

OLEFIN AND ACETYLENE COMPLEXES OF PLATINUM AND PALLADIUM

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I. Introduction

Since the first olefin complex, $K^+[PtCl_3(C_2H_4)] \cdot H_2O$, known as Zeise's salt, was prepared in 1830,¹ a very large number of olefin and acetylene complexes have been reported. Reviews in 1941² and 1952³ summarized the early preparative and qualitative stability data. During the early fifties the currently accepted explanation of the bonding was put forward, initially for silver⁴ and later for platinum.⁵ This stimulated much research on the structure of metal-olefin complexes which was reviewed in 1962.^{6,7} Since these reviews were published further, structural studies have been undertaken. A number of these have been directed to determining which complexes involve the "classical" metal-olefin bonding⁵ and which involve the more recently discovered π -allyl type of bonding.⁸ Most of the recent work, however, has been devoted to relating the earlier structural information to the reactions of metal-olefin complexes both on an industrial and on a laboratory scale. For example, the Wacker process for the oxidation of ethylene to acetaldehyde using a $PdCl_2$ catalyst has been developed into a full-scale industrial process,^{9,10} while mixtures of platinum(II) and tin(II) chlorides have been widely studied for their specificity in catalyzing the hydrogenation of certain olefinic double bonds.¹¹

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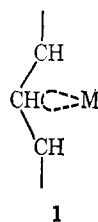
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This review surveys the work on olefin and acetylene complexes of platinum and palladium reported since the previous review in 1962.⁶ An attempt has been made to survey all the literature published up to July 1968.

A number of papers published since then have also been included, but a complete coverage was not possible. The closely related field of π -allyl complexes will be mentioned only for the purpose of comparison. For a more detailed discussion of this field the reader is referred to a recent review.⁸ In view of the current controversy regarding the nature of the bonding in π -allyl complexes, these have been represented as in **1** to avoid favoring either the π -olefin plus σ -carbon bonded species or the π -allyl species.¹²⁻¹⁴



This review includes only those compounds involving a π bond between the metal ion and the olefin or acetylene; no mention is made of either olefin or acetylene complexes involving a σ bond from carbon to metal; these have been reviewed elsewhere.¹⁵ The homogeneous catalysis of olefin reactions by salts of platinum and palladium is discussed, but the related field of heterogeneous catalysis by these metals is excluded, except for the purpose of comparison. Heterogeneous catalysis by platinum, palladium, and other metals has been reviewed recently.¹⁶

II. Nature of the Bonding

A. MOLECULAR ORBITAL TREATMENT

The molecular orbital treatment, which was first applied to silver-olefin complexes⁴ and later extended to platinum-olefin complexes,⁵ gives the currently accepted explanation of the nature of the metal-olefin bond. This essentially involves a σ bond (olefin to metal) and a π bond (metal to olefin) as shown in Figure 1. The σ bond, which in the case of platinum is formed between the filled olefin π orbitals and the empty $5d6s6p^2$ hybrid orbital on platinum, causes an unfavorable distribution of negative charge on the metal ion; however, the π back-donation from the filled $5d6p$ hybrid on platinum to the empty olefin π^* (antibonding) orbital relieves this, thus giving a synergic effect. The bonding in palladium-olefin complexes is similar. Such a bonding scheme requires the carbon-carbon double bond of the olefin to be perpendicular to the plane containing the metal and other ligand atoms in such complexes as $[MX_3(\text{olefin})]^-$ and $[MX_2(\text{olefin})]_2$ (M = metal and X = other ligand).

When first put forward, this interpretation of the bonding depended for support largely on the infrared data available. Thus the carbon-carbon double-bond stretching frequency

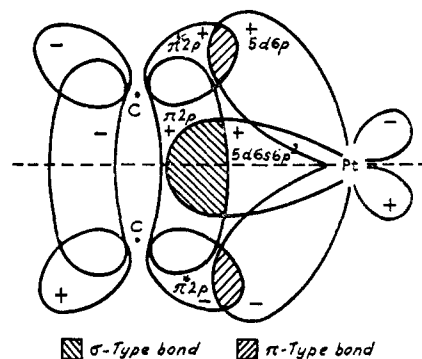


Figure 1. Bonding in metal-olefin complexes (from ref 5).

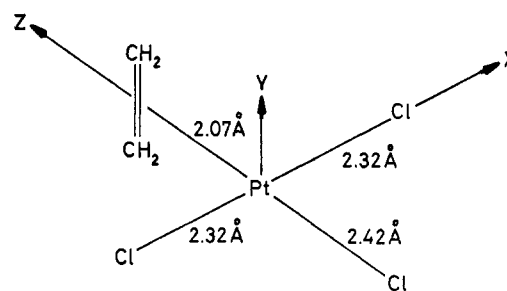


Figure 2. The structure of Zeise's salt. The bond lengths are from ref 18, and the axes are those used throughout this review.

of olefins is lowered by about 140 cm^{-1} on coordination to platinum,¹⁷ which is consistent with a weakened carbon-carbon double bond such as would result from the bonding described above. The best confirmation of this bonding scheme was provided by the X-ray determination of the structure of Zeise's salt¹⁸ (Figure 2) which showed that the carbon-carbon double bond was perpendicular to the plane containing the platinum and chlorine atoms, and situated symmetrically about it. This is exactly the arrangement required by the molecular orbital treatment. Similar structures have been calculated from the X-ray diffraction patterns of a number of platinum(II)- and palladium(II)-olefin complexes. Slight distortions are observed in complexes such as $[\text{PtCl}_2(\text{dipentene})]^{19}$ in which the ligand is very strained.

The X-ray diffraction pattern of dichloro(*p*-toluidine)-(di-*t*-butylacetylene)platinum(II)²⁰ indicates that the bonding in acetylene complexes is similar to that in olefin complexes; the acetylenic bond is perpendicular to the platinum-acetylene bond and situated symmetrically about it. This confirms the earlier conclusions based on the lowering of about 220 cm^{-1} in the infrared stretching frequency of the carbon-carbon triple bond on coordination to platinum(II).²¹

Recent nuclear magnetic resonance studies have indicated that the molecular orbital scheme described above is too rigid, since ethylene in Zeise's salt undergoes rotational oscillations of large amplitude about the platinum-ethylene bond.²² The molecular orbital scheme can be made less rigid

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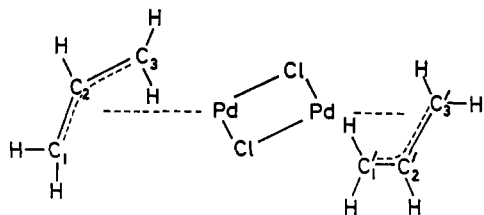


Figure 3. The structure of π -allylpalladium(II) chloride (from ref 26).

if the π back-donation to the olefin π^* (antibonding) orbital can occur from both the metal d_{yz} and metal d_{xz} orbitals or any linear combination of these.²³

In the closely related π -allyl complexes, the arrangement of the atoms, and hence the nature of the bonding, is rather different. The three carbon atoms joined by the delocalized double bond are still in a plane which is approximately perpendicular to that containing the metal and other ligands. However, the line joining C_1 to C_3 (Figure 3) is now parallel to the plane containing the palladium and halogen atoms.²⁴⁻²⁶ The allyl group is symmetrical about a plane which passes through the palladium atoms and is perpendicular to both the $(PdCl)_2$ and allyl group planes.

B. X-RAY STRUCTURAL STUDIES

The X-ray structure determinations have shown that both olefin and acetylene complexes of platinum and palladium can be divided into two distinct groups. In the first group, in addition to the olefin, negative ligands such as halide ions are coordinated to the metal, which is in the +2 oxidation state, whereas in the second group all the ligands are neutral and the metal is formally in the zero oxidation state.

1. Complexes of Divalent Platinum and Palladium

There is general agreement that the plane of the olefin bond is perpendicular to the metal-olefin bond,^{18,27} except in special cases where strain exists.¹⁹ However, a controversy has arisen over the bond lengths, because the accurate location of light atoms such as carbon or even chlorine in the presence of strong X-ray scatterers such as platinum or palladium is difficult and much of the early work is consequently inaccurate.²⁸ The difficulties are exemplified by the X-ray structure of dichloro(norbornadiene)palladium(II). Initially the carbon-carbon double-bond lengths were found to be 1.52 ± 0.036 Å;²⁹ remeasurement gave a value of 1.46 ± 0.037 Å.²⁸ A further determination at the temperature of liquid nitrogen gave a value of 1.366 ± 0.010 Å.³⁰ This value, which is com-

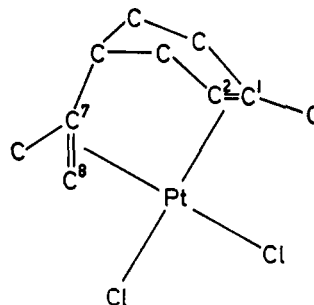


Figure 4. X-Ray structure of dichloro(dipentene)platinum(II) (from ref 19).

patible with the infrared spectrum of the complexed olefin, is barely significantly greater than the carbon-carbon double-bond distance in free ethylene (1.33 Å).³¹ Both double bonds in dichloro(norbornadiene)palladium(II) are ideally situated for bonding in that they are parallel to each other and perpendicular to and situated symmetrically about the palladium-olefin bond. The crystal structure of the red isomer of dichloro(cyclooctatetraene)palladium(II), in which the ligand is again ideally situated for bonding, indicated that the coordinated double-bond lengths were 1.42 Å, which is just significantly longer than the 1.33 Å in free cyclooctatetraene.³² The diolefin dipentene is not ideally suited for forming a chelate complex because the double bonds are not parallel. The X-ray structure of dichloro(dipentene)platinum(II)¹⁹ (Figure 4) has shown that one double bond (C_1-C_2) is perpendicular to the plane containing the $PtCl_2$ group, whereas the other double bond (C_7-C_8) is at an angle of 62.1° .

The complex $[Pt_3(SnCl_3)_2(cycloocta-1,5-diene)_3]$ contains a platinum-tin cluster in which the two tin atoms are on each side of the plane containing the three platinum atoms.³³ Each platinum atom is associated with the two double bonds of one cycloocta-1,5-diene group bonded at right angles to the plane containing the platinum atoms. The bonding within the cluster involves platinum-platinum single bonds with the $SnCl_3^-$ groups each donating an electron to orbitals delocalized over the cluster.

The acetylene bond length in dichloro(*p*-toluidine)(*di-t*-butylacetylene)platinum(II) is 1.27 Å, which is midway between a carbon-carbon double- and triple-bond length.³⁰ The bonds joining the *t*-butyl groups to the acetylenic group are bent away from the metal by 15° .

The π back-donation of charge from the metal d_{xz} orbital to the olefin π^* (antibonding) orbital accounts for the high *trans* effect of olefins. This causes bond weakening if the ligand *trans* to the olefin forms π bonds to the metal, but may even cause a slight strengthening if the *trans* ligand forms pure σ bonds to the metal.³⁴ There is some controversy over whether a metal-halogen bond *trans* to an olefin is lengthened or not. One study of $K^+[PtX_3(C_2H_4)]^-$ ($X = Cl$ and Br) found that the *trans* platinum-halogen bond lengths were 2.39 and 2.52 Å for chlorine and bromine, respectively, whereas the *cis* platinum-halogen bond lengths were appreciably shorter

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(2.28 and 2.42 Å, respectively).³⁵ Similarly in the complex *cis*-[PtBr₂(NH₃)(C₂H₄)] the platinum–bromine bond length *trans* to ethylene was found to be 2.51 Å, whereas the *cis* bond was only 2.40 Å.^{36,37} By contrast a very careful determination indicated a value of 2.33 Å for the platinum–chlorine bond length¹⁹ in [PtCl₂(dipentene)], in close agreement with the platinum–chlorine bond lengths in both *cis*- and *trans*-[PtCl₂(NH₃)₂] (2.33 and 2.32 Å, respectively).³⁸ Similarly the palladium–chlorine bond lengths in dichloro-(norbornadiene)palladium(II) were found to average 2.316 ± 0.0014 Å,³⁰ which is in close agreement with the palladium–chlorine bond lengths of 2.30 to 2.31 Å *trans* to either chlorine or nitrogen that have been observed in a number of complexes.³¹

2. Complexes of Zerovalent Platinum and Palladium

A number of olefin and acetylene complexes in which platinum is formally in the zero oxidation state have been prepared and their structures determined by X-ray diffraction. In contrast to complexes of the divalent metals, the plane of the double or triple bond lies close to the plane of the metal–olefin or –acetylene bond. If the atoms are arranged as in Figure 5, then the observed angles are as follows: bis(triphenylphosphine)(tetracyanoethylene)platinum,^{39,40} $\alpha = 10^\circ$, $\beta = 42^\circ$; bis(triphenylphosphine)(diphenylacetylene)platinum,⁴¹ $\alpha = 14^\circ$, $\beta = 39^\circ$; bis(triphenylphosphine)(ethylene)nickel,⁴² which is isomorphous with the corresponding platinum complex,⁴³ $\alpha = 12^\circ$, $\beta = 42^\circ$.

The observation that in all three complexes the value of α lies between 10 and 14° is explained at present by assuming that the bonding is a hybrid between two extremes. In the first of these the carbon–carbon bond lies perpendicular to the metal–olefin or –acetylene bond as in Zeise's salt. The σ bond is formed by donation of olefin or acetylene π electrons to a d_{sp^2} hybrid orbital on platinum, and the π bond is formed by back-donation from the filled d_{yz} or $d_{yz}p_z$ hybrid orbital on platinum to the π^* (antibonding) orbital. In the second extreme, the carbon–carbon bond lies in the plane of the metal–olefin or –acetylene bond. In this case there are essentially two ways of describing the bonding. In the valence-bond description the olefin or acetylene is considered to be a dicarbanion which forms two σ bonds to platinum, which is itself in the +2 oxidation state. The small values observed for β (Figure 5) suggest that the three-membered ring would be very strained. However, since the tetracyanoethylene complex melts at 268–270° (with decomposition),⁴⁰ the considerable thermal stability of the complex suggests that little strain is present. On the other hand, the finding that the

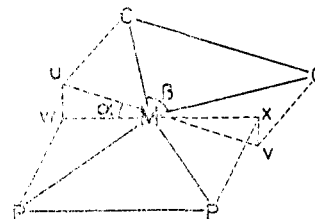


Figure 5. The structure of olefin and acetylene complexes of platinum(0). The plane containing the points u, v, w, and x together with atom M is perpendicular to both the MCC and MPP planes.

fluorine–fluorine coupling constant in the nuclear magnetic resonance spectrum of [Pt(PPh₃)₂(hexafluoropropene)] is of the same order as that observed in saturated fluorocarbon systems suggests that the hexafluoropropene moiety is σ -bonded to platinum.⁴⁴ In the molecular orbital description a σ bond from the olefin or acetylene π orbital to the platinum d_{sp^2} hybrid orbital is complemented by back-bonding from the metal d_{zz} orbital to the olefin π^* (antibonding) orbital. Although these two bonding schemes are essentially equivalent,⁴⁰ the molecular orbital description has the advantage of greater flexibility.

Since the σ -donor properties of tetracyanoethylene are negligible, this ligand is virtually “pure π -bonded” to the platinum. The observed carbon–carbon single-bond length and the shortening of the C–CN distance on coordination are both consistent with this. The acetylenes also exhibit a preference for π - rather than σ -bonding since the weaker the σ -donor capacity, the more stable the complex.⁴⁵

In the diphenylacetylene complex the bonds joining the phenyl and acetylene groups are bent 40° out of the acetylenic bond plane away from the platinum.⁴¹ This angle, which arises from nonbonded interactions with the metal, is almost equal to that in the *cis*-bent excited state of ethylene, suggesting that in the complex the diphenylacetylene resembles one of its excited forms.⁴⁶ In the tetracyanoethylene complex the bonds joining the cyano and ethylene groups are similarly bent 10° out of plane away from the platinum atom with the result that the stereochemistry of the coordinated carbon atoms in the tetracyanoethylene complex is essentially pyramidal, which is similar to the geometry present in the excited states of ethylene.⁴⁶ Thus any wave function that describes the bonding must contain functions representing the excited states of both the metal ion and the ligands.

C. INFRARED SPECTRA

On coordination of the olefin to the metal the carbon–carbon double-bond stretching frequency is generally lowered by about 140 cm⁻¹ for platinum¹⁷ and 120 cm⁻¹ for palladium.⁴⁷ For acetylenes the carbon–carbon triple-bond stretching frequency is lowered by about 250 cm⁻¹ on coordination to platinum(II).⁴⁸ Acetylenes are polymerized so rapidly by palladium(II) that no comparable figure is available for

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coordination to palladium(II).⁴⁸ The infrared spectra of metal-olefin and -acetylene complexes have been widely used to give preliminary evidence for the structure of the complexes.⁴⁹ However, infrared studies alone cannot be relied on to distinguish between a normal olefin complex and a π -allyl complex, although in conjunction with nuclear magnetic resonance measurements such a distinction can often be made. Thus it was shown by nuclear magnetic resonance and infrared studies that butadienepalladium(II) chloride has the π -allyl structure $[(\pi\text{-CH}_2\text{CHCHCH}_2\text{Cl})\text{PdCl}_2\text{Pd}(\pi\text{-CH}_2\text{-CHCHCH}_2\text{Cl})]^{50,51}$ and not the bridged structure, $[\text{Cl}_2\text{Pd}(\text{C}_4\text{H}_6)_2\text{PdCl}_2]$, put forward earlier as a possible interpretation of the infrared data alone.^{52,53}

The complex formed between tetramethylbutynediol and PdCl_2 is a good example where an unexpected structure has been deduced from the infrared spectrum; a band at 1700 cm^{-1} was assigned to a carbonyl stretching frequency,⁵⁴ which together with the elemental analysis led to the structure $(\text{CH}_3)_2(\text{HO})\text{CC}(\text{PdCl})=\text{C}(\text{C}(\text{OH})(\text{CH}_3)_2)\text{CH}(\text{C}(\text{OH})(\text{CH}_3)_2)-\text{C}(=\text{O})\text{C}(\text{OH})(\text{CH}_3)_2$ being put forward. This is in contrast to the platinum(II) complex of this ligand which exhibits a coordinated triple-bond stretching frequency in the infrared at 2010 cm^{-1} and has the normal divalent metal-acetylene complex structure²¹ $\text{K}^+[\text{PtCl}_3\{(\text{CH}_3)_2(\text{HO})\text{CC}\equiv\text{CC}(\text{OH})(\text{CH}_3)_2\}]^-$.

The infrared spectra of Zeise's salt, of its dimer, and of the palladium(II) analogs have been studied in detail.⁵⁵⁻⁶¹ The bands arising from the olefin are virtually identical in the monomer and dimer. A normal coordinate analysis has indicated that bands of 408 (platinum) and 427 cm^{-1} (palladium) are due to the metal-ethylene stretching modes.^{58,60} An earlier assignment⁵⁹ of bands at 485 and 364 cm^{-1} as well as the band at 408 cm^{-1} to platinum-ethylene stretching modes has been questioned.⁶⁰ The band at 485 cm^{-1} , which was observed at 490 cm^{-1} in the Raman spectrum of Zeise's salt and assigned to the platinum-olefin asymmetric stretching frequency,⁶² was found to be very solvent dependent and was therefore assigned to a combination or overtone band.⁶⁰ The band at 364 cm^{-1} was assigned to the platinum-terminal chlorine stretching mode⁶⁰ in agreement with an independent assignment obtained from a number of platinum(II)- and palladium(II)-bridged chloro complexes.⁶³ The force constants

of the metal-olefin stretching mode in $[\text{MCl}_2(\text{C}_2\text{H}_4)]_2$ were calculated to be 2.25 and 2.14 mdyne/\AA for platinum and palladium, respectively, indicating that it is the lighter mass of palladium than platinum rather than a stronger palladium-olefin bond which causes the metal-olefin stretching frequency to be higher in the palladium complex.⁶⁰

An attempt was made to relate the strength of the metal-olefin bond to the lowering of the carbon-carbon double-bond stretching frequency on coordination.⁶⁴ This correlation was later withdrawn since the bands assigned to the olefin were found to be due to another ligand present (pyridine N-oxide).⁶⁵ The carbon-carbon double bond in the complexes is perpendicular to the metal-olefin bond so that the motions of the carbon atoms in the double-bond vibration will be perpendicular to the rest of the molecule. There will therefore be little interaction between the motion of the carbon atoms and that of the central metal group, so that the lowering of the double-bond stretching frequency on coordination might be expected to correlate with the strength of the metal-olefin bond. No correlation does exist^{57,65,66} because of three factors.

1. Coupling to Other Vibrations

The motion of the carbon atoms in the double bond will couple with other motions of the same symmetry representation, for example, in ethylene with the in-plane $>\text{CH}_2$ scissoring vibration.^{58,67} These vibrations will be different for each olefin, and so will give rise to differences in the carbon-carbon double-bond stretching frequencies. These interactions will alter on coordination, particularly when a change of symmetry occurs. Hence the molecular structure will affect not only the frequency of the uncoordinated double bond, but also the frequency shift caused by coordination.

2. Effect of Strain

When an olefin is in a strained form, the carbon-carbon double bond is weakened and lengthened.⁶⁸ As a result the lowering of the carbon-carbon double-bond frequency of a strained olefin on coordination is less, relative to the metal-olefin bond strength, than that of an unstrained olefin.

3. Electronic Effects

The proximity of different polar groups to the carbon-carbon double bond modifies the stretching frequency of that bond (Table I). This modification, which is not readily pre-

Table I

Carbon-Carbon Double-Bond Stretching Frequencies in Olefins Containing Polar Substituents⁶⁶

Olefin	$\nu_{\text{C}=\text{C}}$, cm^{-1}	Olefin	$\nu_{\text{C}=\text{C}}$, cm^{-1}
$\text{CH}_2=\text{CHCH}_2\text{OH}$	1645	$\text{CH}_2\text{CH}=\text{CHCH}_2\text{NH}_3^+$	1673
$\text{CH}_2=\text{CHCH}_2\text{NH}_2$	1642	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH}$	1645
$\text{CH}_2=\text{CHCH}_2\text{NH}_3^+$	1650	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{NH}_2$	1640
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$	1690	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{NH}_3^+$	1640
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{NH}_2$	1670		

dictable in terms of an inductive effect, will be different when the olefin is coordinated to a metal.

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Correlations of the double-bond stretching frequency with the metal-olefin bond strength for a single olefin with different metals are useful as a rough guide to bond strength. For different olefins with a single metal, the metal-olefin stretching force constant serves as the best measure of the bond strength.⁶⁰

The platinum-chlorine stretching frequencies in the metal-olefin complexes have been well studied.^{55-61,63,69} The positions of the peaks are virtually unchanged on increasing the pressure to 50,000 atm. The intensity of the symmetric stretching frequency decreases with increasing pressure, but the asymmetric stretching frequency is hardly altered.⁶⁹ This has been used to confirm the assignment of these bands in dichloro(norbornadiene)platinum(II).⁷⁰ The platinum-chlorine stretching frequencies of a series of complexes $[\text{PtCl}_3\text{L}]^-$ (L = olefin or acetylene) have been determined and the platinum-chlorine stretching frequency *trans* to the olefin was found to be lower than that *cis* to the olefin.^{66,69,61} This has been claimed to be consistent with the high *trans*-effect of olefins.⁵⁶ However, as mentioned earlier, ligands which exert a *trans*-effect by a mesomeric or π -acceptor mechanism will only cause bond weakening if the *trans* bond has any π -bonding, and may cause a slight strengthening if the *trans* bond is a pure σ bond.³⁴ In agreement with this, olefins give a *trans* strengthening of the metal-chlorine stretching frequency relative to phosphines.⁶¹ This could occur by ethylene drawing the metal $d\pi$ electrons away from the non-bonding lone pairs on the chlorine atom.

An examination of the metal-halogen stretching frequencies in chloro-bridged complexes has indicated that the metal-chlorine bridging bonds are probably not equivalent.⁶⁸ Although relatively little evidence is as yet available, the structure of $[\text{PtCl}(\text{MeO}(\text{cyclopentadiene}))_2]$ as determined by X-ray diffraction has shown that the platinum-chlorine bond *trans* to the σ -bonded carbon is 0.17 Å longer than that *trans* to the platinum-olefin bond.⁷¹ This is consistent with the *trans*-effect theory cited above.³⁴

The platinum-olefin stretching frequencies in $[\text{PtX}_2(1,5\text{-cyclooctadiene})]$ (X = Cl, Br, I, CH_3 , and C_6H_5) and $[\text{PtX}_2(\text{cyclooctatetraene})]$ (X = Cl, Br, and I) were assigned⁷² to bands at about 460 cm^{-1} . This is similar in frequency to the bands at about 480 cm^{-1} in Zeise's salt and $[\text{PtCl}_2\text{L}(\text{C}_2\text{H}_4)]$ (L = neutral ligand) which were assigned to the platinum-olefin stretching frequency by the same authors.⁵⁷ Other workers have assigned a much lower frequency to the platinum-olefin stretching frequency in Zeise's salt.^{58,60} It was concluded that the extra stability of the cyclic olefin complexes was due either to their extreme insolubility or to the thermodynamic chelate effect. However, if the platinum-olefin stretching frequency is compared with the accepted value in Zeise's salt (408 cm^{-1}), the extra stability may also be due to a greater bond strength in the cyclic olefin complexes.

The changes in the platinum-olefin bond strength, as indicated by changes in the infrared spectra of the complexes *trans*- $[\text{PtCl}_2\text{L}(\text{C}_2\text{H}_4)]$ as L was changed from chloride to amine to pyridine N-oxide, were shown to result from changes in the relative magnitudes of the σ and π components of the

platinum-olefin bond and were not the result of a change in the hybridization of the olefinic carbon atoms (*e.g.*, from sp^2 to sp^3).⁷⁸ The infrared spectra of a series of complexes of the type *trans*- $[\text{PtCl}_2\text{L}(\text{ac})]$ (L = 4-substituted pyridine N-oxide and ac = acetylene) were determined.⁷⁴ The variation in the triple-bond stretching frequency was not linearly related to the electron-withdrawing power of the 4-substituent, which was thought to indicate that there is a limit to which the π back-bonding may be increased by the *trans* ligand before the σ bond from acetylene to platinum is appreciably weakened.

Complexes of platinum(0) with olefins exhibit no infrared bands assignable to the olefinic double bond.^{44,75} On coordination to platinum(0) the triple-bond stretching frequency of acetylenes is lowered by 460 to 1705 cm^{-1} , which is similar to that observed for an uncoordinated double bond.⁷⁶ This reduction in the multiple-bond order on complex formation with platinum(0) is consistent with the mode of binding in these complexes discussed above in connection with their X-ray structures.

D. NUCLEAR MAGNETIC RESONANCE STUDIES

Nuclear magnetic resonance studies have been widely used in conjunction with infrared spectroscopy to provide preliminary evidence for the structure of olefin complexes. In particular nuclear magnetic resonance has frequently been successful in distinguishing between olefinic and π -allylic complexes.^{50,51} The details of the application of nuclear magnetic resonance to metal-olefin complexes are given in a recent review.⁷⁷

The nuclear magnetic resonance spectrum of polycrystalline $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$ did not show any evidence for the rotation of the olefin about the platinum-olefin bond, although there was evidence for a rocking motion perpendicular to the platinum-olefin bond and "wagging" about the carbon-carbon double-bond axis.⁷⁸ The nuclear magnetic resonance data also suggested that the olefinic bond was lengthened and the hydrogen atoms were bent out of the olefinic bond plane away from the platinum atom, giving a geometry similar to that which exists in the excited states of ethylene.⁴⁶

The nuclear magnetic resonance spectra of single crystals of $\text{K}^+[\text{PtCl}_2(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ and its deuterium oxide analog were recorded at a number of orientations relative to the magnetic field. The results, in contrast to the earlier work with the polycrystalline dimer, suggested that the ethylene molecule was undergoing large amplitude rotational oscillations about both the platinum-olefin bond and the carbon-carbon double-bond axis.²² Rotation about the platinum-olefin bond has also been claimed in the complexes *trans*-dichloro(olefin)(2,4,6-trimethylpyridine)platinum(II) where the olefin is styrene or *t*-butylethylene.^{79,80} Molecular models indicate that the 2- and 6-methyl groups on pyridine maintain the plane of the pyridine molecule perpendicular to the PtCl_2

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plane, so that when an unsymmetrical olefin is coordinated *trans* to the pyridine the two methyl groups are no longer magnetically equivalent. With styrene and *n*-butylethylene only one methyl signal was observed at room temperature although on cooling to -50° two signals were observed. This was interpreted as indicating a rapid (on the nuclear magnetic resonance time scale) rotation of the olefin about its coordination axis, which ceased below -50° . Since at -75° the rate of exchange of free and coordinated olefins is high⁸¹ ($>70 \text{ sec}^{-1}$ for ethylene in Zeise's salt),⁸² the observed single methyl signal could be explained equally well as being due to the rapid intermolecular exchange of free and coordinated olefins. Since it is likely that the bulkier the olefin, the slower the rate of exchange, an intermolecular exchange mechanism would account for the fact that no splitting of the methyl signals was observed for propylene complexes.⁷⁹

Rotation about the axis of the olefinic double bond has been observed in a number of complexes containing unsymmetrical olefins. This rotation forces the substituents on the double bond further away from the metal.^{81,83,84} In addition a slight rotation about an axis perpendicular to both the platinum-olefin bond and the olefinic double bond, which forces the substituted end of the double bond further away from the platinum atom, has been observed.⁸³ This is similar to the situation in $[\text{PdCl}_2(\text{PhCH}=\text{CH}_2)]_2$ in which the X-ray measurements have shown that the olefinic double-bond axis is displaced 20° from the perpendicular.⁸⁵

A rotation about the carbon-carbon double bond was also observed in the chloroacetylacetonato(olefin)platinum(II) complexes due to nonbonding interactions between the chlorine and oxygen atoms which forced the olefin to twist. The two geometrical isomers formed by twisting in opposite directions did not exist in equal abundance which suggests that although twisting reduces the steric repulsion, it also reduces the platinum(II)-olefin orbital overlap, as predicted by the molecular orbital description of the bonding.⁸⁶

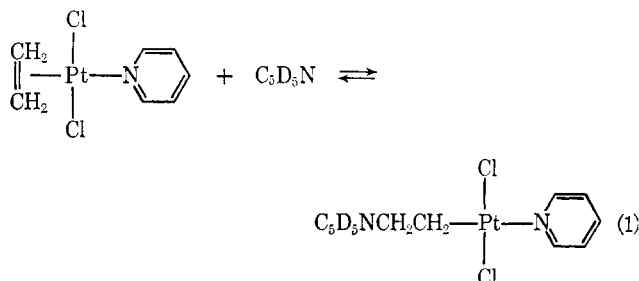
Since the coupling of ^{195}Pt with the olefinic protons increases with decreasing platinum-hydrogen distance whereas coupling of ^{195}Pt with the protons on the methylene (or methyl) group adjacent to the double bond decreases with decreasing platinum-hydrogen distance, the coupling constants $J(\text{Pt}-\text{CH})$ and $J(\text{Pt}-\text{C}-\text{CH})$ must have opposite signs.⁸⁶

The chemical shifts of the olefinic protons in a series of *trans*- $[\text{PtCl}_2(\textit{para}$ -substituted pyridine N-oxide)(C_2H_4)] complexes were found to move downfield as the electron-withdrawing character of the *para* substituent increased.^{80,87} This was ascribed to a reduction in the π back-donation of charge from platinum to ethylene which weakened the ethylene-platinum interaction.⁸⁷ In addition it was found that the coupling between platinum and the olefinic protons increased with increasing electron-withdrawing character of the *para* substituent on pyridine N-oxide. This was interpreted in terms of electron withdrawal by the substituents

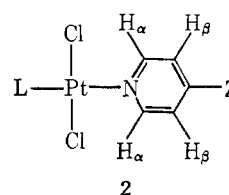
leading to a decrease in the platinum-olefin bond length.⁸⁷ However, a simpler explanation, which does not involve a variation in the platinum-ethylene bond length, is that the electron-withdrawing *para* substituent will reduce the pyridine N-oxide to platinum σ bonding and so make the platinum a better acceptor in the ethylene to platinum σ bond. This will lead to increased $^{195}\text{Pt}-^1\text{H}$ coupling by increasing the platinum s character in the platinum-ethylene bond.⁸⁸

Nuclear magnetic resonance has indicated that the rate of exchange of free and coordinated ethylene in Zeise's salt is greater than 70 sec^{-1} at 75° .⁸² From studies of the mutarotation of diastereoisomers of platinum-olefin complexes, it has been suggested that this exchange occurs by an $\text{S}_{\text{N}}2$ mechanism.⁸⁹

The addition of fully deuterated pyridine to a solution of $[\text{PtCl}_2(\text{C}_5\text{H}_5\text{N})(\text{C}_2\text{H}_4)]$ in chloroform shifts the methylene resonance peak in the nuclear magnetic resonance spectrum to a higher field. This, together with the fact that this peak has been split into a triplet, has been tentatively ascribed to the conversion of the platinum-olefin π bond into a platinum-carbon σ bond (eq 1).⁹⁰



The nuclear magnetic resonance spectra of **2** show that the



coupling of the H_α protons to the platinum atom depends on the temperature, the solvent, and the nature of L and Z .⁹¹ It was assumed that failure to observe such coupling was due to a rapid exchange of pyridine, either with the solvent or between complexes. When Z and the solvent are kept constant, the temperature at which coupling is observed is related to the *trans*-labilizing effect of L : the lower the temperature, the greater the *trans*-labilizing effect. In chloroform with $\text{Z} = \text{H}$, it was found that the *trans*-labilizing effect of a number of ligands was in the order $\text{C}_2\text{H}_4 \gg \text{PhCH}=\text{CH}_2 \sim \textit{cis}$ - and *trans*- $\text{CH}_3\text{CH}=\text{CHCH}_3 \approx \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2 > \text{CO}$.

The nuclear magnetic resonance studies of the formally zerovalent platinum complex $[\text{Pt}(\text{PPh}_3)_2(\text{MeC}\equiv\text{CPh})]$ showed

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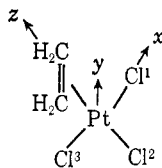
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Table II
Ultraviolet and Visible Spectra of Zeise's Salt Together with Assignments of the Observed Bands^a

Obsd bands ^b		Assignment 1 ^c	Assignment 2 ^d	Assignment 3 ^{b,e}
λ , cm ⁻¹	ϵ			
23,900	40.1		{ Pt 5d → Pt 5d (unspecified) }	0.70(Cl ^{1,3} 3p _x) + 0.25(Pt 5d _{z²}) + 0.04(Cl ² 3p _x) → A
30,350	340	Pt 5d _{z²} → Pt 5d _{z²}	{ Pt 5d → Pt 5d (unspecified) }	0.67(Cl ^{1,3} 3p _y) + 0.33(Pt 5d _{xy}) → B
33,450	605	Pt 5d _{x²-y²} → Pt 5d _{z²}	Pt 5d _{x²-y²} → C ₂ H ₄ π*	0.70(Cl ^{1,3} 3p _x) + 0.25(Pt 5d _{z²}) + 0.04(Cl ² 3p _x) → A
37,450	3100	{ Pt 5d _{xy} → Pt 5d _{z²} } (augmented by charge transfer)	Pt 5d _{xy} → C ₂ H ₄ π*	{ 0.70(Cl ^{1,3} 3p _x) + 0.25(Pt 5d _{z²}) + 0.04(Cl ² 3p _x) → B } { 0.67(Cl ^{1,3} 3p _y) + 0.33(Pt 5d _{xy}) → A }
40,700	3260	Charge transfer	Pt 5d _{yz} → C ₂ H ₄ π*	0.64(Cl ² 3p _x) + 0.19(Cl ^{1,3} 3p _x) + 0.16(Pt 5d _{z²}) → B

^a The axes and numbers of the chlorine atoms are as shown



^b Reference 96. ^c Reference 95. ^d Reference 97. ^e A = 0.51(C₂H₄ π*) + 0.28 (Pt 6p_y) + 0.14(Pt 5d_{yz}) + 0.06(Cl² 3p_y). B = 0.24(Pt 5d_{z²}) + 0.20(Cl² 3p_x) + 0.17(Cl^{1,3} 3p_x) + 0.10(Pt 5d_{x²-y²}) + 0.10(C₂H₄ π*) + 0.09(Pt 6p) + 0.04(Pt 6s) + 0.03(Cl^{1,3} 3p_x) + 0.01(Cl² 3s).

that rotation about the platinum-acetylene bond was slow relative to the nuclear magnetic resonance time scale (*i.e.*, less than 1.2 sec⁻¹) indicating a high activation energy for rotation.⁹² The complex is therefore constrained in an approximately planar geometry in solution as has been shown in the solid state from the X-ray structure of the diphenylacetylene analog.⁴¹

E. ULTRAVIOLET AND VISIBLE SPECTRA

Ultraviolet and visible spectra have been recorded for Zeise's salt⁹³⁻⁹⁶ and a number of its analogs containing different olefins.^{94,97} Three attempts have been made to assign the observed bands to particular electron transitions within the complex (Table II). In the earliest attempt the order of the d orbitals in Zeise's salt was assumed to be identical with that in PtCl₄²⁻ except for removal of the degeneracy of the d_{yz} and d_{xy} orbitals.⁹⁵ Although this assumption is open to a number of criticisms, one of which is that the relative energies of the d orbitals in PtCl₄²⁻ are uncertain,⁹⁸ the values coincide with the relative energies of the d orbitals deduced from the ultraviolet spectra of the platinum(II)-olefin complexes.⁹⁷ However, the assignment of the bands at 33,450 and 37,450 cm⁻¹ to d-d transitions, the latter band being augmented by charge transfer, is unsatisfactory since the extinction coefficients of each of these bands are too large for either of them to arise solely from a d-d transition.⁹⁷ A later assignment based on a semiempirical self-consistent charge and configuration molecular orbital calculation indicated that there was considerable mixing of the component atomic orbitals.⁹⁹ Although the bands calculated by this approach were in qualitative agreement with the observed bands, the quantitative

agreement was poor. A further independent assignment based on comparisons with similar complexes assigned the ultraviolet bands to transitions between platinum 5d and olefin π* (antibonding) orbitals.⁹⁷ By observing the spectral shifts that occurred both on changing the solvent and on altering the ligand *trans* to the olefin, the relative energies of the d orbitals were shown to be d_{z²} > d_{z²} > d_{x²-y²} > d_{xy} > d_{yz}, using the axes of Figure 2.⁹⁷

The circular dichroism of optically active olefins is instrumentally difficult to observe since olefins absorb at about 50,000 cm⁻¹. However, when the olefin is coordinated to platinum(II), the disymmetric olefin perturbs the d-d transitions which occur between 20,000 and 30,000 cm⁻¹, giving rise to a circular dichroism band in a region that is instrumentally convenient. This technique, which allows the relative and absolute configurations of the olefins to be determined, has been applied to β-pinene and (+)-limonene.⁹⁹ The sign of the circular dichroism band depends solely on the optical activity of the olefin and is independent of both the optical activity of the amine and the relative positions (*cis* or *trans*) of the olefin and the amine in [PtCl₂(RNH₂)(olefin)].¹⁰⁰

F. MAGNETIC SUSCEPTIBILITY STUDIES

The magnetic susceptibilities of a number of platinum(II)-olefin complexes have been determined and analyzed in terms of susceptibilities of the individual bonds formed between platinum and the ligands.¹⁰¹ The results indicate that the magnetic susceptibility of the platinum(II)-olefin bond is approximately twice that of the olefin itself.¹⁰² A similar result was found for other ligands such as carbon monoxide which are known to be π-bonded to the metal. In contrast, σ-bonded complexes gave smaller differences between the magnetic susceptibility of the platinum(II)-ligand bond and

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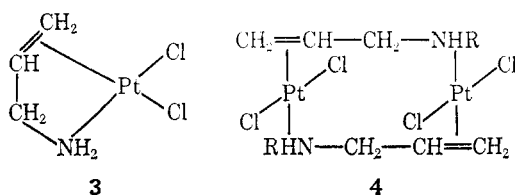
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that of the ligand itself. Until these results are confirmed they should be treated with caution since the compound dichloro(allylamine)platinum(II) was assumed to have structure 3. It has since been shown that secondary allylamines form complexes of type 4 (R = alkyl group) in which platinum-platinum interaction occurs.^{94, 103} This interaction was

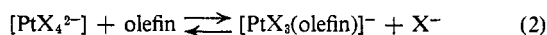


not considered in the magnetic susceptibility calculations.

G. STABILITY CONSTANT STUDIES

Qualitative information about the relative stabilities of the platinum(II)-olefin complexes was first obtained in 1936.¹⁰⁴ Since then the results of a number of workers have shown that the stability of platinum(II)-olefin complexes decreases as the over-all charge on the complex ion becomes more positive,¹⁰⁵ indicating that when π bonding is greatly reduced as in cationic platinum(II)-olefin complexes the stability of the platinum(II)-olefin bond is greatly decreased, despite the enhancement of the σ bond between the olefin and platinum(II).¹⁰⁶

Systematic quantitative stability constants have only recently become available. A spectrophotometric study of the system

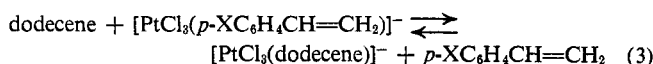


indicated that the olefins gave higher stability constants than water, lower than amines, and comparable with the heavier halides.¹⁰⁷ The stability constants for a series of olefins¹⁰⁷⁻¹¹² (Table III) indicated that the stabilities of the complexes increased as the structure of the olefin was modified in such a way as to decrease the electron density at the olefin bond. Thus the strength of the π back-bond from platinum(II) to olefin would appear to be more important than that of the σ bond from olefin to platinum(II) for the formation of stable platinum(II)-olefin bonds. The platinum(II)-olefin bond strength was greater in the bromo than in the chloro complexes, probably due to the fact that the PtBr_3^- group is a poorer σ acceptor and a better π donor than the PtCl_3^- group.¹¹¹ It was also found that in addition to electronic

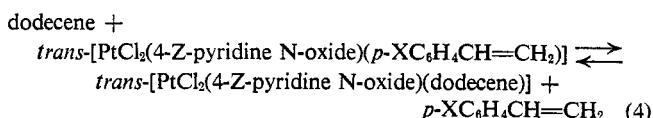
factors, steric factors were important in determining the strength of the platinum(II)-olefin bond.

A study of the kinetics of the forward direction of reaction 2 showed that the reaction was first order in both olefin and tetrachloroplatinate(II) ion.¹¹² It was suggested that the olefin first becomes coordinated in the axial position *via* a rapidly established preequilibrium and then displaces an equatorial chloride ligand in the rate-determining step. Unexpectedly it was found that the aquo species $[\text{PtCl}_3(\text{H}_2\text{O})]^-$ was not involved in the reaction. It was suggested that this was because the d orbitals were more compact in the less negatively charged aquo complex, giving less overlap with the olefin orbitals. This would lead to large differences in the rate of reaction of olefins with $[\text{PtCl}_4]^{2-}$ and $[\text{PtCl}_3(\text{H}_2\text{O})]^-$.

A study of the system



showed that both electron-releasing and electron-withdrawing *para* substituents (X) on the styrene increased the stability of the styrene-platinum(II) complex.¹¹³ On treating Zeise's salt with 4-substituted pyridine N-oxides, the chloride ligand *trans* to ethylene is displaced by the pyridine N-oxide¹¹⁴ giving a series of complexes containing a platinum(II)-oxygen bond. The insensitivity of the platinum-oxygen stretching frequency at 323 cm^{-1} in the infrared spectrum to changes in the 4-substituent suggests that this is essentially a σ bond.¹¹⁵ Since the donor strengths of the substituted pyridine N-oxide ligands correlate well with the Taft σ values of the substituents,¹¹⁶ the equilibria which are shown in eq 4 were studied for a series of 4-substituted pyridine N-oxides



and *meta*- and *para*-substituted styrenes.⁹⁵ The results, for which the authors claim an accuracy of only $\pm 20\%$, showed little correlation between the stability constant and the electron-withdrawing or electron-releasing ability of the substituent on either the styrene or the pyridine N-oxide. However, on comparison of complexes containing a series of *para*-substituted styrenes and a particular pyridine N-oxide ligand (e.g., 4-nitropyridine N-oxide), or alternatively on comparison of complexes containing a series of 4-substituted pyridine N-oxide ligands and a particular styrene (e.g., unsubstituted styrene), it was found that both electron-withdrawing and electron-releasing substituents increased the stability of the styrene-platinum(II) complex relative to the dodecene-platinum(II) complex. Although there are many as yet unexplained contradictions to this generalization, if it is an enthalpy effect, it can be understood if the σ bond (styrene to platinum(II)) and the π back-bond (platinum(II) to styrene) are of approximately equal strength.

Palladium(II)-olefin stability constants have been determined for the simple olefins using solubility methods (Table

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Table III
Stability Constants of Platinum-Olefin Complexes^a

$$\text{PtX}_4^{2-} + \text{L} \xrightleftharpoons{K} \text{PtX}_3\text{L}^- + \text{X}^-$$

$$K = \frac{[\text{PtX}_3\text{L}^-][\text{X}^-]}{[\text{PtX}_4^{2-}][\text{L}]}$$

Ligand X	Olefin (L) ^b	Temp, °C	Stability constant	ΔH, kcal/mole	ΔS, eu	Ref
Cl	allNH ₃ ⁺	59.0	1022	-7.1	-7.6	107
		44.0	1737			
		30.2	2829			
Cl	allNH ₂ Et ⁺	59.0	806	-5.9	-4.4	107
		44.0	1233			
		24.0	2348			
Cl	allNHEt ₂ ⁺	59.0	386	-5.6	-5.0	107
		45.3	551			
		30.0	865			
Cl	allNEt ₃ ⁺	59.0	112	-4.9	-4.6	107
		45.0	153			
		25.0	260			
Cl	allPEt ₃ ⁺	59.0	505	-5.9	-4.3	107
Cl	allAsEt ₃ ⁺	58.0	917			
45.0	1320					
Cl	allNMe ₃ ⁺	60.0	117	-5.3(5)	-6.6	107
		44.5	173			
		30.0	259			
Cl	allNPr ⁿ ₃ ⁺	60.0	131			107
Cl	allNBu ⁿ ₃ ⁺	60.0	308			107
Cl	allNH(CH ₂) ₄ ⁺	60.0	649			107
Cl	allNH(CH ₂) ₅ ⁺	60.0	437			107
Cl	butNH ₃ ⁺	60.0	2038	-5.1	-0.2	107
		44.5	3017			
		30.0	4396			
Cl	butNEt ₃ ⁺	60.0	4449	-3.8	+5.4	107
		44.8	5911			
		30.0	7778			
Cl	butAsEt ₃ ⁺	60.0	5459	-3.3	+7.2	107
		44.8	7014			
		30.0	8962			
Cl	pentNH ₃ ⁺	60.0	1124			110
Cl	<i>trans</i> -CH ₃ CH=CHCH ₂ NH ₃ ⁺	60.2	209	-5.1	-4.6(5)	109
		44.5	304			
		30.0	450			
Cl	CH ₂ =CHCH(CH ₃)-NH ₃ ⁺	60.0	804	-6.7	-6.9	109
		45.3	1282			
		30.0	2194			
Cl	CH ₂ =C(CH ₃)-CH ₂ NH ₃ ⁺	60.0	3.2			109
Cl	(CH ₃) ₂ C=CHCH ₂ NH ₃ ⁺	60.0	2.6			109
Cl	allOH	60.0	3890	-8.1	-7.6	110
		44.5	7250			
		30.0	13011			
Cl	pentOH	60.0	2525			110
Cl	<i>trans</i> -CH ₃ -CH=CHCH ₂ OH	60.0	3008			110
Cl	allSO ₃ ⁻	55.6	1539	-6.1	-4.1	112
		45.0	2123			
		35.0	2884			
Br	allNH ₃ ⁺	24.5	306			111
Br	allNH ₂ Et ⁺	35.0	184			111
		25.0	241			
		0.0	506			
Br	allNHEt ₂ ⁺	24.5	127			111
Br	allNEt ₃ ⁺	24.5	44.1			111
Br	butNEt ₃ ⁺	24.5	1190			111

^a Determined in a medium of 1.9 M KX + 0.1 M HX using a spectrophotometric technique. ^b all = CH₂=CHCH₂-; but = CH₂=CH(CH₂)₂-; pent = CH₂=CH(CH₂)₃-.

Table IV
Stability Constants of Palladium-Olefin Complexes^a

$$\text{PdCl}_4^{2-} + \text{L} \rightleftharpoons \text{PdCl}_3\text{L}^- + \text{Cl}^-$$

$$K = \frac{[\text{PdCl}_3\text{L}^-][\text{Cl}^-]}{[\text{PdCl}_4^{2-}][\text{L}]}$$

Olefin (L)	Temp, °C	Ionic strength, M	Stability constant	ΔH , kcal/mole	ΔS , eu	Ref
C ₂ H ₄	15.0	2	18.7			117
	25.0		17.4			
	35.0		9.7			
C ₂ H ₄	8.0	4	15.6	-1.5	0	118, 120
	13.4		16.3			
	20.0		15.2			
	25.0		13.1			
	20.0		16.9			121
C ₂ H ₄	14.8	2	18.7			122
		2.1-2.2	15.5			
		3.1-3.2	15.9			
		4.5	16.3			
C ₃ H ₆	10.3	4	8.4	0	4	120
	14.9		8.6			
	20.1		7.9			
	20.0		7.6			121
1-Butene	5.0	4	13.9	0	5	119, 120
	10.0		12.6			
	14.8		13.6			
	20.0		12.4			
	20.0		14.3			121
1-Butene	14.8	2.1-2.2	13.8			122
		3.1-3.2	13.6			
		4.1-4.2	13.6			
		5.1-5.2	11.3			

^a All constants were obtained by measuring the solubility of olefins in aqueous palladium chloride solutions.

IV).¹¹⁷⁻¹²² The results indicated that $[\text{PdCl}_3(\text{olefin})]^-$ and $\text{trans-}[\text{PdCl}_2(\text{H}_2\text{O})(\text{olefin})]$ were present in solution as is found with the corresponding platinum(II) complexes.¹²³ The enthalpies and entropies of formation of $[\text{PdCl}_3(\text{olefin})]^-$ were very close to zero. By an argument analogous to that used previously,¹⁰⁷ the solvation energies of the free olefins would be expected to vary more than those of the complexes so that the observed differences in enthalpy values do not arise from solvation energy changes. The observed increase in enthalpy on replacing ethylene by propylene could therefore arise from steric effects. It could also arise from electronic effects, if the observation¹⁰⁷ that the strength of the π back-bond from metal to olefin is more important than that of the σ bond from olefin to metal, for the formation of stable platinum(II)-olefin bonds also applies to palladium(II) complexes, since the higher electron density in the olefinic bond of propylene than ethylene should lead to a weaker palladium(II)-olefin bond in the propylene complex.

Although a strict comparison of the palladium(II)-olefin

stability constants with those obtained for platinum(II) complexes is not possible because of the use of different olefins, the values of the stability constants of the palladium(II)-olefin complexes are about a factor of 100 less than those of the platinum(II)-olefin complexes. Thus, when comparable values are obtained, they will probably support the infrared data obtained from the metal-olefin stretching force constants⁶⁰ in showing that platinum(II)-olefin complexes are thermodynamically more stable than palladium(II)-olefin complexes.

The greater stability of the platinum(II)- relative to palladium(II)-olefin complexes can be understood in terms of the molecular orbital theory of bonding. Using the coordinate axes of Figure 2, the relative energies of the d orbitals in platinum(II)-olefin complexes⁹⁷ are $d_{z^2} > d_{xz} > d_{x^2-y^2} > d_{xy} > d_{yz}$. If it is assumed that the same order applies in palladium(II)-olefin complexes, then the molecular orbital scheme shown in Figure 6 is obtained. The stability of the complexes will increase with an increase in the energy difference between the highest filled and the lowest unfilled molecular orbital (ΔE). Since the value of ΔE increases on going from palladium(II) to platinum(II) (for example, for $[\text{PdCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ ΔE has the values¹²⁴ 19,150 and 23,450 cm^{-1} respectively), the stability of the platinum(II)-olefin complexes will be greater than that of the palladium(II)-olefin complexes.

The greater spacial extension of the d orbitals of platinum(II) relative to palladium(II) will confer greater stability on the platinum(II)- relative to palladium(II)-olefin bond by giving greater overlap between the metal and olefin orbitals if both metals form metal-olefin bonds of equal length. Although no exactly comparable bond lengths have been determined, the mean palladium(II)-olefin bond lengths in dichloro(norbornadiene)palladium(II) (2.08 Å)⁸⁰ and dichloro(cyclooctatetraene)palladium(II) (2.08 Å)⁸² are, within experimental error, equal to the 2.07 Å found for the platinum(II)-olefin bond length in Zeise's salt.¹⁸

The observation that *cis* olefins form complexes with higher stability constants than *trans* olefins¹²⁵ is probably the result of two effects.

(1) *cis* olefins are more strained than *trans* olefins, and this strain is reduced on complex formation. The higher heats of hydrogenation of *cis* olefins as compared with *trans* olefins are indicative of the greater strain present in the former.¹²⁶ It has been suggested¹²⁷ that on complex formation a slight rotation about the double bond can occur to relieve the bond oppositions present in a planar *cis* olefin. Since this rotation is not observed in the free olefin, it must lead to considerable bond weakening. In support of this theory the lowering of the double-bond stretching frequency in the infrared and the slight lengthening of the olefin bond on complex formation both indicate that bond weakening does occur on complex formation.

(2) The actual bonds formed between *cis* olefins and metals are stronger than between *trans* olefins and metals. It has been suggested⁶⁶ that whereas in Zeise's salt the mean position of the plane of the ethylene molecule is perpendicular to the

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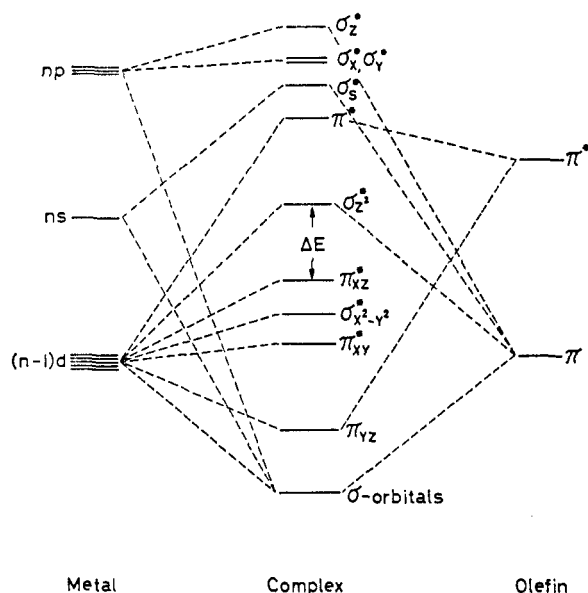


Figure 6. Molecular orbital scheme for platinum(II)- and palladium(II)-olefin complexes. For simplicity the ligand orbitals associated with the ligands other than the olefin have been excluded.

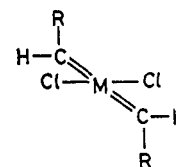


Figure 7. The rotation necessary to remove steric interference in a *cis*-disubstituted olefin complex.

platinum(II)-ethylene bond and parallel to the *cis*-chlorine-platinum(II) bond, in the complex of a *cis*-disubstituted olefin the plane of the olefin would twist about the double-bond axis in such a way as to reduce the steric interference between the substituents and the *cis*-chlorine ligands. This rotation, which would leave the double bond still vertical (Figure 7), has been observed in the nuclear magnetic resonance spectra of a number of complexes containing unsymmetrical olefins.^{81,82,84,91} The small reduction in the orbital overlap caused by this rotation would result in a slight weakening of the metal-olefin bond relative to that formed by ethylene. To reduce the steric interference between the substituents in a *trans*-substituted olefin and the *cis*-chlorine ligands, a rotation about the metal-olefin bond axis is necessary (Figure 8). While not affecting the σ bond, this will markedly reduce the overlap between the filled d orbitals of the metal and the empty π^* (antibonding) orbitals of the olefin, thus considerably reducing the over-all bond strength. A nuclear magnetic resonance study of Zeise's salt has shown that rotation about the metal-olefin bond does occur, even in the solid state.²²

The equilibrium constants for the solvation of Zeise's salt in ethanol and water have been determined, and the value in water was found to be 50 times that in ethanol.¹²⁸⁻¹³⁰

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View along metal-olefin bond

Figure 8. The rotation necessary to remove steric interference in a *trans*-disubstituted olefin complex.



L does not form π -bonds L forms π -bonds

Figure 9. Schematic representation of the π -bonding mechanism for the *trans*-effect.

In addition, it was found that at low platinum concentration Zeise's dimer dissolved in ethanol to give the monomeric complex *trans*-[PtCl₂(EtOH)(C₂H₄)]. The rate of exchange of the chloride ion *cis* to ethylene in Zeise's salt was studied in ethanol and found to be first order in both [PtCl₂(C₂H₄)]⁻ and [PtCl₂(EtOH)(C₂H₄)]. A mechanism for this exchange involving a dimeric chloro-bridged intermediate was suggested.¹³⁰

Both kinetic and equilibrium measurements have been made for the replacement of one acetylene (ac) coordinated to platinum(0) by another (ac') (eq 5).^{131,132} The rate is proportional to the concentration of the platinum(0)-acetylene complex but independent of the concentration of the reacting



acetylene (ac'), suggesting that the rate-determining step involves loss of the coordinated acetylene (ac). Thus the rate coefficient is a measure of the platinum(0)-acetylene bond strength. Both the rate and equilibrium constants for eq 5 coupled with the chemical shifts of the acetylenic protons in the nuclear magnetic resonance spectra of the free acetylenes¹³³ indicate that the π -acceptor capacity of the acetylene is more important than its σ -donor capacity for the formation of a stable platinum(0)-acetylene bond.

H. THE *trans*-EFFECT

The *trans*-effect, as derived from kinetic data, may be defined as the ability of one ligand to modify the properties of a second ligand bound to a metal in the *trans* position. It has long been recognized that in terms of this definition olefins exhibit a high *trans*-effect. A review¹³⁴ of the *trans*-effect written in 1962 favored the π -bonding mechanism for the *trans*-effect of olefins¹³⁵ in which a ligand L (Figure 9) which can form π bonds will withdraw some of the electron density of the d_{yz} orbital from the ligand (X) in the *trans* position.

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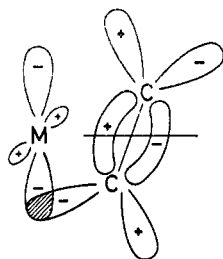


Figure 10. Distortion of the metal-olefin bonding arising from interaction of the metal $d_{x^2-y^2}$ and olefin π^* (antibonding) orbitals.

This should weaken the Pt-X bond as well as direct an incoming nucleophile toward X, which is the region of lowest electron density. More recently the *trans*-effect of olefins has been ascribed to three factors.

(1) Olefins have empty π^* (antibonding) orbitals with energies comparable to the platinum $d_{x^2-y^2}$ orbital, so that by distortion (Figure 10) the $d_{x^2-y^2}$ orbital can donate charge to the olefin π^* (antibonding) orbital. Thus the availability of the π^* (antibonding) orbitals distorts the olefin out of the plane, facilitating the approach of the entering group.¹³⁶

(2) The withdrawal of charge from the metal to the olefin π^* (antibonding) orbitals stabilizes the five-coordinate trigonal-bipyramidal state. Since the electron density is highest in the equatorial plane where both the entering and leaving groups are located, the olefin will be more effective if it is located in this plane rather than axially.¹³⁶ The excess negative charge on the electron-withdrawing ligand will repel the other ligands, the strongest repulsions being with those ligands bonded at 90° to the olefin. In the trigonal-bipyramidal intermediate there are two such ligands for replacement of a *trans* ligand, but three for replacement of a *cis* ligand, so that electron withdrawal may deactivate *cis* substitution while activating *trans* substitution.¹³⁷ Thus in Zeise's salt, ethylene labilizes the *trans*-chloride ligand^{93,138} but reduces the rate of exchange of *cis*-chloride ligands¹³⁸ and also reduces the acid hydrolysis of the *cis*-chloride ligand by a factor of 0.15.⁹³

(3) Olefins, because they carry no charge, only leave the activated complex with difficulty. By contrast, a negatively charged ligand leaves more readily because not only is it repelled by the other negative ligands present, but also it is readily solvated once it has left the activated complex, providing energy to make the reaction favorable.¹³⁶

Since the *trans*-effect, as observed from kinetic data, depends on the energy relationships present in both the original complex and the transition state, the new term "*trans*-influence" has been introduced. The *trans*-influence is defined as the tendency of a ligand to weaken the bond *trans* to itself.^{139,140} Ligands which exert their *trans*-effect by a π -acceptor mechanism will only cause *trans*-bond weakening if the *trans* bond contains π -bonding. If there is only weak π -bonding in the *trans* bond, that bond may either not be

weakened, or may even be strengthened.³⁴ Thus the *trans*-influence of a ligand depends not only on that ligand but also on the nature of the ligand in the *trans* position.

The early qualitative evidence for the *trans*-effect of olefins was obtained from preparative studies, while the more recent quantitative evidence has been obtained from kinetic data.¹⁴¹ By contrast the evidence for the *trans*-influence of olefins is based on static data obtained from X-ray and infrared studies as well as the acid strengths of aquo complexes. The X-ray and infrared data, which have been discussed in detail under the appropriate headings, may be summarized as follows. The X-ray structure determinations give conflicting results about the possible lengthening or otherwise of the *trans* metal to ligand distance. However, the more recent and accurate work suggests that when chloride or bromide ligands are *trans* to olefin in platinum(II) or palladium(II) complexes, there is no significant bond lengthening.^{19,30,38} In the complex $[\text{PtCl}(\text{MeO}dicyclopentadiene)]_2$ the platinum-chlorine bond *trans* to the σ -bonded carbon atom is 0.17 Å longer than that *trans* to the platinum-olefin bond, indicating that olefins give *trans*-bond shortening relative to alkyl groups.⁷¹

The infrared data have shown that the platinum-chlorine stretching frequency *trans* to an olefin is lower than that *cis* to an olefin.^{56,59,61} However, it has also been found, in agreement with the π -acceptor mechanism for the *trans*-effect of olefins,³⁴ that olefins give a *trans* strengthening of the metal-chlorine stretching frequency relative to phosphines.⁶¹ Nuclear magnetic resonance studies of the complex *trans*- $[\text{PtCl}_2(\text{C}_5\text{H}_5\text{N})(\text{ligand})]$, where the ligand is ethylene or carbon monoxide, have indicated that the rate of exchange of coordinated pyridine with solvent pyridine is much greater for ethylenic than carbonyl complexes suggesting that ethylene is a stronger *trans*-labilizing group than carbon monoxide.¹⁴²

Evidence that olefins may actually cause *trans* bond strengthening if the *trans* bond is a pure σ bond is provided by the acid strengths of the two complexes¹⁴³ $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]^{2+}$ ($\text{p}K_a = 5.6$) and *trans*- $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})(\text{C}_2\text{H}_4)]^{2+}$ ($\text{p}K_a = 3.5$). The greater acidity of the ethylene complex is due to two factors. The *trans*-effect of ethylene strengthens the platinum-oxygen bond and simultaneously weakens the oxygen-hydrogen bond. In addition the π back-donation of charge from platinum to olefin reduces the d electron density on the platinum, decreasing the electrostatic attraction between the platinum d electron density and the hydrogen atoms.

In conclusion there is no unambiguous evidence for bond weakening of σ -bonded ligands bound *trans* to an olefin. σ -Bonded ligands include oxygen, nitrogen, and even chlorine which nuclear quadrupole resonance studies have shown to be an essentially σ -bonded ligand.¹⁴⁴ Thus the high kinetic *trans*-effect of olefins is due to the ability of olefins to stabilize the transition intermediate and direct the incoming nucleophile to the *trans* position, rather than to actual bond weakening of the *trans* metal-ligand bond.

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I. RELATIVE STRENGTHS OF σ AND π COMPONENTS OF THE METAL-OLEFIN BOND

The present discussion is limited to a consideration of the relative strengths of the σ and π components of the platinum-olefin bond, since no data have been obtained for the palladium-olefin bond. Historically the σ bond from metal to ligand was introduced before π back-bonding from metal to ligand. As a result in metal-olefin complexes the σ component has tended to be considered as the main component with the π component adding valuable extra strength but not being dominant. This idea was supported by the dipole moment studies of the platinum(II)-olefin bond which suggested that the olefin was at the positive end of the dipole so that the σ component of the platinum(II)-olefin bond was stronger than the π component.^{5,145} This conclusion has been questioned⁶⁶ on the grounds that it was based on the doubtful value of 6 D for the nitrogen-aluminum σ bond. This value was obtained by considering the complex $C_2H_5NH_2AlCl_3$, which has a dipole moment of 6.9 D.¹⁴⁶ Since the dipole moment of the pyramidal $AlCl_3$ group, which is present in $C_2H_5NH_2AlCl_3$, is about 4 D,¹⁴⁷ a value of 6 D for the nitrogen-aluminum σ bond would seem excessive. There is therefore doubt as to whether the dipole moment studies support a stronger σ than π component of the platinum(II)-olefin bond.

A number of workers have found that the stability of platinum(II)-olefin complexes decreases as the over-all charge on the complex ion becomes more positive.¹⁰⁵ This indicates that when π bonding is greatly reduced as in cationic platinum(II)-olefin complexes the stability of the platinum(II)-olefin bond is greatly decreased, despite the corresponding enhancement of the σ bonding. More recently studies of the stability constants of both platinum(II)-olefin¹⁰⁷⁻¹¹¹ and platinum(0)-acetylene¹²² complexes have suggested that the π component of the platinum-olefin or -acetylene bond is more important for the stability of that bond than the σ component. This suggestion is compatible with other data obtained for these bonds that were previously used to support the reverse conclusion. For example, if the π component is stronger than the σ component, there will be less weakening of the π (bonding) component of the olefin bond than if the reverse is true. However, the greater buildup of electron density in the π^* (antibonding) olefin orbital will greatly weaken the olefin bond. Thus the weakening of the olefin bond on coordination that results in both the lowering of the carbon-carbon double-bond stretching frequency in the infrared spectrum and the lengthening of the olefin bond as observed by X-ray diffraction is consistent with a stronger π than σ component in the platinum-olefin bond.

The decrease in the platinum-olefin stretching frequency on changing the ligand X in [(cyclooctadiene)PtX₂] from chloride to bromide to iodide to methyl to phenyl has been interpreted by assuming that the π component of the platinum(II)-olefin bond is greater than the σ component.¹⁴⁸ The constancy of the ¹⁹⁵Pt-¹H coupling constant, as observed

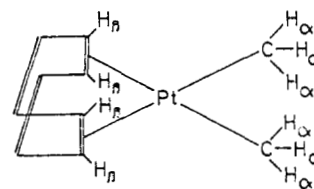


Figure 11. Labeling of the hydrogen atoms in $[Pt(CH_3)_2(COT)]$.

in the nuclear magnetic resonance spectrum, as the halogen is altered, suggests that the σ component has an approximately constant value and that the observed lowering in frequency is due to the easier conjugation between the olefin π^* (antibonding), platinum d, and halogen d orbitals as the halogen increases in atomic weight and radius.¹⁴⁸

The ability of nucleophiles to attack coordinated olefins has also been used to support the idea of a stronger σ than π component. However, even if the π component is stronger than the σ component, there will still be a region of low electron density, suitable for attack by nucleophiles, between the carbon atoms of the double bond.¹⁴⁹ This idea is developed further in section V.A.

The results discussed so far have either suggested that the π component of the platinum-olefin bond is stronger than the σ component, or have been consistent with this concept. However, the nuclear magnetic resonance¹⁵⁰ and infrared data¹⁴⁸ obtained for a series of cyclooctatetraene (COT) complexes, $[PtX_2(COT)]$, have been used to deduce that the percentage contributions of the π components to the platinum(II)-cyclooctatetraene bond were 35, 33, 30, and 56% for X equal to chloride, bromide, iodide, and methyl, respectively.¹⁵⁰ These values were obtained by assuming that for $[Pt(CH_3)_2(COT)]$ (Figure 11) the ratio $(J_{Pt-H_\alpha})/(K_{Pt-CH_3})$ was equal to $(J_{Pt-H_\beta})/(K_{Pt-olefin(\sigma\text{ bond})})$, where J is the nuclear magnetic resonance coupling constant and K is the force constant of the σ bond. In view of the very different nature of the σ bonds between the platinum atom and the olefinic protons on the one hand and the methyl groups on the other hand, the validity of this assumption is open to question. Furthermore the percentages recorded were then obtained by comparing this calculated stretching force constant for the σ bond with the stretching force constant for the platinum(II)-cyclooctatetraene bond evaluated from the infrared data. In calculating this total stretching force constant, the authors appear to have treated the system as containing two independent olefinic bonds, rather than making allowance for the effect of chelation. The presence of chelation will result in the observed platinum-olefin stretching frequency being higher than would have been observed if the platinum(II)-olefin bonds had been of the same strength, but the olefin groups had not been part of a chelate ring. This has the effect that the calculated percentage contributions of the π components of the platinum(II)-olefin bond in cyclooctatetraene-platinum(II) complexes are probably low.

It can be seen that a great deal of work remains to be done on the relative strengths of the σ and π components of the metal-olefin bond. Both components are undoubtedly very important, although on balance it appears that the π component may be slightly more important than the σ component

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for the formation of stable platinum-olefin or -acetylene bonds.

III. Preparation and Properties of Olefin Complexes

A. PREPARATION OF OLEFIN COMPLEXES

1. Complexes of Divalent Platinum and Palladium

There are essentially three methods for the preparation of olefin complexes of divalent platinum and palladium.

1. The treatment of a salt of platinum(II) or palladium(II) with olefin in water has been used where the olefin was soluble in water^{94, 103, 107} (e.g., allylamine), where it was a liquid but insoluble in water (e.g., cyclooctatetraene¹⁵¹ or butadiene¹⁵²), and also with gaseous olefins, such as ethylene, where the use of pressure was necessary.¹⁵³ The reaction, which is normally slow, taking a number of days to go to completion, can be accelerated by the introduction of a trace of stannous chloride catalyst.¹⁵³ Under these conditions the reaction with ethylene is complete within 1.6 hr.

2. The treatment of a salt of platinum(II) or palladium(II) with an olefin in a nonaqueous solvent has been used to prepare the dimer $[\text{PdCl}_2(\text{C}_2\text{H}_4)]_2$ by high-pressure treatment of PdCl_2 in benzene with ethylene,¹⁵⁴ and also to prepare dichloro(norbornadiene)palladium(II) by treating Na_2PdCl_4 with norbornadiene in methanol.¹⁵⁵

3. Displacement of ligands such as benzonitrile has been widely used to prepare olefin complexes of both platinum(II) and palladium(II).^{152, 156} The observation that an excess of one olefin will displace another has also been widely used.¹¹⁴ The olefin to be displaced is generally ethylene since its volatility aids the displacement.

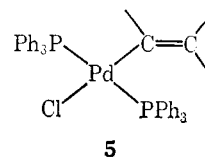
2. Complexes of Zerovalent Platinum and Palladium

A number of methods have been used to prepare complexes of formally zerovalent platinum and palladium.

1. Reduction of $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$ with hydrazine followed by addition of the olefin led to the formation of olefin complexes with *trans*-stilbene, *trans*-4,4'-dinitrostilbene, and acenaphthylene;¹⁵⁷ ethylene, butadiene, hex-1-ene, cyclohexene, allyl alcohol, styrene, and tetraphenylethylene did not react.¹⁵⁷

2. Refluxing $\text{Pt}(\text{PPh}_3)_4$ in benzene with olefins gives olefin complexes with chloroolefins,^{158, 159} fluoroolefins,^{44, 75, 76, 158-160} and tetracyanoethylene.¹⁶¹ By contrast treatment of $\text{Pd}(\text{PPh}_3)_4$

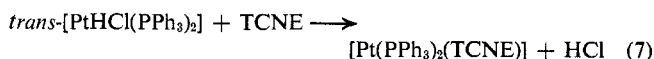
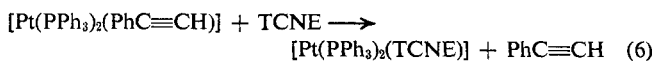
with chloroolefins gives complexes containing palladium-carbon σ bonds (5), although olefins such as maleic anhydride,



ethyl fumarate, and tetracyanoethylene react to give normal olefin complexes of zerovalent palladium.¹⁶²⁻¹⁶⁴ The reaction of chloroolefins is typical of organic halogen compounds, such as methyl iodide, which react with $\text{Pd}(\text{PPh}_3)_4$ to give a palladium-carbon σ bond.¹⁶⁵

3. Olefins which coordinate weakly or which interact with hydrazine can form complexes by reaction with $\text{Pt}(\text{PPh}_3)_2$. This method has been used to prepare complexes with butadiene, 1,5-cyclooctadiene, *n*-pentene, and octene,¹⁶⁶ as well as acrylonitrile, vinyl acetate, and maleic anhydride.¹⁶⁷ $\text{Pt}(\text{PPh}_3)_2$ is formed initially during the preparation of ethylene¹⁶⁸ and tetracyanoethylene¹⁶¹ complexes of platinum(0) by reduction of $\text{PtO}_2(\text{PPh}_3)_2$ with hydrazine or sodium borohydride in the presence of the olefin. The reaction of tetrafluoroethylene with $[\text{PtH}(\text{PPh}_3)_2]^+\text{BF}_4^-$ to give $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{F}_4)$ occurs by a dissociative mechanism in which $\text{Pt}(\text{PPh}_3)_2$ is initially formed.¹⁶⁹

4. Two further reactions (eq 6 and 7) have been used to



prepare tetracyanoethylene (TCNE) complexes.¹⁷⁰ A kinetic investigation of reaction 7 suggested that the most likely mechanism involved the rapid reversible uptake of tetra-cyanoethylene by the hydrido complex to give the octahedral complex $[\text{PtHCl}(\text{PPh}_3)_2(\text{TCNE})]$, which then undergoes a slow loss of hydrogen chloride to yield the final product.¹⁷¹ The octahedral hydrido olefinic complex $[\text{PtHCN}(\text{PEt}_3)_2(\text{TCNE})]$ was isolated during the reaction of the corresponding cyano complex.^{171, 172}

5. The first purely olefinic complex of platinum(0) bis(1,5-cyclooctadiene)platinum(0) was prepared by the ultraviolet irradiation of bis(isopropyl)(1,5-cyclooctadiene)platinum(II) at room temperature under nitrogen for 22 hr.¹⁷³ Attempts to prepare the norbornadiene analog failed.

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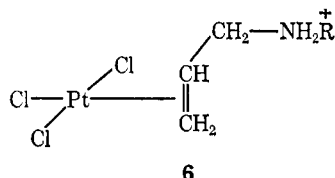
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B. PROPERTIES OF OLEFIN COMPLEXES

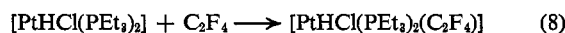
1. Complexes of Monoolefins

a. Complexes of Divalent Platinum and Palladium

Monomeric platinum(II) complexes with unsaturated amines have been prepared and shown, contrary to earlier suggestions,¹⁷⁴⁻¹⁷⁸ to have structure **6** (R = H or alkyl group) in which only the olefin is coordinated to platinum(II).^{94,103} On treatment with alkali the dimeric *trans*-complex **4** in which



both olefin and nitrogen are coordinated to platinum(II) is formed.^{94,103} When the dimeric complex $[\text{PtCl}_2(\text{1-octene})]_2$ is allowed to stand in 1-octene, a white crystalline complex, which is considered on the grounds of color and insolubility to be the monomeric *cis*- $[\text{PtCl}_2(\text{1-octene})_2]$, is formed.¹⁷⁹ Treatment of the dimeric complexes $[\text{PtCl}_2(\text{olefin})]_2$, where olefin = 1-hexene, 1-octene, or styrene, with carbon monoxide gives monomeric *cis*- and *trans*- $[\text{PtCl}_2\text{CO}(\text{olefin})]$ containing both olefin and carbon monoxide,¹⁸⁰ whereas carbon monoxide displaces ethylene from Zeise's salt to give the carbonyl complex¹⁸¹ $\text{K}^+[\text{PtCl}_3\text{CO}]^-$. Although a π -olefin complex of tetrafluoroethylene with platinum(II) was postulated, on the basis of infrared evidence,^{182,183} to be formed in eq 8, the claim was withdrawn¹⁸⁴ when the X-ray structure and chemical analysis showed that the product was *trans*- $[\text{PtCl}$



$(\text{CO})(\text{PEt}_3)_2]^+\text{SiF}_6^-$. This product was formed by insertion of tetrafluoroethylene into the platinum-hydrogen bond, followed by elimination of hydrogen fluoride and hydrolysis of the platinum-carbon σ -bonded complex formed (Figure 12).¹⁸⁵ A series of platinum(II)-olefin complexes containing the oxygen-bonded ligands pyridine N-oxide¹¹⁴ and diphenylcyclopropenone¹⁸⁶ *trans* to the olefin have been prepared. A number of stable nonionic platinum(II)-olefin complexes containing amino acids have been prepared. Infrared and

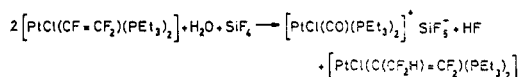
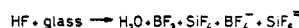
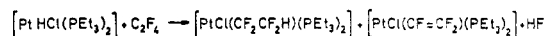
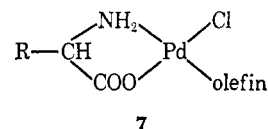


Figure 12. Mechanism for the interaction of platinum(II) complexes with tetrafluoroethylene.

chemical evidence has shown that the olefin is coordinated *trans* to the amino group as in **7**.¹⁸⁷



Monomeric monoolefin complexes of palladium(II) have been detected in solution.¹¹⁷⁻¹²² The only examples of such complexes that have been isolated are those with pyridine N-oxide *trans* to the olefin.¹⁸⁸ Although a number of such complexes have been prepared, only the ethylene complex has been purified. It decomposes rapidly in water to give acetaldehyde and is only stable under an atmosphere of ethylene.¹⁸⁸ When pure PdCl_2 is treated with oct-1-ene or dec-1-ene, it is probable that the initial product is a π -olefin complex which rapidly forms the π -allyl complex with liberation of hydrogen chloride. The π -allyl complex adds a further mole of PdCl_2 giving the π -allyl complex, $[\text{Pd}_3\text{Cl}_4(\text{C}_n\text{H}_{2n-1})_2]$, as the final product.¹⁸⁹ With lower olefins (*e.g.*, ethylene,¹⁹⁰ propylene,¹⁹⁰ butene,¹⁹⁰ pentene,¹⁹⁰ cycloheptene,¹⁹¹ and cyclooctene¹⁹¹) dimeric π -olefin complexes $[\text{PdCl}_2(\text{olefin})]_2$, which are stable in air for a few hours, are formed. The cyclooctene complex is very stable and unlike the cycloheptene complex is not converted into the π -allyl complex on heating.¹⁹¹ But-1-ene, pent-1-ene, hex-1-ene, and oct-1-ene all react with PdCl_2 in dimethylformamide to give π -allylpalladium(II) complexes.¹⁹² The isolation of $[(\text{dimethylformamide})_2\text{H}]_2[\text{Pd}_2\text{Cl}_4]$ from the reaction mixture suggests that dimethylformamide promotes π -allyl complex formation by withdrawing protons from the olefin. In agreement with this, sodium carbonate in chloroform will convert π -olefin-palladium(II) complexes of propene and butene into π -allyl complexes.¹⁹³ Tertiary allylamines react with Li_2PdCl_4 in methanol at room temperature to give complexes such as **8** which contain a palladium(II)-carbon σ bond.¹⁸⁴

Olefins can be recovered from mixtures of gases by forming the palladium(II)-olefin complex, which on heating releases

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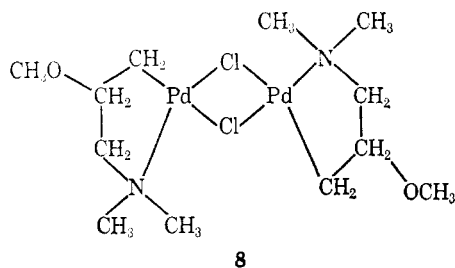
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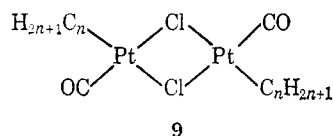
the olefin.¹⁹⁵ Palladium(II) complexes have been used in gas-liquid chromatography columns for the separation of olefins.¹⁹⁶ Platinum(II) complexes have also been examined, but they react too strongly with olefins giving excessively broad peaks.¹⁹⁶

Hydrido complexes of platinum(II) react reversibly with ethylene to give alkyl complexes (eq 9) rather than complexes containing both hydride and olefin ligands.¹⁹⁷ From a study of



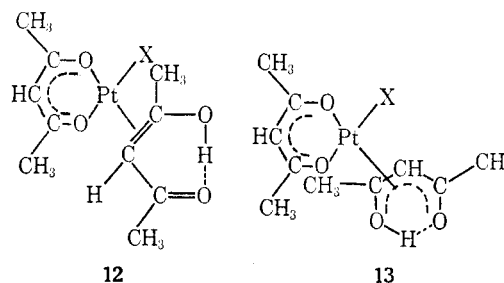
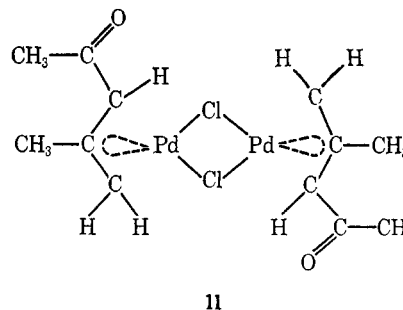
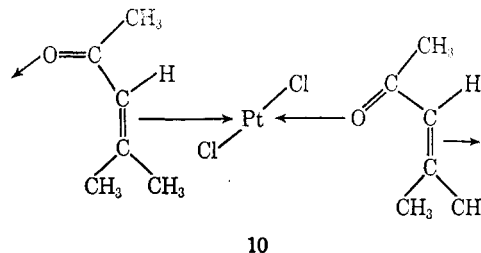
deuterium-labeled complexes, it was shown that the hydrogen atoms attached to either of the carbon atoms of the ethyl group can provide the hydrido ligand.¹⁹⁸ No hydrogen-deuterium exchange between fully deuterated ethylene and undeuterated Zeise's dimer to give monodeuterioethylene was observed at 100° in dilute hydrochloric acid, although a slow exchange was observed in toluene at the same temperature.¹⁹⁹

When platinum(II) complexes were treated with terminal olefins in a dimethylformamide-formic acid solvent, dimeric complexes such as **9** containing both σ -bonded alkyl groups and coordinated carbon monoxide, liberated from the formic

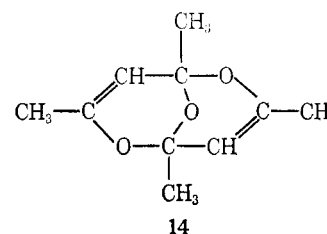


acid, were obtained.^{200,201} Mesityl oxide complexes of platinum(II) and palladium(II) differ markedly in structure. While platinum(II) forms a polymeric olefin complex **10**, palladium(II) forms a π -allyl complex (**11**).^{202,203} This reflects the relative tendencies of the two metals to form olefin and π -allyl complexes.

On acidifying the complexes $\text{K}^+[\text{PtX}(\text{acac})_2]^-$ where acac = acetylacetonate and X = Cl or Br, a complex originally thought to be **12** was isolated.²⁰⁴ However, a reexamination of the data found that the π -allyl structure **13** fitted better.²⁰⁵ On



acidification of the tris(acetylacetonato)platinum(II) complex which contains one conventional oxygen-bonded acetylacetonate ligand and two γ -carbon-bonded ligands in a square-planar arrangement around the platinum, a complex of the diolefin **14**, formed by elimination of water between two acetylacetonate ligands, was formed.²⁰⁶ This unexpected product was con-



firmed by X-ray diffraction.

b. Complexes of Zerovalent Platinum and Palladium

The zerovalent metal-olefin complexes are white crystalline solids that are stable to oxidation by air. They readily exchange the olefin with other ligands.¹⁶⁶ The presence of electronegative substituents seems to be important for the formation of a stable metal(0)-olefin bond,^{157,168,167} suggesting that π back-donation of charge from the metal to the olefin may be even more important than in the divalent metal-olefin complexes. In accordance with this $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ decomposes at¹⁶⁸ 122–125°, whereas the tetracyanoethylene analog decomposes at⁴⁰ 268–270°. A detailed dis-

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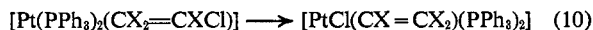
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cussion of the bonding in metal(0)-olefin complexes has been given above under their X-ray structural determinations.

It has been found that $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ dissociates reversibly in benzene solution to give $\text{Pt}(\text{PPh}_3)_2$ and ethylene.²⁰⁷ As a result addition of phenylacetylene to a solution of $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ in benzene gives an immeasurably fast initial reaction due to combination of phenylacetylene with free $\text{Pt}(\text{PPh}_3)_2$ followed by a slower reaction, the kinetics of which are consistent with the formation of $\text{Pt}(\text{PPh}_3)_2$ by loss of ethylene, followed by combination of $\text{Pt}(\text{PPh}_3)_2$ with phenylacetylene.²⁰⁷

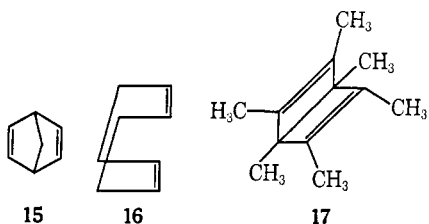
Platinum(0)-olefin complexes of chloroolefins rearrange on heating to give platinum(II) complexes containing platinum-carbon σ bonds (eq 10 where $X = \text{F}$ or Cl).^{44,159} This rearrangement occurs in polar solvents such as ethanol,



which facilitate cleavage of the carbon-chlorine bond, but not in nonpolar solvents.¹⁵⁹ Palladium(0) complexes react with chloroolefins to give complexes containing palladium(II)-carbon σ bonds directly.¹⁶⁴

2. Complexes of Nonconjugated Polyolefins

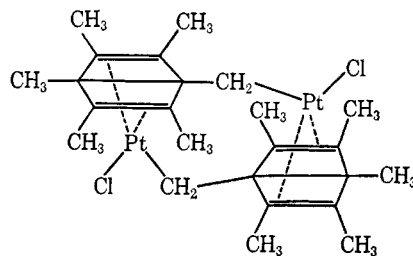
A number of nonconjugated diolefins and higher polyolefins exist in conformations which present the olefinic bonds in ideal arrangements for coordination to metal atoms. Examples of such ligands are norbornadiene (**15**), 1,5-cyclooctadiene (**16**), and Dewar hexamethylbenzene (**17**). Both norbornadiene and 1,5-cyclooctadiene give mononuclear chelate complexes of the



type $[\text{PtX}_2(\text{diolefin})]$, where $X = \text{halogen}$ or alkyl .²⁰⁸⁻²¹⁰ The conditions of reaction of platinum(II) and palladium(II) complexes with cyclooctadiene are critical in determining whether or not the olefin isomerizes during complex formation. Thus complexes of 1,4- and 1,5-cyclooctadiene with both metals have been prepared without any apparent isomerization,^{211,212} whereas under different conditions phosphine complexes of both palladium(II)²¹³ and platinum(II)²¹⁴ isomerize the nonconjugated cyclooctadienes to the 1,3 isomer. The norbornadienepalladium(II) complexes are useful as antiknock additives for fuels.²¹⁵

Dewar hexamethylbenzene (**17**) displaces benzonitrile from

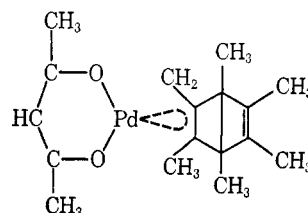
$[\text{PdCl}_2(\text{PhCN})_2]$ to give a monomeric chelate complex which is unstable even in the solid. On adding triphenylphosphine to a solution of the complex, Dewar hexamethylbenzene is liberated, whereas on standing in chloroform solution Kekulé hexamethylbenzene is formed.²¹⁶ A monomeric Dewar hexamethylbenzene complex, $[\text{PtCl}_2(\text{C}_{12}\text{H}_{18})]$, is formed by reaction of Dewar hexamethylbenzene with Na_2PtCl_4 in ethanol.²¹⁷ On treatment with methanolic sodium methoxide, $[\text{PtCl}_2(\text{C}_{12}\text{H}_{18})]$ gives a yellow dehydro complex, which has structure **18**. The platinum-olefin bond *trans* to chlorine in **18**



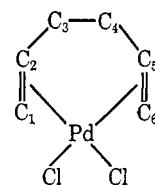
18

is 0.19 Å shorter than that *trans* to the methylene group. This is reflected²¹⁷ in the difference of 0.10 Å in the two olefin bond lengths and the fact that there are two double-bond stretching frequencies in the infrared spectrum, one at 1570 and the other at 1497 cm^{-1} . The iodo analog of $[\text{PtCl}_2(\text{C}_{12}\text{H}_{18})]$ has a π -allylic structure analogous to that of (acetylacetonato)-(Dewar hexamethylbenzene)palladium(II) (**19**).²¹⁸

An X-ray structural investigation²¹⁹ finally established that $[\text{PdCl}_2(\text{hexa-1,5-diene})]$ (**20**) is formed by the addition of allyl chloride to $[\text{PdCl}_2(\text{PhCN})_2]$ at 3-5°. The C_3 - C_4 bond is shortened to 1.46 Å on coordination. Since such a shortening



19



20

requires about 20 kcal/mole of energy, the combined strengths of the two palladium(II)-olefin bonds must be in excess of 20 kcal/mole. Although hexa-1,5-diene can readily displace the olefin in Zeise's salt¹⁵¹ to form $[\text{PtCl}_2(\text{hexa-1,5-diene})]$, it cannot displace the olefin in $[\text{PtCl}_2(\text{pyridine N-oxide})(\text{olefin})]$ complexes.²²⁰ This, together with the observation that pyridine

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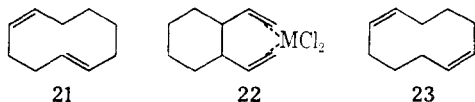
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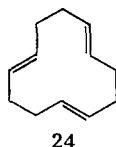
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N-oxide is inert toward complex formation with $[\text{PtCl}_2(\text{hexa-1,5-diene})]$ may be due to the structure of $[\text{PtCl}_2(\text{hexa-1,5-diene})]$, making it impossible to form a trigonal-bipyramidal intermediate.²²⁰

4-Vinylcyclohexene gives monomeric chelate complexes with platinum(II),²²¹ whereas in the presence of $[\text{PdCl}_2(\text{PhCN})_2]$ it rearranges to give $[\text{PdCl}_2(1,5\text{-cyclooctadiene})]$.²²² The driving force for this rearrangement is the greater stability of the palladium(II) complex of 1,5-cyclooctadiene as compared to 4-vinylcyclohexene. 1,5-Cyclodecadiene (**21**) re-

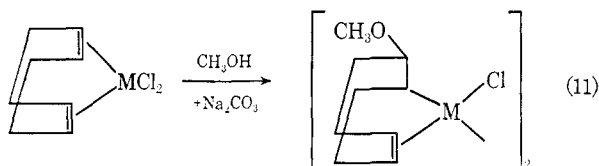


arranges during complex formation to give both platinum(II) and palladium(II) complexes of 1,2-divinylcyclohexane (**22**). It has been suggested that rearrangement occurs via a closed-ring π -allyl intermediate.^{223,224} By contrast 1,6-cyclodecadiene (**23**) gave a palladium(II) complex without rearrangement.²²³ Both the *cis-trans-trans* and *trans-trans-trans* isomers of 1,5,9-cyclododecatriene (CDT) (**24**) give normal π olefin complexes of platinum(II)^{225,226} and palladium-



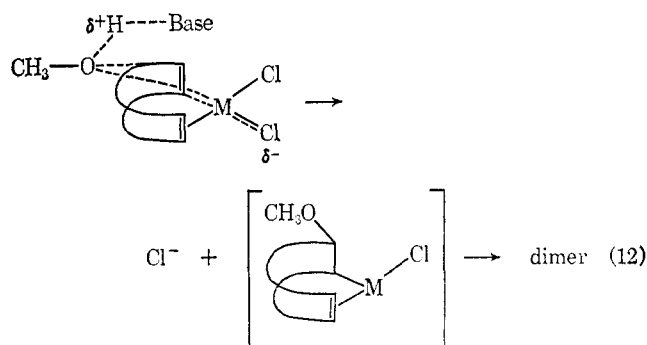
(II).^{225,227} Although the complexes are stable crystalline solids, there must be a certain amount of strain because in solution the platinum(II) complex forms $[\text{Pt}_6\text{Cl}_{12}(\text{CDT})_4]$ in which each olefin molecule is bound to three platinum atoms.²²⁸

Di-olefin complexes of platinum(II)²²⁸ and palladium(II)²²⁹ react with alkaline methanol to give complexes containing a metal-olefin π bond and a metal-carbon σ bond (eq 11). In hot methanol some decomposition to palladium metal is



observed,²²⁹ although in cold methanol the product is obtained in 93% yield.²³⁰ An X-ray determination of the struc-

ture of the dimeric methoxydicyclopentadiene-platinum(II) complex has confirmed the presence of a metal-olefin π bond and a metal-carbon σ bond and excluded the possibility of a π -allyl structure.⁷¹ The coordination around the platinum atom is square planar. A number of studies have been made of the stereochemistry of eq 11 with dicyclopentadiene, norbornadiene, and bicyclo[2.2.1]heptadiene complexes of platinum(II) and palladium(II).²³¹⁻²³⁵ In all cases the methoxy group was found to have an *exo* configuration, indicating that nucleophilic attack of the double bond had occurred from the side opposite to the metal (eq 12). The chloro bridge



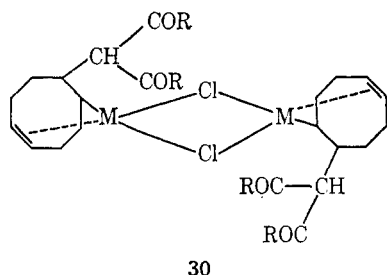
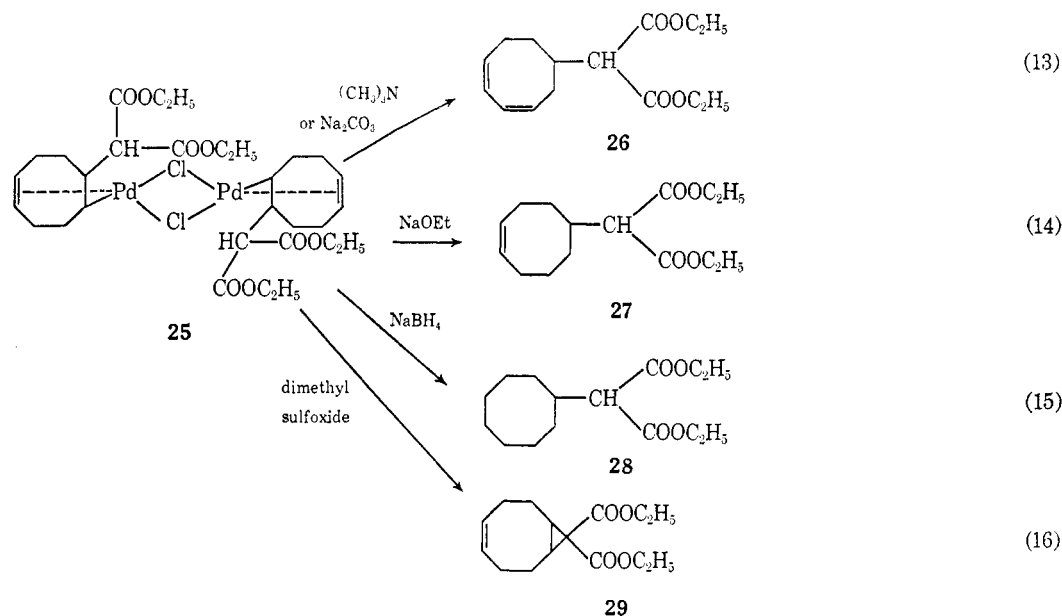
in the dimeric methoxydicyclopentadiene-platinum(II) complex can be split using sodium cyclopentadienide to give π -cyclopentadienyl(methoxydicyclopentadiene)platinum(II).²³⁶

Nucleophiles such as amines and carboxylate ions react with di-olefin complexes in a similar manner to alkoxides.²³⁷ The products obtained by the addition of carbanions such as ethyl malonate to $[\text{PdCl}_2(\text{cycloocta-1,5-diene})]$ (**25**) undergo interesting decomposition reactions in the presence of bases.^{238,239} Thus with trimethylamine or sodium carbonate the conjugated di-olefin **26** is formed (eq 13), with sodium ethoxide the mono-olefin **27** is formed (eq 14), and with sodium borohydride the saturated compound **28** is formed (eq 15). The cyclopropane derivative **29** is formed when the complex is decomposed in dimethyl sulfoxide (eq 16).

A number of compounds containing both metal-carbon σ bonds and metal-olefin π bonds of the general formula $[(\text{diene-diketone})\text{M}(\text{diketone})]$ (where $\text{M} = \text{Pt}$ or Pd and diene = cycloocta-1,5-diene, norbornadiene, or dicyclopentadiene) have been prepared.²⁴⁰ With halogen acids these give dimeric complexes such as **30**. When dimeric complexes containing a metal-carbon σ bond and a metal-olefin π bond (e.g., **25** or **30**) are treated with triphenylphosphine, the halogen bridge is split and a monomeric complex with triphenylphosphine *cis* to the metal-carbon σ bond is formed.²⁴⁰

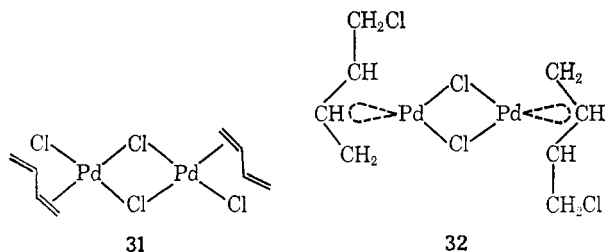
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3. Complexes of Conjugated Polyolefins

Conjugated diolefins generally form π -allylic complexes with palladium(II), although platinum(II) forms true olefin complexes with these ligands.²⁴¹ 1,3-Butadiene reacts with dimeric complexes $[\text{PtX}_2(\text{PEt}_3)_2]_2$, where X = halogen, to give the butadiene-bridged complexes $[(\text{PEt}_3)_2\text{X}_2\text{Pt}(\text{C}_4\text{H}_6)\text{PtX}_2(\text{PEt}_3)]_2$ in which butadiene coordinates to both platinum atoms.²⁴² At -40° 1,3-butadiene gives quantitative displacement of pentene from $[\text{PdCl}_2(\text{pentene})]_2$ to give the olefin complex 31.²⁴³ Above -20° this complex is unstable, and at room temperature it isomerizes to give the π -allylic complex 32, which is the normal product obtained at room temperature.⁵⁰ By contrast 1,3-cyclooctadiene displaced pentene to give an olefin complex that was stable up to its melting point (110°).²⁴³ The infrared spectra of 31 and its 1,3-cyclooctadiene analog both



showed one free olefin (1660 cm^{-1}) and one coordinated

olefin (1500 cm^{-1}) stretching frequency, indicating that the ligands were truly monodentate. Although 1,3- and 1,5-cyclooctadiene gave two distinct complexes with palladium(II),^{191,212,244} displacement of benzonitrile from $[\text{PdCl}_2(\text{PhCN})_2]$ by 1,3-cyclooctadiene led exclusively to the formation of $[\text{PdCl}_2(1,5\text{-cyclooctadiene})]$.²⁴⁵ Spectroscopic studies indicated that the complex $[\text{Pt}(\text{CH}_3)_2(\text{cyclopentadiene})]$ was a diolefin rather than π -allylic complex.²⁴⁶ Cycloheptatriene reacts with Zeise's salt or its dimer to give the olefin complex $[\text{PtCl}_2(\text{C}_7\text{H}_8)]$, which is also formed together with the cycloheptatrienylium salt $(\text{C}_7\text{H}_7^+)_2(\text{PtCl}_6)^{2-}$ on addition of cycloheptatriene to a solution of chloroplatinic acid in glacial acetic acid.^{209,247}

A spectroscopic investigation of the cyclooctatetraene complexes $[\text{PdCl}_2(\text{C}_8\text{H}_8)]$ and $[\text{PtI}_2(\text{C}_8\text{H}_8)]$ has shown no frequencies in the infrared assignable to free double bonds and a single proton resonance signal in the nuclear magnetic resonance spectrum of the palladium(II) complex in dimethylformamide or benzonitrile.¹⁵⁶ This evidence, which led to the conclusion that the cyclooctatetraene ring must be almost planar, has been questioned since it is possible that in the polar solvents used the olefin is displaced from the complex giving rise to the single proton resonance signal that is observed in the free olefin.²⁴⁸ This together with the weak band at 1635 cm^{-1} observed subsequently in the platinum complex suggests that the cyclooctatetraene exists in the tub conformation.²¹⁰ $[\text{PtI}_2(\text{C}_8\text{H}_8)]$ reacts with Grignard reagents to form both mononuclear (33) and binuclear (34) cyclooctatetraene alkyls and aryls, which are thermally very stable.^{210,249} The mononuclear complexes exhibit a weak band at about 1635 cm^{-1} in the infrared which may be due to the uncoordinated double bonds, whereas the binuclear complexes do not exhibit such a band. Although $[\text{PdBr}_2(\text{C}_8\text{H}_8)]$ could not be prepared

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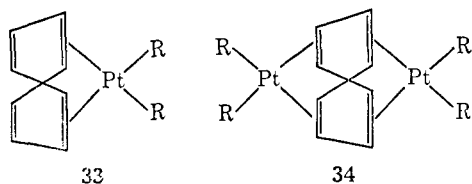
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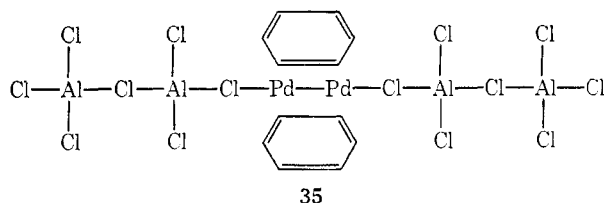
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from Na_2PdBr_4 , it has been prepared from $[\text{PdBr}_2(\text{PhCN})_2]$.²⁵⁰

The "conjugated polyolefin" benzene gives an interesting bisarene complex of palladium(II) (35). The palladium-palladium bond length²⁵¹ is 2.58 Å, which is the shortest distance found so far for this metal-metal bond.²⁵²



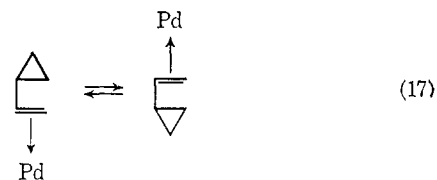
4. Complexes of Three-Membered Ring Systems

Attempts to prepare a triphenylcyclopropene complex of platinum by displacement of ethylene from Ziese's salt failed to yield the desired product. Instead $(\text{Ph}_3\text{C}_3)^+[\text{PtCl}_3(\text{C}_3\text{H}_4)]^-$ was obtained, indicating that the triphenylcyclopropenyl ion is too electronegative to act as a symmetrical π ligand even with platinum(II) where a strong back-donation of charge from the metal d orbitals is possible.²⁵³ The palladium π complex $[(\text{Ph}_3\text{C}_3)\text{PdCl}_2\text{PdCl}_2\text{Pd}(\text{C}_3\text{Ph}_3)]$ has been claimed to result from the reduction of PdCl_2 in aqueous methyl cyanide in the presence of triphenylcyclopropenyl chloride.²⁵⁴

Cyclopropane reacts with platinum(IV) complexes to give a polymeric complex $[\text{PtCl}_2(\text{C}_3\text{H}_6)]_n$. With pyridine this gives a monomeric complex $[\text{PtCl}(\text{pyridine})_2(\text{C}_3\text{H}_6)]$ which has been shown by X-ray diffraction to contain a four-membered C-C-C-Pt ring.²⁵⁵ It has been claimed that the cyclopropyl group is present in $[\text{Pd}_2\text{Cl}_4(\text{C}_3\text{H}_6)_2]$ prepared by treating $[\text{PdCl}_2(\text{PhCN})_2]$ with allyl chloride in benzene at room temperature.²⁵⁷ This is surprising since allyl chloride reacts with PdCl_2 in 50% acetic acid,²⁵⁸ or in methanol in the presence of carbon monoxide,²⁵⁹ to give the π -allyl complex $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$.

A vinylcyclopropane complex of palladium was prepared by treating the dimeric $[\text{PdCl}_2(\text{C}_2\text{H}_4)]_2$ with vinylcyclopropane.²⁶⁰ Although the infrared spectrum indicates the presence

of both a double bond and a cyclopropyl group, the nuclear magnetic resonance spectrum shows neither, indicating that a rapid hydrogen transfer occurs (eq 17). On heating to 40° in benzene the complex forms two π -allyl complexes of 1,3-



pentadiene,²⁶⁰ $[\text{PdCl}(\pi\text{-CH}_3\text{CHClCHCH}_2)]_2$ and $[\text{PdCl}(\pi\text{-CH}_2\text{ClCH}_2\text{CHCH}_2)]_2$.

5. Complexes of Olefins That Contain Additional Donor Groups

A number of olefins have been prepared which contain additional donor groups. For example, 2-allylpyridine binds to platinum through both nitrogen and olefin,²⁶¹ to give the monomeric complex *cis*- $[\text{PtCl}_2(2\text{-CH}_2=\text{CHCH}_2\text{C}_5\text{H}_4\text{N})]$. By contrast a series of primary and secondary amines of the type $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{NHR}$ (where R = H or *n*-octyl and *n* = 1 or 3) were found to give *trans*-dimeric complexes (4).^{94,103} The ligands analogous to 2-allylpyridine with *n* = 2 give insoluble polymeric materials.¹⁰³ The pentenylphosphine and -arsine ligands $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{LPh}_2$ (L = P or As) give monomeric chelate complexes in which both the group V donor atom and olefin are bound to platinum.^{262,263} With palladium dimeric complexes are formed in which the olefinic double bond is not coordinated to palladium.²⁶³ This could indicate that only platinum has the correct steric requirements for chelation by these ligands or may be due to the complexes formed by palladium(II) with the group V donors being more stable than palladium(II)-olefin complexes. The more sterically constrained *o*-styryldiphenylphosphine, *o*-styryldimethylarsine, and but-3-enyl di(cyclohexyl)phosphine form chelate complexes $[\text{MX}_2(\text{ligand})]$, where M = Pt and X = Cl and Br, in which both the group V atom and the olefin are both bound to platinum.²⁶⁴⁻²⁶⁶ These complexes react with iodide and thiocyanate to give a variety of complexes in which the double bond may or may not remain coordinated. These studies, together with the double-bond stretching frequencies in the infrared spectra (Pt(II), 1500 cm^{-1} ; Pd(II), 1530 cm^{-1}), suggested that the platinum(II)-olefin bond is stronger than the palladium(II)-olefin bond.²⁶⁶

The results obtained with unsaturated sulfides are similar to those obtained with unsaturated phosphines in that but-3-enyl (butyl) sulfide gives chelate complexes with both platinum(II) and palladium(II), whereas pent-4-enyl (butyl) sulfide only forms chelate complexes with platinum(II).²⁶⁷ The two ligands 36 with *n* = 2 and 3 both form chelate complexes with platinum(II) and palladium(II) in which only the sulfur atoms are bound to the metal.²⁶⁷ A study of the platinum(II) and

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(257) I. A. Zakharova and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1914 (1964); *Chem. Abstr.*, **62**, 4052a (1965).

(258) R. Huettel and J. Kratzer, *Angew. Chem.*, **71**, 456 (1959).

(259) W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964).

(260) A. D. Ketley and J. A. Braatz, *J. Organometal. Chem. (Amsterdam)*, **9**, 5 (1967).

(261) R. E. Yingst and B. E. Douglas, *Inorg. Chem.*, **3**, 1177 (1964).

(262) H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *Proc. Chem. Soc.*, 220 (1961).

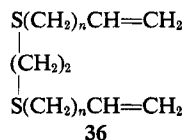
(263) M. A. Bennett, H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 4570 (1964).

(264) K. Issleib and M. Haftendorn, *Z. Anorg. Allgem. Chem.*, **351**, 9 (1967).

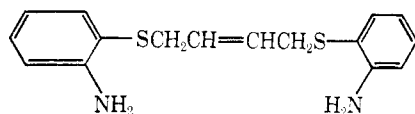
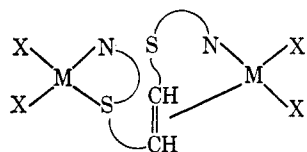
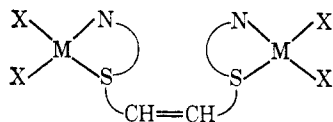
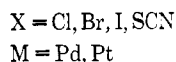
(265) M. A. Bennett, J. Chatt, G. J. Erskin, J. Lewis, R. F. Long, and R. S. Nyholm, *J. Chem. Soc., A*, 501 (1967).

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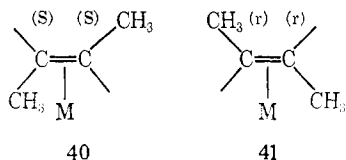
palladium(II) complexes of **37** has shown that the two metal atoms present in each complex are in different environments. This is consistent with structure **38** but not **39** and indicates

**37****38****39**

that olefins coordinate more strongly than thioethers to platinum(II) and palladium(II).²⁶⁸

6. Complexes of Optically Active Olefins

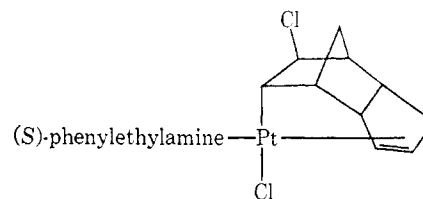
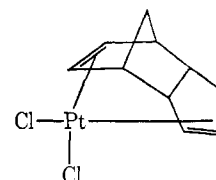
Olefins which have no symmetry planes perpendicular to the plane of the double bond (*e.g.*, *trans*-but-2-ene or propene) can coordinate to a metal in two enantiomorphous ways (**40** and **41**). If an optically active ligand (*e.g.*, 1-phenylethylamine) is also incorporated in the complex, then two diastereo-

**40****41**

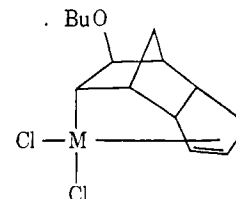
isomers are formed, which can be separated by fractional crystallization. The two diastereoisomers of [PtCl₂{(-)-(*S*)-1-phenylethylamine}(olefin)], where olefin = *trans*-but-2-ene, propylene, and styrene, have been observed in solution,²⁶⁹ although with propylene and styrene only one diastereoisomer can be obtained as a crystalline product.²⁷⁰ With *trans*-but-2-ene only one crystalline diastereoisomer can be obtained from one particular solvent, but the particular diastereoisomer obtained depends on the solvent used.²⁷⁰ Preliminary X-ray analyses have been commenced to determine the absolute configuration of these complexes.^{271, 272} Platinum(II) com-

plexes containing optically active 1-phenylethylamine have been used to partially resolve a number of 1-olefins in which the asymmetric carbon atom is α or β to the double bond. When *cis*-platinum(II) complexes are used, the 1-olefin whose chirality is the same as that of the amine is preferentially complexed, whereas the reverse is true when *trans*-platinum(II) complexes are used.²⁷³

The two diastereoisomers of **42** were separated and after treatment with hydrochloric acid optically active **43** was isolated, from which by addition of sodium cyanide optically active *endo*-dicyclopentadiene was obtained for the first

**42****43**

time.^{274, 275} The enantiomeric [MCl₂(*endo*-dicyclopentadiene)] complexes, where M = Pt or Pd, both react with an excess of *DL*-*sec*-butyl alcohol to give the corresponding *sec*-butoxy-dicyclopentadiene complexes **44**. The unreacted alcohol was recovered and found to be optically active indicating an asym-

**44**

metric induction in the butoxylation reaction.²⁷⁵

cis,trans-1,5-Cyclooctadiene was partially resolved into its two enantiomorphs using 1-methylphenylethylamine as the optically active ligand²⁷⁶ and completely resolved using 1-methylbenzylamine,²⁷⁷ which was also used to resolve *trans*-cyclooctene.²⁷⁸ The failure of 1-methylbenzylamine to achieve a resolution of the optically active **45** was ascribed to a rapid rotation of the *trans*-olefinic linkage causing spontaneous racemization of the olefin.²⁷⁹ Equilibrium constants for reaction 18 were found to be unity for *trans* complexes,²⁸⁰ but

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(269) G. Paiaro, P. Corradini, R. Palumbo, and A. Panunzi, *Makromol. Chem.*, **71**, 184 (1964).

(270) G. Paiaro and A. Panunzi, *J. Am. Chem. Soc.*, **86**, 5148 (1964).

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(272) P. Corradini, P. Ganis, and C. Pedone, *Acta Cryst.*, **20**, 458 (1966).

(273) R. Lazzaroni, P. Salvadori, and P. Pino, *Tetrahedron Lett.*, 2507 (1968).

(274) G. Paiaro, A. Panunzi, and A. De Renzi, *ibid.*, 3905 (1966).

(275) A. Panunzi, A. De Renzi, and G. Paiaro, *Inorg. Chim. Acta*, **1**, 475 (1967).

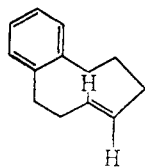
(276) A. C. Cope, C. R. Ganellin, and H. W. Johnson, *J. Am. Chem. Soc.*, **84**, 3191 (1962).

(277) A. C. Cope, J. K. Hecht, H. W. Johnson, H. Keller, and H. J. S. Winkler, *ibid.*, **88**, 761 (1966).

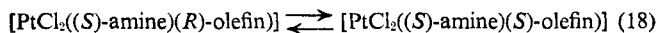
(278) A. C. Cope, C. R. Ganellin, H. W. Johnson, T. V. Van Auken, and H. J. S. Winkler, *ibid.*, **85**, 3276 (1963).

(279) A. C. Cope and M. W. Fordice, *ibid.*, **89**, 6187 (1967).

(280) G. Paiaro and A. Panunzi, *Tetrahedron Lett.*, 441 (1965).



45



noticeably different from unity for *cis* complexes, because of steric interaction between the amine and the *cis*-coordinated olefin, although this effect was only observable for 1,2-disubstituted olefins.²⁸¹ As a result of this when *cis*-[PtCl₂(1-phenylethylamine)(C₂H₄)] was equilibrated with (*R,S*)-*trans*-cyclooctene, the unreacted olefin contained an excess of the (−) isomer, whereas treatment of the complex with potassium cyanide and examination of the olefin liberated indicated an excess of the (+) isomer to be present.²⁸²

IV. Preparation and Properties of Acetylene Complexes

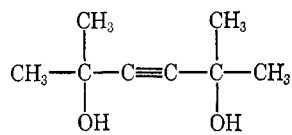
A. PREPARATION OF ACETYLENE COMPLEXES

Acetylene complexes are prepared by the same general methods as have already been described for olefin complexes.

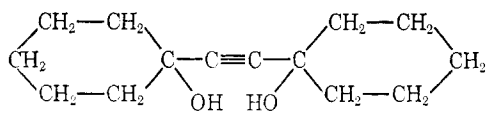
B. PROPERTIES OF ACETYLENE COMPLEXES

1. Complexes of Divalent Platinum and Palladium

Hydroxyacetylenes such as **46** and **47** coordinate more strongly



46



47

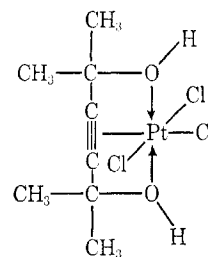
to platinum(II) than ethylene or styrene to form stable complexes of the type [PtCl₂(ac)][−] where ac = acetylene.^{283–285} On coordination to platinum(II) the triple-bond stretching frequency in the infrared is lowered by about 200 cm^{−1}, which is consistent with the formation of a platinum(II)–acetylene π bond.²¹ In addition the O–H stretching frequency is lowered by about 125 cm^{−1} on coordination.^{21, 286, 287} There are three possible explanations for this.

1. One is coordination of the hydroxyl oxygen to platinum(II). This was originally rejected on the infrared evidence that the hydroxyl hydrogen atom was not free to form a

hydrogen bond with a base such as dioxane (0.1 *M*) in carbon tetrachloride.²¹ However, more recent work has shown that intermolecular hydrogen bonding can be observed if either higher concentrations of dioxane or stronger bases are used.^{286, 287} The weakness of this hydrogen bonding is consistent with the presence of essentially tertiary alcohols. The observation that the corresponding methoxyacetylenes give complexes that are as stable as those of the hydroxyacetylenes further supports the suggestion of oxygen to platinum bonding.²⁸⁸

2. Hydrogen bonding between the hydroxyl group and the metal atom is most unlikely since the hydroxyl proton resonance occurs at lower field than in the free ligand.²¹ This is consistent with alternatives 1 or 3 but not 2.

3. Hydrogen bonding between the hydroxyl group and the *cis*-chlorine ligands in K⁺[PtCl₃{(CH₃)₂(HO)CC≡CC(OH)(CH₃)₂}][−] was considered the most likely explanation on the grounds that the platinum(0) complex [Pt(PPh₃)₂{(CH₃)(C₂H₅)(HO)CC≡CC(OH)(C₂H₅)(CH₃)}], which contains no chlorine atoms, has an O–H stretching frequency identical with that of the free ligand.²¹ This argument may not be valid since platinum(II) is a much better electron-acceptor than platinum(0) so that coordination of the hydroxyl oxygen to platinum may well occur in the platinum(II) but not platinum(0) complexes.^{286, 287} Since a hydrogen bond to chlorine and bromine would be expected to give rise to different O–H stretching frequencies, the fact that this frequency in the analogous bromo complex is almost identical with that in the chloro complex is strong evidence for hydroxyl oxygen to platinum(II) bonding.^{286, 287} Thus the most probable structure of the platinum(II)–hydroxyacetylene complexes is **48**. The thermal decomposition of these complexes to yield platinum



48

has been used to prepare active platinum metal catalysts.²⁸⁹

A series of cationic platinum(II) complexes of the general formula [PtX(en)(ac)]_n⁺, where *n* = 1 or 2, X = Cl, Br, and I, ac = **46**, and en = ethylenediamine, have been prepared.²⁹⁰ In contrast to the cationic olefin complexes, which are unstable,²⁹¹ the acetylene complexes are stable for long periods in a desiccator and short periods in moist air. In aqueous solution they decompose to give the free acetylene and *cis*-[PtX₂(en)].

Alkynylsilanes react with platinum(II)–olefin complexes to give carbon–silicon bond cleavage (eq 19) rather than forming a π complex.²⁹²

(281) A. Panunzi and G. Paiaro, *J. Am. Chem. Soc.*, **88**, 4843 (1966).

(282) P. Corradini, G. Paiaro, A. Panunzi, S. F. Mason, and G. H. Searle, *ibid.*, **88**, 2863 (1966).

(283) K. A. Molodova, *Uch. Zap. Leningr. Gos. Ped. Inst. im A. I. Gertsieva*, **160**, 151 (1959); *Chem. Abstr.*, **55**, 6236g (1961).

(284) S. V. Bukhovets and A. O. Sheveleva, *Zh. Neorgan. Khim.*, **9**, 471 (1964); *Chem. Abstr.*, **60**, 10182b (1964).

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(286) T. Theophanides, *Dissertation Abstr.*, **25**, 821 (1964).

(287) A. D. Allen and T. Theophanides, *Can. J. Chem.*, **44**, 2703 (1966).

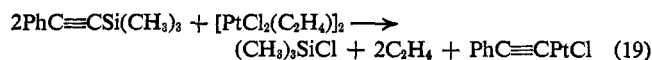
(288) A. D. Allen and T. Theophanides, *ibid.*, **43**, 290 (1965).

(289) S. V. Bukhovets, USSR Patent 105,486 (1965); *Chem. Abstr.*, **64**, 16700c (1966).

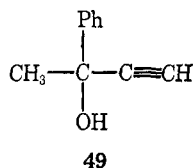
(290) P. Kong and T. Theophanides, *Can. J. Chem.*, **45**, 3193 (1967).

(291) A. D. Gel'man and E. A. Meilakh, *Compt. Rend. Acad. Sci. URSS*, **51**, 207 (1946); *Chem. Abstr.*, **40**, 7042^g (1946).

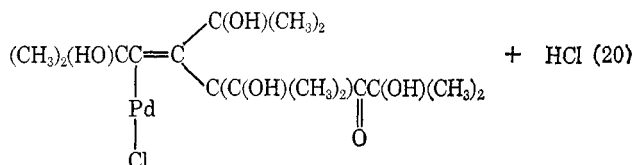
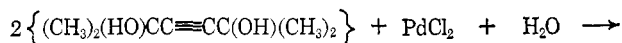
(292) J. E. Poist and C. S. Kraihanzel, *Chem. Commun.*, 607 (1968).



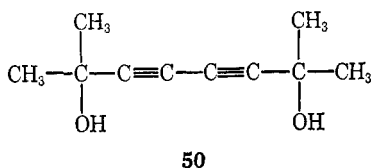
The palladium(II) complexes of acetylenes are more complex and less well understood than the platinum(II) complexes because of the fact that acetylenes are very rapidly polymerized by palladium(II) compounds.⁴⁸ Thus **49** forms complexes of the type $[\text{PdX}(\text{ac})_4]$,²⁹³ where X = Cl, Br, I, and SCN, and ac = **49**, in which weak bands at about 1540 cm^{-1} in the



infrared spectra have been assigned to olefinic double bonds coordinated to palladium(II).²⁹⁴ **46** when treated with PdCl_2 in the ratios 1:1, 2:1, and 4:1 always gives the complex $[\text{PdCl}(\text{ac})_2]$.²⁹⁵ This complex shows no infrared bands that can be identified with the triple bond. However, bands at about 1700 and 1630 cm^{-1} have been assigned to carbonyl and double-bond stretching frequencies, respectively.²⁹⁴ Equation 20 has been suggested to account for these observations.⁶⁴ The formation of a carbonyl group is consistent



with the ability of palladium(II) salts to oxidize acetylenes to carbonyl compounds.²⁹⁶ **50** gives stable complexes²⁹⁷ of the type $[\text{Pd}(\text{OH})\text{X}(\text{ac})]$ where X = Cl, Br, I, and SCN



and ac = **50**. No spectral or structural information on these complexes has yet been published.

51 reacts with PdCl_2 in benzene to give $[\text{PdCl}_2(\text{C}_{14}\text{H}_{28})]$ which exhibits a triple-bond stretching frequency in the infrared at 2220 cm^{-1} . When the reaction is carried out in methanol, $[\text{PdCl}_2(\text{C}_{14}\text{H}_{28}\text{O})]$ is formed.²⁹⁸ Both these complexes have been assigned cyclobutadiene-type structures (**52**).²⁹⁹ On

(293) A. V. Babaeva and T. I. Beresneva, *Zh. Neorgan. Khim.*, **11**, 2671 (1966); *Chem. Abstr.*, **66**, 43298 (1967).

(294) A. V. Babaeva, T. I. Beresneva, and Yu. Ya. Kharitonov, *Dokl. Akad. Nauk. SSSR*, **175**, 591 (1967); *Chem. Abstr.*, **68**, 68388 (1968).

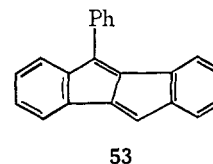
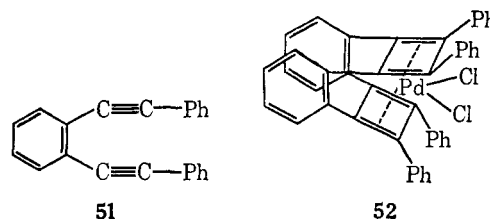
(295) A. V. Babaeva and T. I. Beresneva, *Zh. Neorgan. Khim.*, **11**, 1966 (1966); *Chem. Abstr.*, **65**, 16477b (1966).

(296) O. N. Temkin, S. M. Brailovskii, R. M. Flid, M. P. Strukova, V. B. Belyanin, and M. G. Zaitseva, *Kinetika i Kataliz*, **5**, 192 (1964); *Chem. Abstr.*, **60**, 13127h (1964).

(297) A. V. Babaeva and T. I. Beresneva, *Zh. Neorgan. Khim.*, **12**, 2520 (1967); *Chem. Abstr.*, **67**, 121895 (1967).

(298) E. Mueller, K. Munk, P. Ziemek, and M. Sauerbier, *Naturwissenschaften*, **54**, 563 (1967).

(299) E. Mueller, K. Munk, P. Ziemek, and M. Sauerbier, *Ann. Chem.*, **713**, 40 (1968).

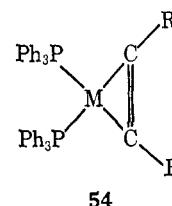


addition of triphenylphosphine to $[\text{PdCl}_2(\text{C}_{14}\text{H}_{28})]$, palladium metal and five hydrocarbons, one of which was shown to be **53**, are formed.²⁹⁸

The complexes formed between palladium(II) and either isopropenylacetylene or ethynylbenzene have been used in the photometric determination of palladium.³⁰⁰ None of the metals iron, cobalt, nickel, copper, manganese, gold, chromium, and platinum interfere, although some of these metals can form complexes with acetylenes.

2. Complexes of Zerovalent Platinum and Palladium

A number of acetylene complexes of formally zerovalent platinum and palladium have been prepared. Platinum complexes of the type **54** have been prepared by hydrazine reduction of $[\text{PtCl}_2(\text{PPh}_3)_2]$ in the presence of the acetylene,



although with palladium this route was unsuccessful.⁴⁸ The platinum complexes can, however, be prepared by displacement of two of the phosphine ligands in $[\text{Pt}(\text{PPh}_3)_4]$ by the acetylene.⁴⁸ Other preparative routes to these complexes that have been used are reaction of the acetylene with $[\text{Pt}(\text{PPh}_3)_2]$ ¹⁶⁶ and exchange of one acetylene with another.^{166, 301} Equilibrium and kinetic studies on this latter reaction have indicated that the metal-acetylene bond strength is increased when electron-withdrawing substituents are adjacent to the acetylenic bond.^{181, 182} The greater strength of the platinum(0)-acetylene bond than the palladium(0)-acetylene bond is indicated by the greater lowering of the triple-bond stretching frequency in the infrared spectrum on coordination to platinum(0) as compared with palladium(0) (Table V).

A benzene complex of nickel has recently been reported.³⁰² However, attempts to prepare benzyne complexes of platinum by treating $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ with either benzenediazonium-1,2-carboxylate or benzo-1,2,3-thiadiazole 1,1-dioxide, which are diazonium precursors of benzyne, have so far failed,

(300) M. Ziegler and W. Buchholz, *Z. Anal. Chem.*, **210**, 344 (1965).

(301) J. L. Boston, S. O. Grim, and G. Wilkinson, *J. Chem. Soc.*, 3468 (1963).

(302) E. W. Gowling, S. F. A. Kettle, and G. M. Sharples, *Chem. Commun.*, 21 (1968).

Table V

Stretching Frequencies of the Triple Bond in the Infrared

Compound	$\nu_{\text{C}\equiv\text{C}}, \text{cm}^{-1}$	Ref
$\text{CF}_3\text{C}\equiv\text{CCF}_3$	2300 ^a	c
$(\text{Ph}_3\text{P})_2\text{Pd}(\text{C}_4\text{F}_6)$	1811, 1838	48
$(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_4\text{F}_6)$	1775	301
$\text{CH}_3\text{OOC}\equiv\text{CCOOCCH}_3$	2150	55
$(\text{Ph}_3\text{P})_2\text{Pd}(\text{CCOOMe})_2$	1845, 1830 ^b	d
$(\text{Ph}_3\text{P})_2\text{Pt}(\text{CCOOMe})_2$	1782, 1765 ^b	48

^a Raman. ^b Shoulder. ^c F. A. Miller and R. P. Bauman, *J. Chem. Phys.*, **22**, 1544 (1954). ^d E. Dallwigk, H. Paillard, and E. Briner, *Helv. Chim. Acta*, **36**, 1757 (1953).

although interesting cyclic azo complexes of platinum have been isolated.³⁰³ Until further investigations have been made, it is impossible to decide whether the failure to prepare the benzyne complex is due to an inherent instability in the platinum-benzyne bond or to the stability of the cyclic azo complexes. A cyclooctyne complex of platinum(0), $[\text{Pt}(\text{PPh}_3)_2(\text{C}_8\text{H}_{12})]$, has been prepared by addition of cyclooctyne to $[\text{Pt}(\text{PPh}_3)_4]$.³⁰⁴

The X-ray structure of $[\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CPh})]$ ⁴¹ and the nature of the bonding in these complexes has been discussed in section II.B.

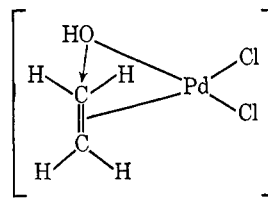
V. Nucleophilic Attack on Coordinated Olefins

A. INTRODUCTION

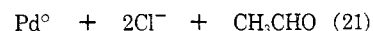
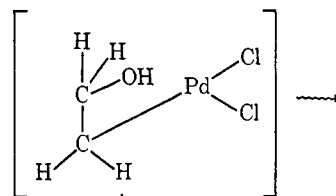
A number of examples of nucleophilic attack on olefins coordinated to metal ions are known. Complex formation reduces the electron density between the carbon atoms, rendering the double bond more susceptible to nucleophilic attack. An interesting difference occurs between the stereochemistry of nucleophilic attack on coordinated chelating diolefins and on monoolefins, since the former give *trans* addition of nucleophiles across the double bond (eq 12),²⁸¹⁻²⁸⁴ whereas the kinetic results for the oxidative hydrolysis of monoolefins coordinated to palladium(II) are only consistent with *cis* addition.^{117,305} Although at low temperature (25°) diolefins give *trans* addition of methoxide ion to the double bond and no reduction to the metal,²⁸⁰ at higher temperatures reduction to palladium metal is observed²²⁹ and vinyl ethers, which are the normal oxidative addition products,³⁰⁶ are isolated.²⁸⁰ Thus for diolefin complexes *trans* addition is favored at low temperatures, whereas for monoolefin complexes it is *cis* addition that is favored at low temperatures. In the oxidative acetylation of monoolefins coordinated to palladium(II), both *cis*- and *trans*-addition mechanisms occur simultaneously.³⁰⁷

It has been suggested³⁰⁸ that *cis* addition to monoolefins occurs at lower temperatures than *trans* addition because the monoolefins are free to rotate about the metal-olefin bond. This rotation would enable the oxidative hydrolysis to occur by a mechanism such as eq 21 in which the two carbon

atoms and the oxygen atom in **55** lie in an approximately straight line. However, such a rotation would present the



55



π^* (antibonding) olefin orbitals to the nucleophile. The observation that for the formation of a stable olefin-platinum(II) bond the π bond from metal to olefin is more important than the σ bond from olefin to metal¹⁰⁷ implies that there will be a considerable buildup of negative charge in the olefin π^* (antibonding) orbitals. An incoming nucleophile would therefore be expected to approach the double bond between the carbon atoms rather than around the end, making the linear model^{308,309} for the nucleophilic attack of coordinated monoolefins unlikely.¹⁴⁹ Attack by the nucleophile at the center of the double bond, which can occur *cis* or *trans* relative to the position of the metal, would give exactly the same products as linear attack.

If the nucleophile attacks the monoolefin when the olefinic double bond is perpendicular to the plane containing the metal and halogen atoms, it remains to be explained why the nucleophilic attack of diolefin complexes, where the double bonds are rigidly fixed in this orientation, occurs by a different stereochemical route. Two reasons can be advanced. Firstly, it has been suggested that in the diolefin complexes steric hindrance by the olefin prevents *cis* addition occurring.²⁸³ Secondly no platinum(II) or palladium(II) complexes containing both a chelating diolefin and a water or methanol ligand, which are essential precursors for the *cis*-addition mechanism,^{117,305} have been reported, although 10% of the complex $[\text{PtCl}_2(\text{H}_2\text{O})(\text{C}_2\text{H}_4)]$ exists in the *cis* configuration.⁹⁸

In general palladium(II) salts catalyze nucleophilic attack on olefins more readily than platinum(II) salts. There are a number of factors which contribute to this.

1. Palladium(II)-olefin complexes are formed more rapidly than platinum(II)-olefin complexes. For example, equilibria between palladium(II) salts and olefins are established in 30-40 min at 14.8°,¹²² whereas equilibria between platinum(II) salts and olefins require 14 days at 30°.¹⁰⁷

2. While the π back-donation of charge from metal to olefin is known to be considerable in the platinum(II)-olefin complexes,¹⁰⁷ it is possible that it is less in the palladium(II)-olefin complexes since the ionization potentials of palladium are greater than those of platinum³¹⁰ indicating that palladium

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will less readily donate electrons back to the olefin than platinum. This will result in the electron density around the olefinic double bond being less when it is coordinated to palladium than platinum, and hence nucleophiles would more readily attack olefins coordinated to palladium than platinum.

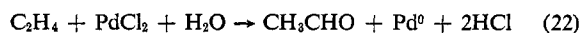
3. The palladium-olefin bond is weaker than the platinum-olefin bond⁶⁰ so that the activation energy of any rearrangement process that may be necessary during the course of the reaction will be lower for palladium- than platinum-olefin complexes.

4. Palladium(II) can more readily expand its coordination sphere to accept a fifth and sixth ligand than can platinum(II).³¹¹⁻³¹³ This allows the incoming nucleophile to coordinate to palladium(II) before attacking the olefin, thus lowering the activation energy of the nucleophilic attack.

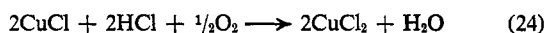
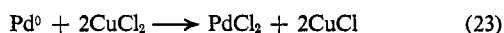
B. OXIDATION

When olefins are introduced into aqueous solutions containing palladium(II) salts, the olefins are oxidized to carbonyl compounds. Similar rapid oxidations by platinum(II) salts have not been observed although carbonyl compounds are formed rapidly when olefins are introduced into Na₂PtF₆ solution.³¹⁴ Although platinum(II) salts do not oxidize olefins rapidly, Zeise's salt is hydrolyzed slowly on heating in water to give some acetaldehyde.³¹⁵

The oxidation of olefins to carbonyl compounds in the presence of palladium(II) salts, which has been developed commercially into the Wacker process,^{9,10,316-318} can be represented schematically by eq 22. Although it is not a



catalytic process, it can be made into a pseudo-catalytic process by the introduction of a suitable oxidant such as cupric chloride, ferric chloride, or benzoquinone, to reoxidize the palladium(0) to palladium(II). Cupric chloride is the preferred oxidant because the reoxidation of cuprous chloride by oxygen is a very fast reaction.⁹ The regeneration of palladium(II) can be represented schematically by eq 23 and 24. The oxygen may be introduced either simultaneously with



the olefin (one-stage process) or in a separate stage (two-stage process); both processes have been investigated on a commercial scale.⁹

The commercial importance of the Wacker process can be gauged by the number of patents and papers that have been published describing modifications that either improve the

yields of particular products or accelerate the reaction.³¹⁹⁻³²⁷ No attempt will be made in this review to define the precise conditions of the reaction; instead further discussion will be confined to the mechanism of the reaction. The considerable experimental data that have been obtained may be summarized as follows.

1. Olefins other than ethylene can also be oxidized although such oxidation occurs more slowly and in lower yields than with ethylene.³²⁷ The presence of at least one hydrogen atom on each of the carbon atoms of the double bond is essential.⁹ Higher olefins often yield a number of products due to isomerization of the olefin.³²⁸

2. One mole of olefin is absorbed and reacted for each mole of PdCl₂,¹⁰ so that the stoichiometry of eq 22 is followed. This together with the fact that the excess solubility of ethylene in PdCl₂ solution over water is independent of the acid concentration, but decreases with increasing chloride concentration, suggests that the first step is the equilibrium formation of a palladium(II)-olefin complex (eq 25).^{117,119,305,339}



3. Although fluoride ions hardly interfere, chloride, bromide, and iodide ions inhibit oxidation to an increasing extent, which is consistent with equilibrium 25 being present,⁹ since for platinum this equilibrium lies further to the left as the atomic weight of the halogen increases.¹¹¹

4. The plots of the concentration of olefin absorbed by PdCl₂ solutions against time for a series of temperatures intersect.⁹ This occurs because as the temperature increases equilibrium 25 shifts to the left giving a reduced olefin absorption, whereas the rate of the hydrolysis (eq 26) increases with increasing temperature.

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5. The carbonyl group appears on the carbon atom that Markovnikov's rule would predict to be attacked by the anionic species.^{9, 317}

6. Ethyl alcohol is not an intermediate oxidation product since ethyl alcohol reacts more slowly than ethylene with PdCl_2 .^{9, 317}

7. Kinetic studies have indicated that for ethylene, propylene, but-1-ene, and *cis*- and *trans*-but-2-ene the reaction is first order with respect to palladium(II)^{10, 117, 305, 340-349} and olefin.^{10, 117, 305, 340-350} In the absence of chloride the reaction is second order in palladium(II).³⁴² The reaction is inhibited by protons (first order)^{117, 305, 342, 348} and chloride ions (second order).^{117, 305, 344, 345} The over-all rate expression can be written

$$\frac{-d[\text{olefin}]}{dt} = \frac{k[\text{PdCl}_4^{2-}][\text{olefin}]}{[\text{Cl}^-]^2[\text{H}_3\text{O}^+]}$$

The oxidation of cyclohexene did not show proton inhibition.³⁵¹ The oxidation of styrene gave two possible products, acetophenone and phenylacetaldehyde, whose formation followed different rate laws,³⁴⁹ viz.

$$\frac{d[\text{acetophenone}]}{dt} = \frac{k[\text{PdCl}_2][\text{styrene}]}{[\text{Cl}^-]^{1.0}[\text{H}_3\text{O}^+]}$$

$$\frac{d[\text{phenylacetaldehyde}]}{dt} = \frac{k[\text{PdCl}_2][\text{styrene}]}{[\text{Cl}^-]^{0.4}}$$

8. Since no deuterium is present in the acetaldehyde formed when ethylene is oxidized by palladium(II) salts in D_2O , all the hydrogen atoms in the acetaldehyde must have been present in the original ethylene, indicating that a hydrogen shift must occur during the reaction.¹⁰ An isotope effect $K_{\text{H}}/K_{\text{D}}$ of 4.05 was observed in D_2O .³⁵²

9. Using water and fully deuterated ethylene a very small isotope effect ($K_{\text{H}}/K_{\text{D}} = 1.07$) is observed indicating that no carbon-hydrogen bond is broken during the rate-determining step.¹¹⁷

A number of mechanisms have been put forward to explain

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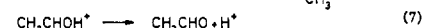
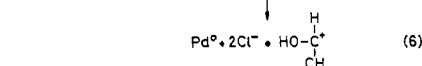
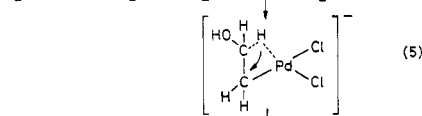
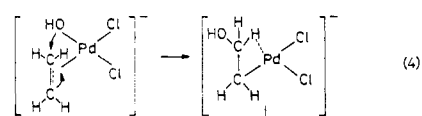
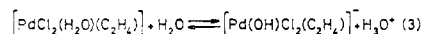
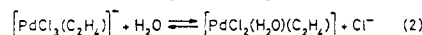
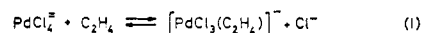


Figure 13. Mechanism for the oxidation of ethylene by aqueous palladium(II) chloride solutions.

the observed kinetic data.^{10, 117, 340, 341, 348, 344, 346, 353-359} A recent review of these³⁰⁹ has suggested that the mechanism in Figure 13 incorporates the best of all the previously proposed mechanisms and accounts for all the experimental data. The first two stages of this mechanism are widely accepted and account for the inhibition of the reaction by chloride ions.^{117, 305, 343-345, 355, 360} The third stage^{117, 305, 355, 360} accounts for the proton inhibition as well as the deuterium isotope effect in D_2O . The last four stages³⁰⁹ were put forward to avoid the necessity of postulating a two-coordinate σ -bonded complex of palladium suggested earlier.¹¹⁷ It has been suggested that stage 4, which involves nucleophilic attack of the coordinated olefin by a coordinated hydroxide ion, would be facilitated by rotation of the ethylene about the palladium-ethylene bond.^{308, 309} This rotation is known from nuclear magnetic resonance studies to occur in both platinum(II)-olefin and rhodium(I)-olefin complexes.^{22, 361} However, such a rotation would present the olefin π^* (antibonding) orbitals to the nucleophile. Since in platinum(II)-olefin complexes and probably in palladium(II)-olefin complexes these orbitals are known to have a high electron density,¹⁰⁷ it is more likely that the nucleophile will attack the center of the double bond, so that rotation of the olefin, which undoubtedly occurs, will not facilitate this attack.¹⁴⁹ The three-coordinate intermediate shown in stage 4 may well contain a molecule of solvent and in reality be four-coordinate. In the oxidation of substituted styrene complexes, electron-releasing substituents favor the formation of a substituted acetophenone, whereas electron-withdrawing substituents favor the formation of a substituted phenylacetaldehyde.³⁶² This has been accounted for by

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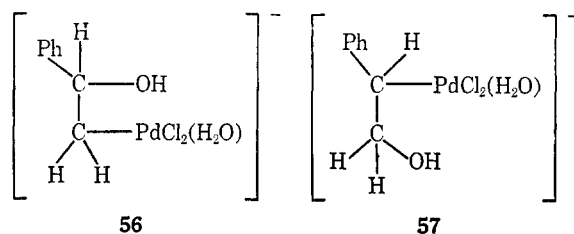
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postulating that, in stage 4 (Figure 13), electron-releasing groups in the aromatic ring, by increasing the electron density at the α -carbon atom, give rise to **56**, whereas electron-withdrawing substituents, by withdrawing charge from the



α -carbon atom, give rise to **57**.³⁶² The formation of a carboanion ion, as in stage 6, had been suggested previously.^{10,363} The palladium(0) formed may either be present as the free metal or as a complex. While this mechanism accounts satisfactorily for all the present experimental data, it may need to be modified later in the light of further data.

Preliminary results on the oxidation of acetylene by aqueous palladium(II) salts have indicated that the reaction is considerably more complex than with ethylene,²⁹⁶ probably due to the ability of palladium(II) salts to polymerize acetylenes.⁴⁸ Thus formaldehyde, acetaldehyde, propionaldehyde, and acraldehyde are formed. A mechanism has been suggested for this reaction,²⁹⁶ but the experimental data at present available are inadequate to enable it to be tested properly.

An investigation of the possibility of adapting the oxidation of ethylene by palladium(II) salts to a fuel cell has shown that a continuous feed of oxygen can establish smooth fuel-cell reactions.³⁶⁴

A solution of PdCl₂ and cupric acetate in acetic acid catalyzes the direct oxidation of unsaturated aldehydes to unsaturated acids.³⁶⁵

C. ACETYLATION

When ethylene is passed into a solution of PdCl₂ in acetic acid containing an excess of a soluble acetate such as sodium or lithium acetate, the ethylene is oxidized to vinyl acetate, ethylidene diacetate, and acetaldehyde. This reaction has been widely investigated as a commercial method for the preparation of unsaturated esters.³⁶⁶⁻³⁸⁸

The experimental data that have been obtained may be summarized as follows.

1. The presence of acetate ions, as opposed to un-ionized acetic acid, is essential for acetylation of the olefin,^{368,368} The reaction involves reduction of palladium(II) to palladium(0), so that oxidizing agents such as cupric salts or benzoquinone are added to reoxidize the palladium(0). In the absence of acetate ions no palladium metal is precipitated, indicating that no oxidation has occurred.

2. The products formed from ethylene are vinyl acetate, acetaldehyde, ethylidene diacetate, and ethylene diacetate. The ratio of vinyl acetate to acetaldehyde can be increased by the addition of solvents such as dimethylformamide or alkyl and aryl nitriles.³⁶⁹

3. Kinetic studies have shown that the reaction rate is first order with respect to both olefin and Pd(OAc)₂.³⁹⁰⁻³⁹² The reaction has a maximum rate at a sodium acetate concentration of 0.2 M. On increasing the sodium acetate concentration from 0.3 to 1.0 M, there was a decrease in rate proportional to the square of the acetate concentration.³⁹¹

4. The ethylidene diacetate obtained in the presence of CH₃COOD contained virtually no deuterium, indicating that it is not formed by addition of acetic acid to vinyl acetate,³⁶⁸ so that at some stage in the reaction a hydride shift must have occurred. Similarly the vinyl acetate does not contain any deuterium.³⁶⁸

5. Using propylene and 2-deuterated propylene it was found that the rate of oxidation of the undeuterated olefin was 2.8 times greater than that of the deuterated olefin.³⁸⁸ In addition the deuterium retention of the product was 75%, which could be consistent with a 1,2 shift of hydride from the carbon atom that is attacked by acetate, followed by loss of a proton from the adjacent carbon atom.³⁸⁸ This explanation, while it may be correct, has been queried on the grounds that it assumes that the hydride shift must occur during the rate-determining step while the subsequent loss of the proton

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(381) Celanese Corporation of America, Netherlands Patent 6,510,481 (1966); *Chem. Abstr.*, 65, 619e (1966).

(382) E. I. du Pont de Nemours and Co., Netherlands Patent 6,509,320 (1966); *Chem. Abstr.*, 65, 2130b (1966).

(383) W. D. Schaeffer, U. S. Patent 3,253,020 (1966); *Chem. Abstr.*, 65, 3754h (1966).

(384) W. D. Schaeffer, U. S. Patent 3,260,739 (1966); *Chem. Abstr.*, 65, 3767d (1966).

(385) W. D. Schaeffer, U. S. Patent 3,277,158 (1966); *Chem. Abstr.*, 65, 20015h (1966).

(386) Union Oil Co. of California, British Patent 1,032,325 (1966); *Chem. Abstr.*, 65, 5372h (1966).

(387) G. H. Rutherford, British Patent 1,067,850 (1967); *Chem. Abstr.*, 67, 21456 (1967).

(388) Pullman, Inc. British Patent 1,104,805 (1968); *Chem. Abstr.*, 68, 104562 (1968).

(389) R. G. Schultz and P. R. Rony, *Am. Chem. Soc. Petrol. Div. Preprint*, 12, 139 (1967).

(390) A. P. Belov, I. I. Moiseev, and N. G. Uvarova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2224 (1965); *Chem. Abstr.*, 64, 11044g (1966).

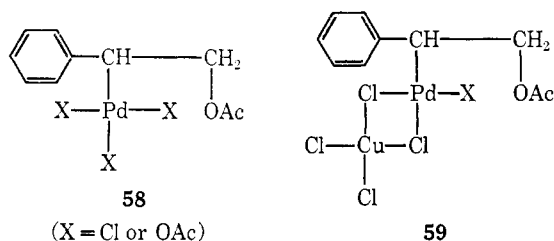
(391) A. P. Belov, I. I. Moiseev, and N. G. Uvarova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1642 (1966); *Chem. Abstr.*, 66, 64832 (1967).

(392) R. Ninomiya, M. Sato, and T. Shiba, *Bull. Japan. Petrol. Inst.*, 7, 31 (1965).

(393) E. W. Stern, *Proc. Chem. Soc.*, 111 (1963).

from the adjacent carbon atom must be fast.³⁰⁹ This assumption should lead to the observation of a lower rate of formation of isopropenyl acetate from 2-deuterated propylene than from unlabeled propylene, whereas in fact the two rates are the same. The situation is further complicated by the possibility of isomerization, which could be partly responsible for the high deuterium retention.³⁰⁹

6. The acetylation of higher olefins has been studied.^{306, 307, 354, 394-400} The products are often complex due to isomerization of the olefin during the reaction, and the course of the reaction is often very sensitive both to the structure of the olefin and to the medium. This sensitivity to the medium is illustrated by the acetylation of styrene in acetic acid in the presence of PdCl₂. Using cupric chloride and sodium acetate in a molar ratio of 1:2, the unsaturated 2-acetoxy-styrene was formed, whereas in a molar ratio of 2:1 the saturated 1-chloro-2-acetoxyethylbenzene and 1,2-diacetoxyethylbenzene were obtained.⁴⁰⁰ In both cases the intermediate **58** was probably formed. At the lower cupric chloride concentration this gave the unsaturated product by a route which



is probably analogous to that of ethylene described below. However, at high cupric chloride concentrations this probably forms a palladium-copper complex, such as **59**, which decomposes to give the observed product and a palladium-copper chloro-bridged species.

7. While the acetylation of 1-olefins gives mainly enol acetate, the acetylation of 2-olefins such as *cis*- or *trans*-but-2-ene,⁴⁰¹ *cis*-pent-2-ene,⁴⁰¹ and cyclohexene²⁸⁵ gives mainly allylic acetate. Propene, however, appears to be an exception to this rule, since it gives quite high yields of allyl acetate.⁴⁰²

A number of mechanisms have been put forward to explain the palladium(II)-catalyzed formation of vinyl acetate and ethylidene diacetate from ethylene.^{307, 309, 353, 368, 403, 404} All are agreed that a π olefin complex is formed in the first stage,

(394) I. I. Moiseev, A. P. Belov, and Ya. K. Syrkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1527 (1963); *Chem. Abstr.*, 59, 14022a (1963).

(395) I. I. Moiseev, A. P. Belov, and G. Yu. Pek, *Zh. Neorgan. Khim.*, 10, 336 (1965); *Chem. Abstr.*, 62, 14724d (1965).

(396) A. P. Belov, G. Yu. Pek, and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2204 (1965); *Chem. Abstr.*, 64, 11079d (1966).

(397) W. C. Baird, *J. Org. Chem.*, 31, 2411 (1966).

(398) A. P. Belov and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 139 (1966); *Chem. Abstr.*, 64, 12542f (1966).

(399) M. Green, R. N. Haszeldine, and J. Lindley, *J. Organometal. Chem.* (Amsterdam), 6, 107 (1966).

(400) S. Uemura and K. Ichikawa, *Nippon Kagaku Zasshi*, 88, 893 (1967); *Chem. Abstr.*, 68, 114224 (1968).

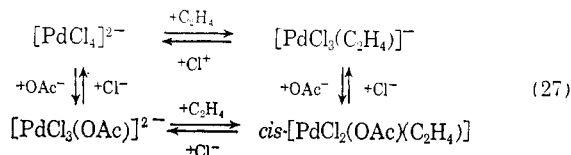
(401) W. Kitching, Z. Rappoport, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, 88, 2054 (1966).

(402) D. R. Bryant, J. R. McKeon, and P. S. Starcher, Abstracts, 2nd International Symposium on Organometallic Chemistry, Madison, Wis., Aug 1965, p 94.

(403) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, 130, 820 (1960); *Chem. Abstr.*, 56, 5813g (1962).

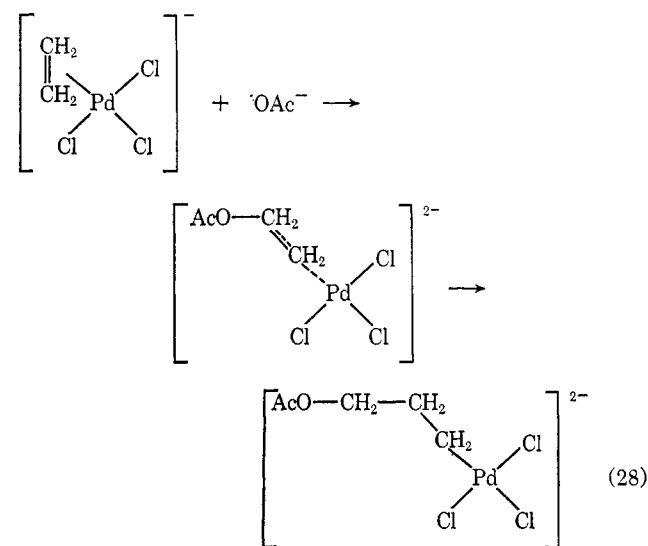
(404) I. I. Moiseev, A. P. Belov, V. A. Igoshin, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, 173, 863 (1967); *Chem. Abstr.*, 67, 53332 (1967).

which allowing for the presence of acetate ions may be represented by eq 27. The observed inhibition by high concentra-

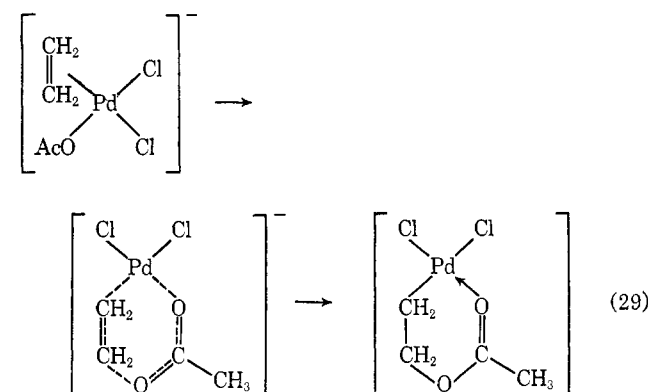


tions of acetate ions has been ascribed to competition between acetate ions and the olefin for coordination to palladium(II).⁴⁰⁴

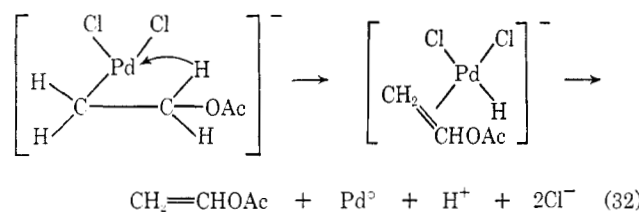
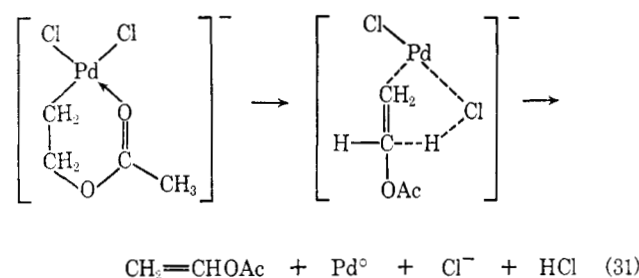
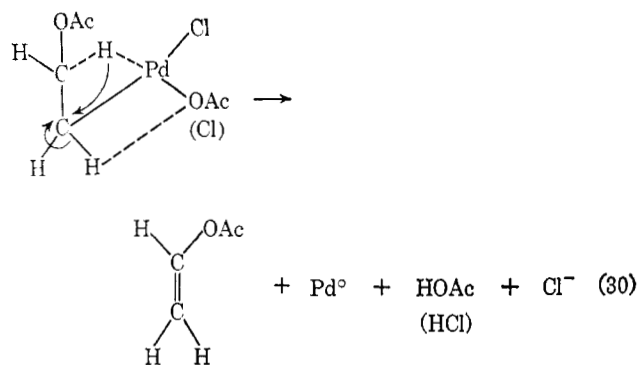
Since, with hexenes, different products are formed at low temperatures in the absence of chloride from those formed at higher temperatures in the presence of chloride, it appears likely that two competing mechanisms occur. In the presence of chloride an intermolecular nucleophilic attack of olefin by acetate ions has been postulated^{307, 309, 353} (eq 28), whereas at low chloride or high acetate concentrations an intramolecular attack of the coordinated acetate ion on the olefin to give a



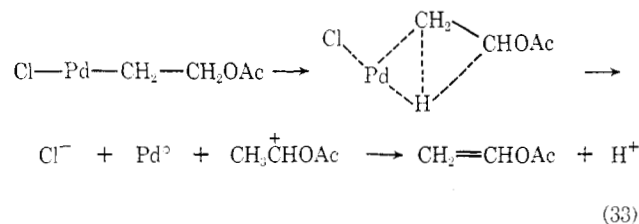
six-membered ring has been suggested (eq 29).³⁰⁷



The decomposition of the σ -bonded palladium-alkyl complex has caused controversy. The deuterium labeling studies^{317, 368, 393} have been used to support a palladium-assisted hydride transfer mechanism. Two distinct routes have been suggested for this. In the first (eq 30), which does not involve the formation of carbonium ions, the hydride shift from the 2- to the 1-carbon atom is assisted by removal of a hydrogen



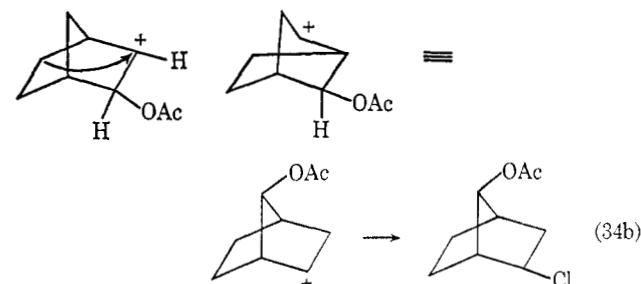
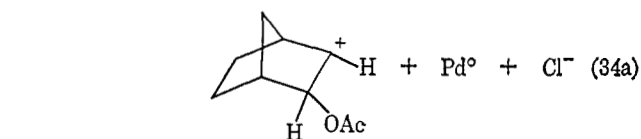
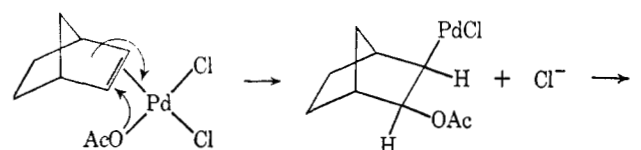
atom from the 1-carbon atom by reaction with a coordinated acetate or chloride ligand.^{9,117,309,398} A slight variation of this in which no 1,2-hydride shift is invoked involves a 2-hydrogen elimination mechanism, which may either occur with the formation of hydrogen chloride³⁰⁷ (eq 31) or may occur with the formation of a palladium-hydrogen bond⁴⁰⁵ (eq 32) which could decompose to palladium(0) and a proton, followed by loss of coordinated vinyl acetate. An alternative mechanism (eq 33), in which an intermediate carbonium ion is formed, has also been put forward,³⁶⁸ but has been criticized³⁰⁷ because,



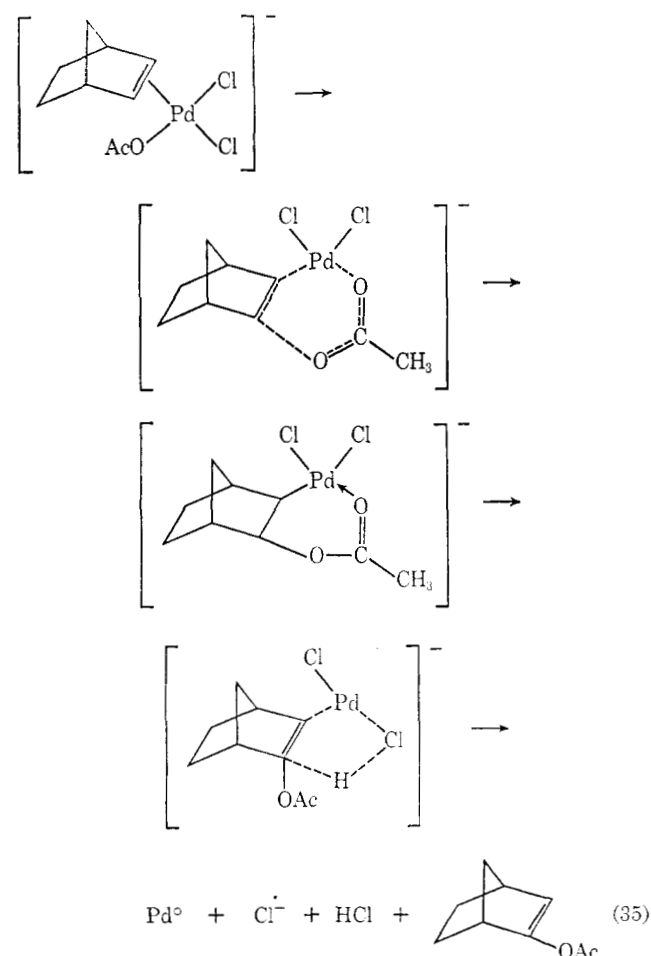
although it accounts well for the absence of deuterium in ethylidene diacetate when the reaction is performed in $\text{CH}_3\text{-COOD}$, the existence of a free carbonium ion in a highly solvating medium such as acetic acid is unlikely. In addition the carbonium ion would be more likely to react with acetic acid to give ethylidene diacetate than to lose a proton to give vinyl acetate, whereas in practice vinyl acetate is formed in greater yield than ethylidene diacetate.

The acetylation of norbornene provides good evidence for a carbonium ion intermediate, since this would lead directly to the formation of *exo*-2-chloro-*syn*-7-acetoxynorbornene

(eq 34), whereas the β -hydrogen elimination, whether this

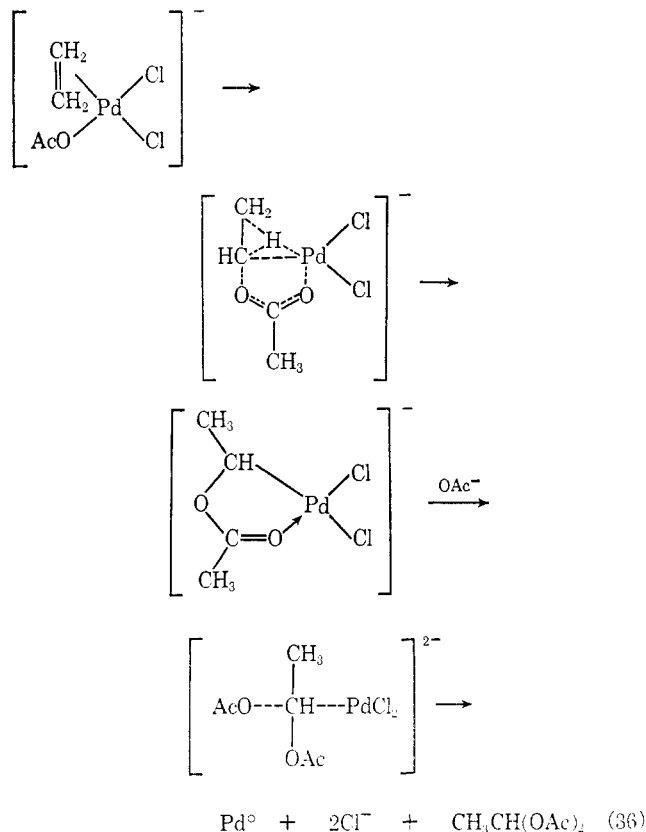


occurs directly or by hydride transfer to the α -carbon atom, would lead to the formation of 2-acetoxy-2-norbornene (eq 35), which is not observed among the products.³⁹⁷

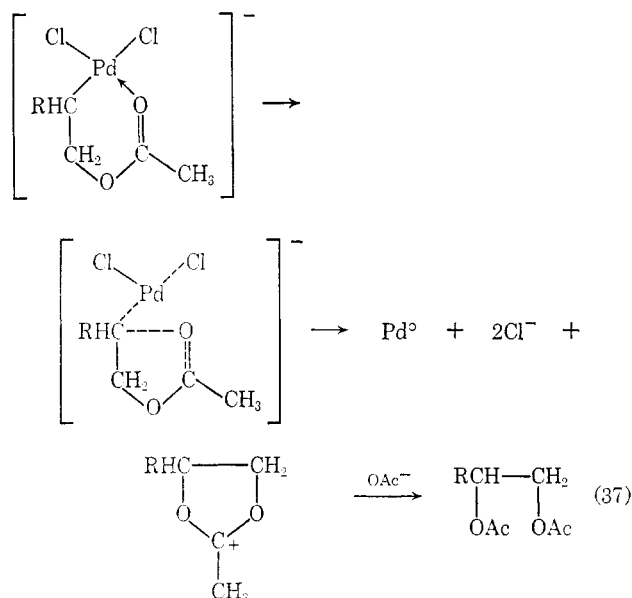


An alternative mechanism which accounts for the formation of ethylidene diacetate without postulating a carbonium ion intermediate involves an acetate displacement of palladium

from the intermediate formed by a 1,2-hydride shift (eq 36).⁸⁰⁷ This mechanism still involves a 1,2-hydride shift, the evidence



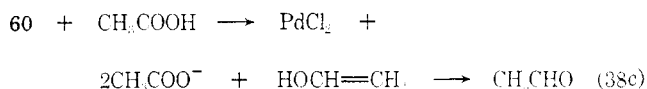
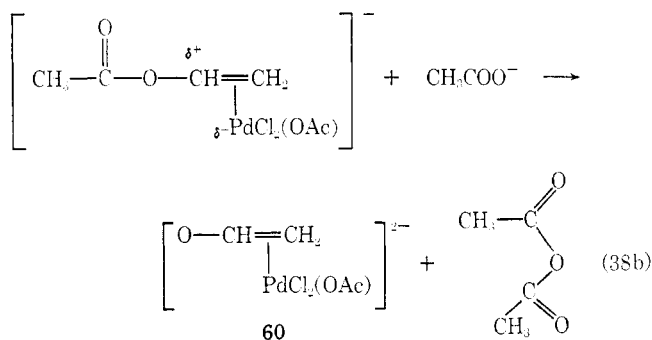
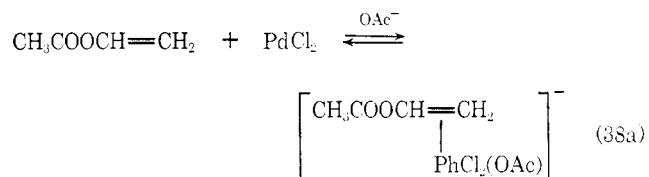
for which has been queried,⁸⁰⁹ emphasizing the importance of further work to establish whether or not such a shift does occur. In addition to 1,1-diacetates, 1,2-diacetates have also been found in the reaction products.⁸⁰⁷ The formation of 1,2-diacetates has been explained by a neighboring group displacement of palladium by acetate (eq 37),⁸⁰⁷ which involves the formation of an intermediate carbonium ion.



It can be seen that while a number of mechanisms have been put forward that are capable of explaining the formation of the observed products, none of these is entirely satisfactory.

A great deal more detailed kinetic and isotope studies are needed to establish an unequivocal mechanism.

The formation of acetaldehyde during the oxidation of olefins in palladium(II) salt solutions can occur by two mechanisms. In one the olefin reacts with the water present in the reaction medium in a manner identical with that described above under oxidation. In addition it has been shown that when vinyl acetate is added to an anhydrous solution of PdCl_2 in acetic acid containing excess sodium acetate, acetaldehyde and acetic anhydride are formed in a 1:1 ratio.^{406, 407} It was established that PdCl_2 and sodium acetate were both essential for this reaction and that ethylidene diacetate was not an intermediate. A mechanism for this reaction has been put forward (eq 38) in which an olefin complex is first formed. This reduces the electron density at the double bond, rendering

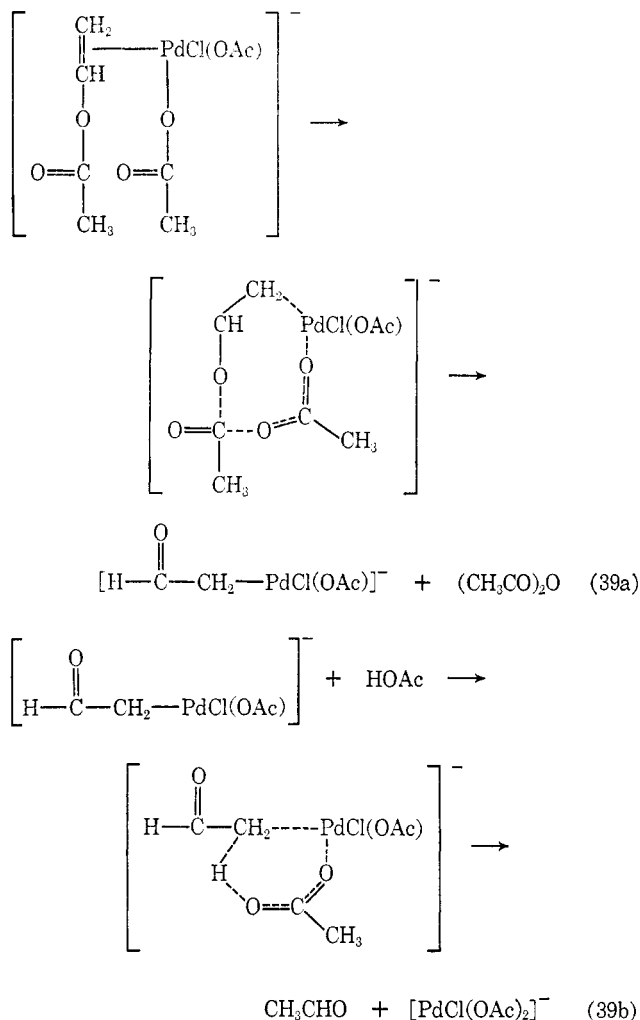


the olefin susceptible to nucleophilic attack by acetate ions giving acetic anhydride and an intermediate, 60, which is then protonated by reaction with acetic acid to give the unstable vinyl alcohol which rearranges to acetaldehyde.⁴⁰⁶ An alternative mechanism (eq 39) which involves intramolecular attack by a coordinated acetate ion has been put forward.⁸⁰⁹ The experimental evidence available at present is insufficient to distinguish between an intermolecular and an intramolecular attack on the olefin by acetate ion. The increased yields of vinyl acetate relative to acetaldehyde in solvents such as alkyl or aryl nitriles indicate that nitriles do not interfere with the vinyl acetate synthesis, but inhibit any further reaction of the palladium(II)-vinyl acetate complex.⁸⁰⁹ This would automatically occur in either of the above mechanisms (eq 38 and 39) if the relative stabilities of the complexes were palladium(II)-ethylene > palladium(II)-nitrile > palladium(II)-vinyl acetate. Unfortunately no stability constant data are available to test this theory.

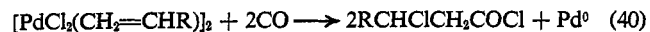
D. CARBONYLATION

The reaction of carbon monoxide with olefins coordinated

(406) W. H. Clement and C. M. Selwitz, *Tetrahedron Lett.*, 1081 (1962).
 (407) D. Clark and P. Hayden, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., 1966, No. U60.



to palladium(II) is another example of a reaction that involves a nucleophilic attack on an olefin coordinated to a metal that has been developed into a commercial process. The basic reaction may be represented by eq 40.⁴⁰⁸ The reaction has been developed commercially to prepare acid chlorides,⁴⁰⁹



carboxylic acids, and esters,⁴¹⁰⁻⁴¹⁸ lactones,⁴¹⁴ and oxo acids.⁴¹⁴

The particular advantage of using palladium salts, as opposed to complexes such as nickel carbonyl, as catalysts in the carbonylation of olefins, is that in the presence of the former the reaction occurs at low temperature (about 80°). This enables heat-sensitive olefins and olefins that would be hydrogenated by hydrogen, formed at higher temperatures by the reaction of carbon monoxide with water, to be car-

bonylated. Two main palladium catalyst systems have been investigated: (1) PdCl_2 in a nonaqueous solvent containing hydrogen chloride;⁴¹⁵ (2) palladium(0) complexes such as $\text{Pd}(\text{PPh}_3)_4$.⁴¹⁶⁻⁴¹⁸ Palladium(0) complexes are only active in the presence of hydrogen chloride when $[\text{PdCl}_2(\text{PPh}_3)_2]$, which is the true catalyst, is formed.⁴¹⁶ The great advantage of complex palladium(II) chloride catalysts over PdCl_2 is that the former permit polyolefins to be selectively carbonylated. Thus mono-, di-, and triesters of 1,5,9-cyclododecatriene can be prepared using complex palladium(II) chloride catalysts and suitably adjusting the reaction conditions.⁴¹⁸

The high pressures necessary to effect the reaction have precluded any kinetic studies. However, the following experimental data have been established.

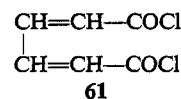
1. Both olefins and acetylenes may be carbonylated in the presence of PdCl_2 .^{408, 419}

2. The reaction must be performed in nonaqueous solvents in the presence of hydrogen chloride. In benzene acid chlorides are formed, whereas in alcoholic solvents these react to give esters as the final products.

3. Where a terminal multiple bond is present carbon monoxide always attacks the terminal carbon atom, in contrast to other nucleophiles such as hydroxide or acetate ions which attack the more substituted carbon atom.⁴⁰⁸

4. During carbonylation palladium metal is formed.^{420, 421} Palladium on charcoal was found to be as effective a catalyst as PdCl_2 ,⁴²⁰⁻⁴²² which may indicate that metallic palladium rather than PdCl_2 is the true catalyst, although it is also possible that carbon monoxide reacts under pressure with palladium metal to give carbonyl complexes which then act as homogeneous catalysts.⁴²³ With propargyl alcohol slightly different products were obtained using palladium on charcoal and PdCl_2 .⁴²⁴

5. Treatment of acetylene with carbon monoxide under pressure in the presence of $[\text{PdCl}_2(\text{PhCN})_2]$ gives initially *cis-cis*-muconyl chloride (**61**), which rapidly isomerizes to the *trans,trans* product.⁴¹⁹ Using low ratios of acetylene to carbon



monoxide in the presence of PdCl_2 , maleic acid derivatives are formed.⁴²⁵ The very small trace of fumaric acid derivative found suggests that the addition of carbon monoxide to acetylene in the presence of PdCl_2 occurs in a stereospecifically *cis* manner, and that the trace of the fumaric acid deriva-

(408) J. Tsuji, M. Morikawa, and J. Kiji, *Tetrahedron Lett.*, 1061 (1963).

(409) I. L. Mador and J. A. Scheben, French Patent 1,419,758 (1965); *Chem. Abstr.*, **65**, 13553d (1966).

(410) G. Jacobsen and H. Spaethe, German Patent 1,138,760 (1962); *Chem. Abstr.*, **58**, 6699f (1963).

(411) J. Tsuji, M. Morikawa, and N. Konochi, Japanese Patent 24,608 (1965); *Chem. Abstr.*, **64**, 4946e (1966).

(412) Shell Internationale Research Maatschappij N. V., Netherlands Patent 6,503,362 (1966); *Chem. Abstr.*, **66**, 65634 (1967).

(413) Badische Anilin- und Soda-Fabrik A.-G., Netherlands Patent 6,516,439 (1966); *Chem. Abstr.*, **65**, 15249a (1966).

(414) Imperial Chemical Industries Ltd., Netherlands Patent 6,511,995 (1966); *Chem. Abstr.*, **65**, 7064f (1966).

(415) J. Tsuji, *Yuki Gosei Kagaku Kyokai Shi*, **25**, 984 (1967); *Chem. Abstr.*, **68**, 86421 (1968).

(416) K. Bittler, N. V. Kutepov, D. Neubauer, and H. Reis, *Angew. Chem. Intern. Ed. Engl.*, **7**, 329 (1968).

(417) Badische Anilin und Soda-Fabrik A.-G., Netherlands Patent 6,409,121 (1965); *Chem. Abstr.*, **63**, 14726b (1965).

(418) N. V. Kutepov, K. Bittler, D. Neubauer, and H. Reis, German Patent 1,237,116 (1967); *Chem. Abstr.*, **68**, 21550 (1968).

(419) J. Tsuji, M. Morikawa, and N. Iwamoto, *J. Am. Chem. Soc.*, **86**, 2095 (1964).

(420) J. Tsuji, M. Morikawa, and J. Kiji, *Tetrahedron Lett.*, 1437 (1963).

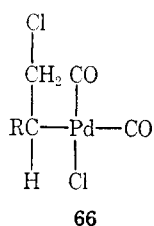
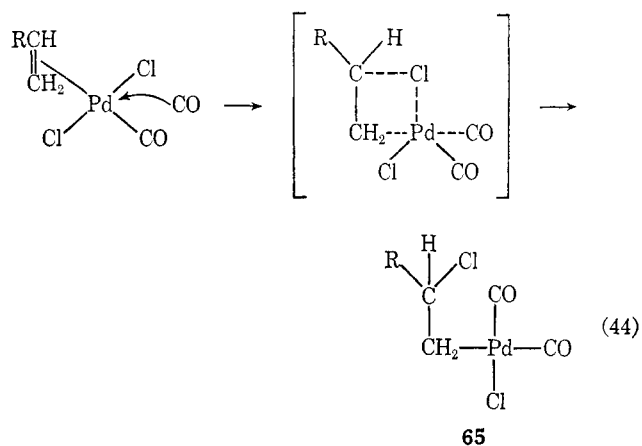
(421) J. Tsuji, M. Morikawa, and J. Kiji, *J. Am. Chem. Soc.*, **86**, 4851 (1964).

(422) J. Tsuji, N. Iwamoto, and M. Morikawa, *Bull. Chem. Soc. Japan*, **38**, 2213 (1965).

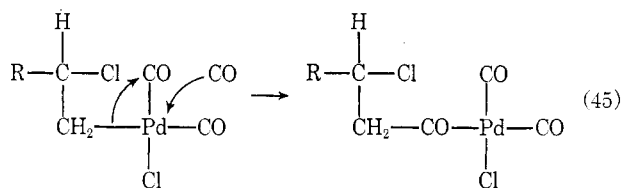
(423) G. C. Bond, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **63**, 42 (1966).

(424) J. Tsuji and T. Nogi, *Tetrahedron Lett.*, 1801 (1966).

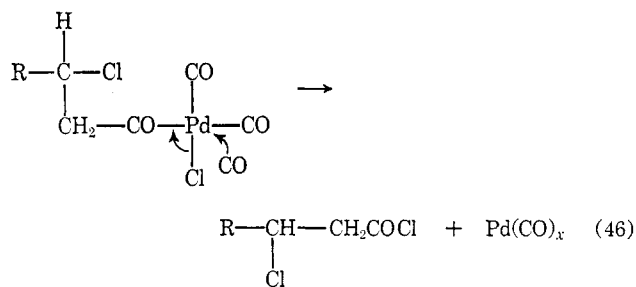
(425) G. P. Chiusoli, C. Venturello, and S. Merzoni, *Chem. Ind. (London)*, 977 (1968).



late the formation of the primary carbanion¹⁸⁰ RCHClCH_2^- . The third stage involves the insertion of carbon monoxide into the palladium-carbon σ bond^{421, 446} (eq 45), which has been shown to occur with both palladium(II) and platinum-



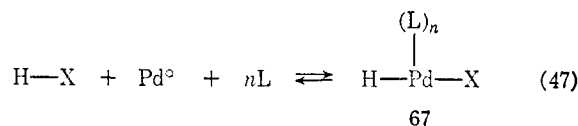
(II) complexes containing phosphine ligands.^{312, 447} The final stage involves attack of the remaining chloride ligand on the acyl group to give the acyl chloride (eq 46). This mechanism is able to explain the observed data and involves a number of intermediates which are very similar to complexes that have already been prepared. It must, however, be emphasized that



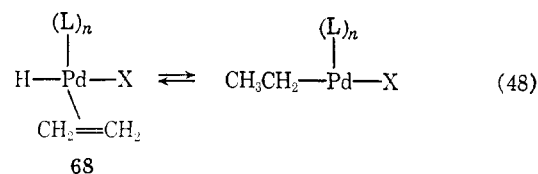
much work remains to be done before this mechanism can be considered to be fully established.

A mechanism, which is similar to that described above for carbonylation in the presence of PdCl_2 , has been proposed for the carbonylation and decarbonylation of olefins in the

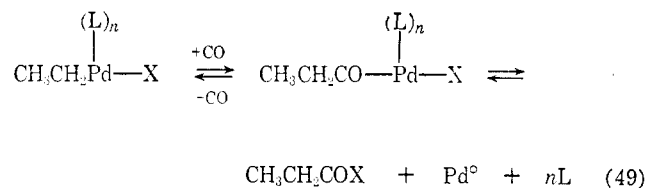
presence of palladium metal.⁴⁴⁸ In the first stage (eq 47), which involves the reaction of palladium metal to give a palladium(II) complex, X is a halogen and L is a molecule that can stabilize palladium(II) (either carbon monoxide or solvent). Although no complexes of the type 67 have been isolated, it was found during the working up that some



palladium metal had gone into solution. 67 then adds a molecule of olefin to give 68. The next stage (eq 48) involves olefin insertion into the palladium-hydrogen bond. Although this reaction has not been established for palladium, it is

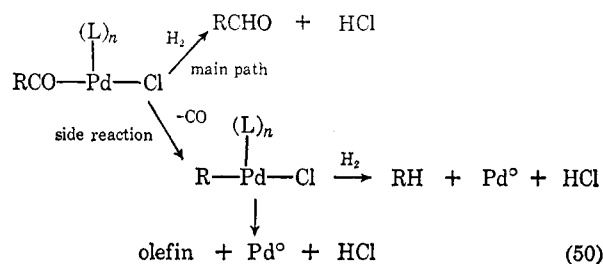
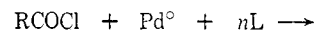


known to occur with platinum(II)-olefin complexes.^{197, 198} The remaining stages of the reaction (eq 49) parallel those discussed above when PdCl_2 was the catalyst. In decarbonyla-



tion the first stage involves oxidative addition of acyl halides or aldehydes to palladium metal. Although there is no direct evidence of complex formation, metallic palladium partially dissolves in acyl halides.⁴⁴⁸ The transformation of acyl-palladium(II) to alkylpalladium(II) complexes on heating in the absence of carbon monoxide is reasonable since acyl-platinum(0) complexes on heating in the absence of carbon monoxide give alkylplatinum(0) complexes.¹⁶² The final stage involves decomposition of the alkylpalladium(II) complexes to give the olefin. This reaction has been observed previously.³⁸⁸

The study of the carbonylation of olefins and the decarbonylation of acid chlorides has enabled a mechanism for the Rosenmund reduction⁴⁴⁹ to be put forward. In this reduction an acid chloride is reduced to an aldehyde by heating with



(446) R. F. Heck, *Advances in Chemistry Series*, No. 49, American Chemical Society, Washington, D. C., 1965, p 181.

447) G. Booth and J. Chatt, *J. Chem. Soc., A*, 634 (1966).

(448) J. Tsuji and K. Ohno, *J. Am. Chem. Soc.*, **90**, 94 (1968).

(449) K. W. Rosenmund, *Chem. Ber.*, **51**, 585 (1918).

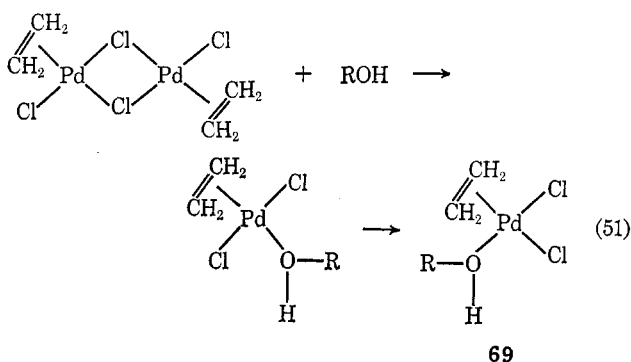
hydrogen in a high-boiling solvent such as xylene in the presence of a palladium metal catalyst. The proposed mechanism (eq 50) involves the formation of an acylpalladium complex which reacts with hydrogen to yield an aldehyde and palladium metal.⁴⁴⁸ The decarbonylated by-products that are obtained from the Rosenmund reduction can be accounted for by an acyl-alkyl rearrangement followed either by decomposition of the alkylpalladium complex to give an olefin or hydrogenolysis to give an alkane.

E. OTHER NUCLEOPHILES THAT ATTACK METAL-OLEFIN COMPLEXES

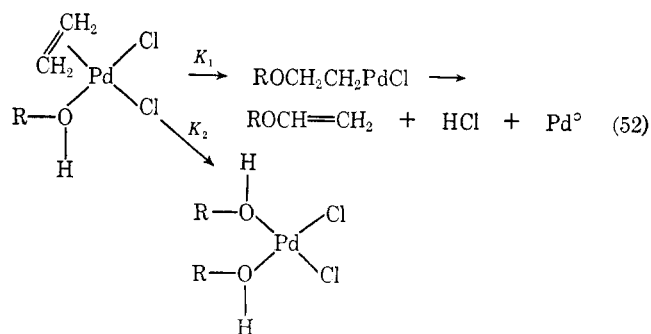
A number of other nucleophiles undergo oxidative addition to olefins that are coordinated to palladium(II).

During these reactions palladium(II) is reduced to palladium(0) and oxidizing agents such as copper(II) salts or benzoquinone must be added if the reaction is to be catalytic. Thus alcohols will undergo nucleophilic addition to olefins coordinated to palladium(II) to give vinyl ethers^{306, 450, 451} or acetals,^{386, 452, 453} primary amines give secondary amines,³⁰⁸ amides give N-alkenylamides,³⁰⁶ chloride gives vinyl chloride,^{451, 454} and cyanide gives vinyl cyanide.⁴⁵⁵ Where higher olefins are involved the nucleophilic attack proceeds according to Markovnikov's rule.

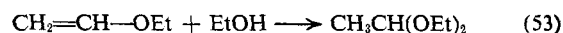
The nucleophilic attack of coordinated olefins by alcohols has been studied in some detail. Methanol and ethanol both react with the coordinated olefin whereas higher alcohols displace the olefin. It has been suggested that the initial reaction of alcohol with $[\text{PdCl}_2(\text{C}_2\text{H}_4)]_2$ to give a *cis* complex (eq 51) is followed by two possible alternatives. Either the alcohol



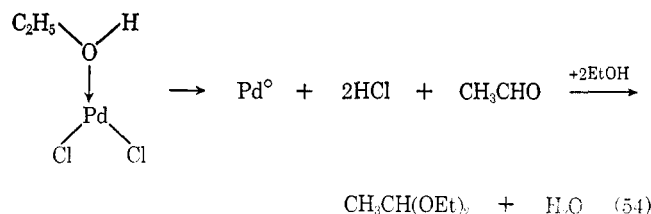
attacks the olefin oxidizing it to an ether or a further molecule of alcohol attacks 69 giving *cis*- $[\text{PdCl}_2(\text{ROH})_2]$ (eq 52).⁴⁵⁶ For R = methyl and ethyl, $K_1 \gg K_2$, whereas for higher alkyl groups, $K_2 \gg K_1$. The acetal formed by reaction of ethanol with $[\text{PdCl}_2(\text{C}_2\text{H}_4)]_2$ can be formed either by addition of



ethanol to vinyl ethyl ether (eq 53) or by oxidation of ethanol,

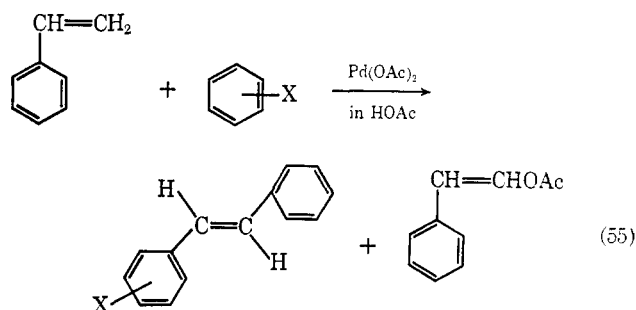


coordinated to palladium(II), to acetaldehyde, which then reacts with further ethanol to give the acetal (eq 54). Using ¹⁴C-



labeled ethylene, it was shown⁴⁵⁶ that only 15% of the acetal was formed by eq 54.

When palladium(II)-olefin complexes are treated with acetic acid in a hydrocarbon solvent such as benzene or toluene, the hydrocarbon becomes substituted on the olefinic double bond.⁴⁵⁷ The reaction was shown to involve substitution, rather than addition across the double bond, followed by dehydrogenation, because when diphenylethane was added it was recovered unchanged. The reaction (eq 55) goes in even better yield if the free olefin is treated with the hydro-



carbon in acetic acid containing $\text{Pd}(\text{OAc})_2$.⁴⁵⁸ During this reaction palladium(II) is reduced to palladium metal, but the reaction can be made catalytic by the addition of silver acetate which reoxidizes the palladium metal to $\text{Pd}(\text{OAc})_2$.⁴⁵⁹

The PdCl_2 -catalyzed oxidative addition of sulfur dioxide to ethylene gives ethyl *trans*-but-2-enyl sulfone as the major product (eq 56) and ethyl vinyl sulfone as a minor by-product.⁴⁶⁰ During the course of the oxidation PdCl_2 is reduced to

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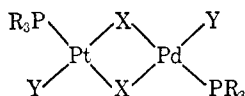
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VII. Homogeneous Hydrogenation of Olefins

The observation that $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$ acted as a catalyst for the hydrogenation of olefins opened up a new field of homogeneous hydrogenation.⁴⁷⁰ This work was later repeated,^{199, 471, 472} and it was shown that if care was taken to avoid a rise in temperature the reaction was homogeneous, but if the temperature rose,⁴⁷¹ or an excess of hydrogen was used,⁴⁷² platinum metal was deposited and the reaction became heterogeneous.

Palladium(II) is generally unstable in the presence of hydrogen,^{473, 474} so that until recently it was rarely used as a homogeneous catalyst although it has often been used as a heterogeneous catalyst.^{16, 475} However, PdCl_2 in dimethylformamide or dimethylacetamide does catalyze the homogeneous hydrogenation of dicyclopentadiene.⁴⁷¹ Aqueous solutions of PdCl_2 have been claimed to catalyze the homogeneous hydrogenation of ethyl crotonate in the presence of promoting ions such as copper(II), nickel(II), silver(I), mercury(II), zinc(II), and cadmium(II). The reaction was claimed to be homogeneous because although palladium metal was deposited the rate decreased as the palladium metal was formed.⁴⁷⁶ 1-Olefins have been homogeneously hydrogenated in the presence of both $[\text{PdCl}_2(\text{PR}_3)_2]$ complexes⁴⁷⁷ and binuclear platinum(II)-palladium(II) complexes of type 72.⁴⁷⁸ It has recently been shown that palladium(II)



72, R = Bu, Pr; X = Cl, Br, PPh_2 ; Y = Cl, Br

complexes containing tin(II) ligands are effective catalysts for the homogeneous hydrogenation of olefins.^{11, 479, 480}

Although platinum(II) complexes that do not contain tin(II) ligands have been used as homogeneous hydrogenation catalysts,⁴⁸¹ by far the greatest effort has been devoted to platinum(II) complexes containing tin(II) ligands. These complexes were found to readily catalyze the homogeneous hydrogenation of ethylene and acetylene.¹⁵³ Higher olefins were hydrogenated more slowly,^{153, 482} which was attributed to the weaker complexes formed between higher olefins and platinum(II).¹⁵⁸ However, the slower rate observed with higher olefins was partly due to the use of methanol as a

solvent since the hydrogenation of higher olefins proceeds smoothly in higher alcohols⁴⁸³ or carboxylic acids and esters.⁴⁸⁴ In general, coordinating solvents decrease the catalytic activity of both platinum(II) and palladium(II) complexes relative to noncoordinating solvents.⁴⁸⁵ The ease of hydrogenation of higher olefins is terminal > 1,2-disubstituted > trisubstituted olefins, which in the case of suitable polyolefins has been used to achieve selective hydrogenation.⁴⁸³ Platinum(II) complexes containing both SnCl_3^- and phosphine ligands catalyze the selective reduction of diolefins and triolefins in soybean oil methyl ester to monoolefins^{11, 486-488} and in methyl linolenate to diolefins and monoolefins.^{11, 479, 489} Studies of this reaction and the hydrogenation of a number of simple polyolefins using both platinum(II) and palladium(II) complexes as catalysts have led to the following observations.

1. The first stage involves the very rapid stepwise migration of double bonds to give a conjugated isomer, which is slowly reduced to the monoolefin.⁴⁸⁰ The importance of conjugated diolefins as intermediates in the hydrogenation of nonconjugated polyolefins is indicated by the formation of unreactive diolefins, in which the double bonds are separated by several methylene groups during the hydrogenation.⁴⁸⁹

2. Olefin isomerization occurs both before hydrogenation, as indicated by the formation of conjugated dienes from nonconjugated dienes, and after hydrogenation as shown by the isomerization of monoolefins under hydrogenation conditions.²¹⁴ *cis-trans* isomerization of the double bond also occurs during the hydrogenation.^{479, 486, 488}

3. A high pressure of hydrogen is necessary for hydrogenation; under atmospheric pressure only isomerization of the double bonds is observed.²¹⁴

4. Since hydridoplatinum(II) complexes can be isolated from the reaction mixture, their formation is essential. However, since $[\text{PtCl}_2(\text{PPh}_3)_2]$ and $[\text{PtHCl}(\text{PPh}_3)_2]$ both give essentially the same rate, hydride formation is not the rate-determining step.²¹⁴

5. Platinum(II)-olefin complexes can also be isolated from the reaction mixture, but again their formation is not rate determining for the same reasons as with the hydridoplatinum(II) complexes.²¹⁴

6. Formation of a hydridometal(II)-olefin complex may be the rate-determining step, since a number of such complexes have been isolated from the reaction medium.⁴⁸⁰

7. Stannous chloride was found to be an essential cocatalyst for all the complexes except $[\text{Pd}(\text{CN})_2(\text{PR}_3)_2]$, which has intrinsic activity of its own.^{214, 486, 488, 490} Stannous chloride reacts with chloride ions to give the SnCl_3^- ion, which exhibits a high *trans*-effect⁴⁹¹ and which is known to be a good ligand

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(491) R. D. Cramer, R. V. Lindsey, C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).

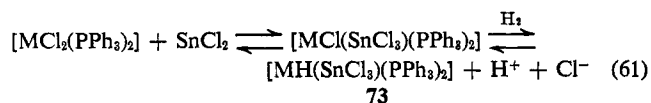
for platinum(II)⁴⁹¹⁻⁴⁹⁵ and palladium(II).⁴⁹⁶ The SnCl_3^- ligand is a weak σ donor and a strong π acceptor because of the presence of vacant 5d orbitals of the right size and energy to accept d electrons from platinum and palladium.⁴⁹⁷ This reduces the electron density on the metal making it susceptible to attack by nucleophiles such as hydride ions and olefins.²¹⁴ Thus a methanolic solution containing 1 mole of $[\text{PtCl}_2(\text{PEt}_3)_2]$ and 2 moles of stannous chloride absorbs 1 mole of hydrogen to give⁴⁹¹ $[\text{PtH}(\text{SnCl}_3)_2(\text{PEt}_3)_2]^-$. It has been suggested that the presence of π -bonding ligands is essential for the formation of stable hydrido complexes,⁴⁹⁸ although the recent demonstration that phosphines are essentially σ -bonding ligands with little or no π -bonding ability^{139,140} has invalidated this. The hydrido complexes of platinum(II) with phosphine ligands are too stable to act as hydrogenation catalysts, whereas when SnCl_3^- ligands are present the complexes have a more suitable lability.⁴⁹⁹

The platinum(II)-tin(II) complex is formed reversibly so that an excess of stannous chloride is necessary for its formation; however, too great an excess results in the SnCl_3^- ligands blocking the sites that would otherwise be available for coordination of hydride ions or olefins.²¹⁴ A platinum to tin ratio of 1:5 has been found to give the best results.^{493, 494, 500} Below a ratio of 1:3 metallic platinum is formed, and above a ratio of 1:7 the rate of hydrogenation gradually decreases.⁴⁸⁴ The addition of extra chloride or bromide ions at low stannous chloride concentrations gives a sharp rise in the rate due to the formation of SnCl_3^- ions.⁴⁸⁴

8. Hydrogenation by H_2 in MeOD and D_2 in MeOH results in all the deuterated ethylenes appearing at the start of the reaction and $\text{C}_2\text{H}_4\text{D}$ being the basic product obtained from ethylene.⁵⁰⁰

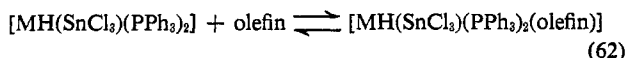
The following mechanism satisfactorily explains all these observations.

Stage 1: Formation of a metal(II)-tin(II) complex which reacts with hydrogen, which may come from molecular hydrogen or the solvent but does not come from the olefin, to form a hydrido complex (eq 61 where $M = \text{Pt}$ or Pd).²¹⁴ **73** with $M = \text{Pt}$ has been isolated and shown to be an effective



catalyst for the hydrogenation of conjugated double bonds that will not hydrogenate isolated double bonds.⁴⁸⁸

Stage 2: The formation of a five-coordinate hydridometal(II)-olefin complex (eq 62). A number of such five-coordinate complexes have been isolated⁴⁸⁰ with $M = \text{Pt}$. The formation

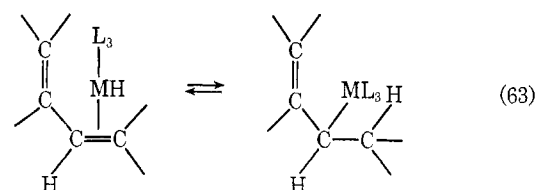


of such a complex would account for the fact that under

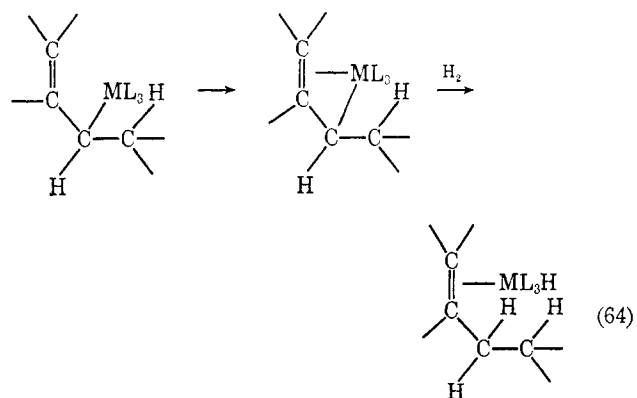
conditions in which palladium(II) complexes are not reduced to palladium metal they are generally better hydrogenation catalysts than platinum(II) complexes,⁴⁷⁹ since palladium(II) can more readily expand its coordination sphere than platinum(II).³¹¹⁻³¹³

Stage 3: Stepwise migration of the double bonds to give a conjugated diene. This is discussed in more detail in section IX.

Stage 4: Rearrangement of the olefin complex to give an alkyl complex (eq 63 where $\text{ML}_3 = \text{Pt}(\text{SnCl}_3)(\text{PPh}_3)_2$ or $\text{Pd}(\text{SnCl}_3)(\text{PPh}_3)_2$). This reaction is well known for platinum(II)-olefin complexes.^{197, 198}



Stage 5: Rearrangement of the alkyl complex by attack of the free double bond on the metal to give a σ - π complex, which then reacts with hydrogen to give the olefin complex (eq 64, where $\text{ML}_3 = \text{Pt}(\text{SnCl}_3)(\text{PPh}_3)_2$ or $\text{Pd}(\text{SnCl}_3)(\text{PPh}_3)_2$). Although the σ - π complex could in theory decompose to a



π -allyl complex which would then be hydrogenated to give the π -olefin complex, this mechanism is unlikely since no π -allyl complexes could be detected by nuclear magnetic resonance.⁴⁸⁰

Stage 6: Displacement of the coordinated monoolefin by free diolefin.

An alternative mechanism⁵⁰¹ involving coordination of two atoms of hydrogen to the metal followed by formation of an alkyldihydrometal(II) complex is less likely than the above mechanism, because none of its postulated intermediates have been isolated.

There are a number of correlations between homogeneous and heterogeneous catalytic hydrogenation, such as the fact that olefins are more weakly absorbed by palladium metal than by platinum metal,⁵⁰² so that heterogeneous hydrogenation can usefully be considered in terms of organometallic

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intermediates.^{490,503-506} This makes it easy to understand the poisoning of metal catalysts by carbon monoxide and sulfur and phosphorus ligands, since such ligands displace olefins from metal-olefin complexes.⁵⁰⁷⁻⁵⁰⁹ The greater selectivity and specificity of homogeneous than heterogeneous catalytic hydrogenation arises from the different environments of the metal atoms in the two systems, rather than from a different form of bonding.⁵⁰⁹

VIII. Homogeneous Hydrosilation of Olefins

The hydrosilation of olefins catalyzed by platinum complexes closely resembles the catalytic hydrogenation of olefins.⁵⁰⁷ Although platinum(II) complexes are effective hydrosilation catalysts,⁵¹⁰ platinum(IV) complexes such as chloroplatinic acid have been more widely studied.⁵¹¹⁻⁵¹⁴ The reaction, which has been used industrially,⁵¹⁵⁻⁵²⁰ is limited to platinum complexes since most palladium complexes are very rapidly reduced by silanes to palladium metal, and in the few cases where reduction does not occur no catalysis has been observed.⁵¹⁰

The extreme similarity between the hydrosilation of olefins catalyzed by platinum metal and by chloroplatinic acid led to the suggestion that the catalysis is heterogeneous with metallic platinum as the true catalyst.⁵²¹ However, since the solutions have been shown to remain optically clear, platinum complexes are true homogeneous catalysts.^{510,514}

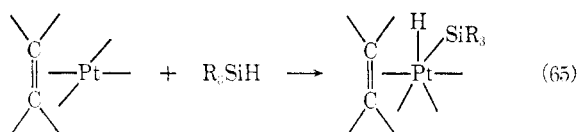
Hydrosilation is often accompanied by considerable isomerization of the olefin, the relative importance of hydrosilation and isomerization being partly determined by the silane present.⁵¹⁰ Terminal olefins give hydrosilation more rapidly than branched olefins.⁵¹⁸ After the addition of methylchlorosilane to an excess of a branched olefin in the presence of chloroplatinic acid, a number of isomers of the olefin were found to be present with the 1-olefin predominating.⁵¹³ A study of the isomerization of hexene by platinum(II) complexes indicated that in the absence of silanes there was a high initial preference for the *cis* isomer to be formed, which declined markedly as the reaction progressed.⁴⁷³ By contrast in the presence of silanes the *cis/trans* ratio, the magnitude of

which depended on the silane present, remained constant throughout the reaction.⁵¹⁰

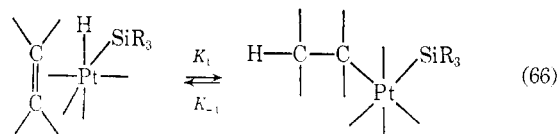
The hydrosilation of acetylenes results in the formation of *trans* products, indicating that *cis* addition of R_3Si-H across the triple bond has occurred.⁵²¹ Similarly the hydrosilation of 1-methylcyclohexene occurs in a stereospecifically *cis* manner⁵²² and the hydrosilation of bicycloheptadiene catalyzed by chloroplatinic acid gives the only known case of *endo* addition to this olefin.⁵²³

Complete hydrogen-deuterium exchange between olefinic hydrogen atoms and deuterated silanes has been observed in most cases, with the final adducts having deuterium widely and randomly distributed throughout.⁵¹⁴ However, there was complete deuterium retention by the olefin during the hydrosilation of 1-methyl-*d*₃-cyclohexene indicating that in this case intramolecular hydrogen exchange had occurred.⁵²²

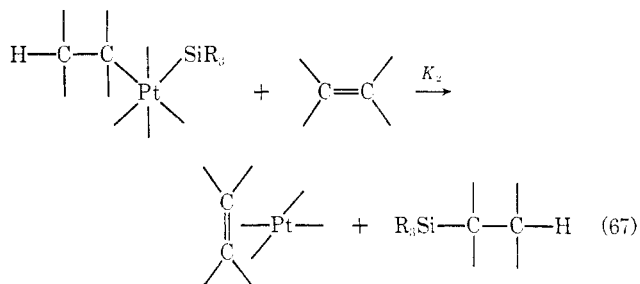
A mechanism for the reaction has been suggested^{510,514} which involves the formation of a platinum(II)-olefin complex by reduction of chloroplatinic acid by the olefin. The platinum(II)-olefin complex then forms a platinum(IV) complex by addition of the silane (eq 65). This adduct then rearranges



to give an alkyl complex (eq 66), from which the alkylsilicon



product is displaced by reaction with further olefin (eq 67).



This mechanism can account for the fact that isomerization sometimes does and sometimes does not occur, since two special cases can be envisaged. In the first the rates of silicon and hydride attack on the olefin are comparable (*i.e.*, $K_1 \sim K_2 > K_{-1}$). This case, which gives a concerted addition of silicon and hydrogen across the double bond and does not give isomerization, is favored by primary alkylsilanes. In the second case, which is favored by secondary and tertiary alkyl derivatives, the hydride attack on the olefin is much faster than the silicon attack (*i.e.*, $K_1 > K_2$) and the lifetime of the alkyl complex is long enough for a reversible alkyl-olefin equilibrium to lead to isomerization of the olefin (*i.e.*, $K_{-1} > K_2$). Thus the 1-olefin adduct predominates in the final

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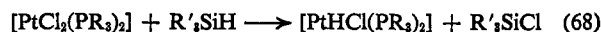
(520) A. J. Chalk, U. S. Patent 3,444,111 (1967); *Chem. Abstr.*, 67, 109343 (1967).

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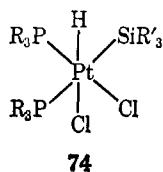
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product obtained from the hydrosilation of internal olefins. Although the addition of silanes to a platinum(II)-olefin complex to give a platinum(IV) complex (eq 65) has not been observed directly, the metathetical exchange between chloride and hydride in eq 68, where R = alkyl and R' = alkyl or aryl, can best be explained in terms of the platinum(IV)



complex 74 being formed as an intermediate.⁵⁰¹ The exceptionally high *trans*-effect of silicon ligands, which is inductive



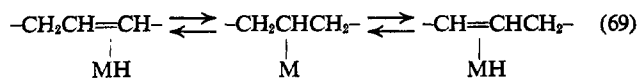
in origin and should therefore be present in octahedral as well as square-planar complexes, indicates that the platinum-silicon σ bond is very strong.⁵²⁴

The addition of germanium hydride derivatives across olefinic double bonds is also homogeneously catalyzed by chloroplatinic acid.⁵²⁵ Extensive isomerization occurs and, as in the homogeneous hydrogenation of olefins,⁴⁸⁰ conjugated dienes undergo germanation more rapidly than unconjugated dienes. As in hydrosilation the *cis* adduct is favored relative to the *trans* and the addition of trimethylgermanium hydride to norbornadiene gives *endo* and *exo* isomers in the ratio of 5:1, which is even greater than the 2.5:1 observed with hydrosilation.^{523,525}

IX. Catalytic Isomerization of Olefins

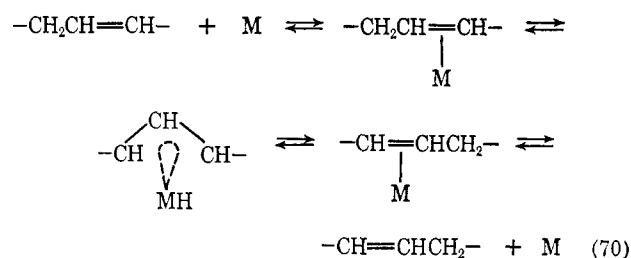
The isomerization of olefins in the presence of palladium(II) and to a lesser extent platinum(II) complexes has been widely observed. For example, the isomerization of unconjugated diolefins to conjugated diolefins is the first stage in the catalytic hydrogenation of polyolefins.⁴⁸⁰ Five mechanisms, which may be conveniently grouped under three headings, have been put forward to account for this isomerization.

1. *Intermolecular Hydrogen Transfer.*⁴⁷³ This mechanism, represented schematically by eq 69, involves the following steps: (a) formation of a metal hydride; (b) coordination

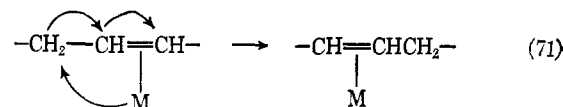


of the olefin to the metal hydride; (c) reversible addition of the metal hydride across the olefin double bond to give a metal alkyl; (d) alkyl complex reverting to a hydrido- π -olefin complex containing the isomerized olefin; (e) displacement of the isomerized olefin from the metal by further unisomerized olefin.

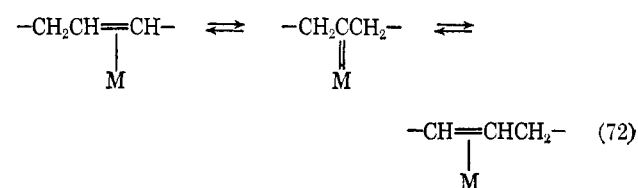
2. *Intramolecular Hydrogen Transfer.* Three possible mechanisms for intramolecular hydrogen transfer have been suggested: (a) formation of an intermediate hydrido- π -allylic complex⁵²⁶ (eq 70); (b) two concerted 1,2 hydrogen shifts accompanied by simultaneous migration of the metal ion⁵²⁷



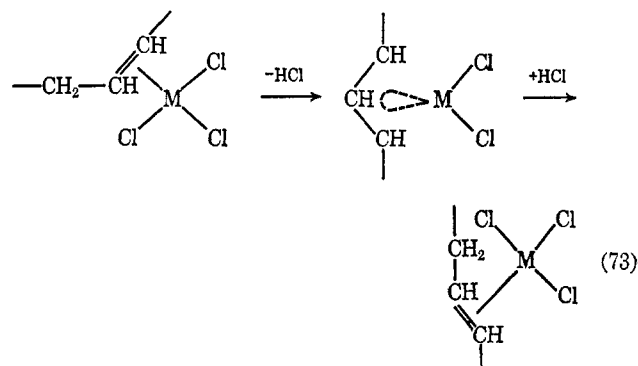
(eq 71); (c) formation of a metal-carbene intermediate⁵²⁸



(eq 72).



3. *Reversible π -Allyl Complex Formation.*⁵²⁸ This mechanism (eq 73) differs from that of eq 70 in that it does not involve a hydrido complex.



Although it has been suggested that there are so many common features between platinum(II) and palladium(II) complexes that two separate mechanisms are unlikely,⁵²⁸ there are sufficient differences to justify considering the two metals separately.

A. ISOMERIZATION OF OLEFINS IN THE PRESENCE OF PLATINUM COMPLEXES

Platinum(II) complexes that have been reported to isomerize olefins include PtCl_2 ,^{526,529} platinum(II)-olefin complexes in chloroform,⁵³⁰ alcohols,⁴⁷³ or acetic acid,⁴⁶⁶ platinum(II)-phosphine complexes either alone⁴⁴⁵ or in the presence of silanes⁵¹⁰ or stannous chloride,²¹⁴ mixtures of chloroplatinic acid and stannous chloride,^{482,531} and bis(acetylacetonato)-platinum(II).⁵³² In general platinum(II) complexes are less active than palladium(II) complexes.

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(531) G. C. Bond and M. Hellier, *J. Catalysis*, **7**, 217 (1967).

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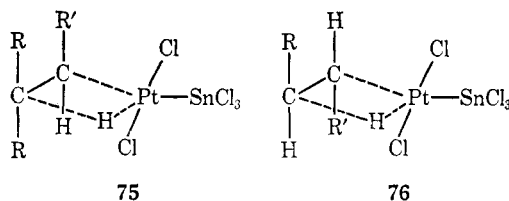
(526) F. Asinger, B. Fell, and P. Krings, *Tetrahedron Lett.*, 633 (1966).

(527) N. R. Davies, *Australian J. Chem.*, **17**, 212 (1964).

The inhibition of isomerization in basic systems,⁴⁶⁶ and the fact that the isomerization proceeds more rapidly in the presence than in the absence of molecular hydrogen,⁴⁷⁴ suggests that a hydride intermediate is formed. However, since the isomerization proceeds at comparable rates in the presence of $[\text{PtCl}_2(\text{PPh}_3)_2]$, $[\text{PtHCl}(\text{PPh}_3)_2]$, and $[\text{PtCl}(\text{PPh}_3)_2(\text{olefin})]$, the true catalyst is more likely to be a hydridoplatinum(II)-olefin complex than any one of these complexes. In agreement with this, a number of such hydridoplatinum(II)-olefin complexes have been isolated from the reaction mixture.²¹⁴ The hydrogen in these complexes was shown to originate either from molecular hydrogen or the solvent, but not from the olefin,²¹⁴ so that in CH_3OD extensive deuteration of the product was observed.⁴⁷⁴

Of the possible mechanisms the hydrido- π -olefin mechanism (eq 69) fits the experimental observations best. The reversible reaction of platinum(II)-olefin complexes with hydrogen to give σ -bonded platinum-alkyl complexes has been studied in detail^{197,198} (see section III.B.1.a). It has been suggested that since, when one olefin containing tritium in the allyl position is isomerized in the presence of another olefin very little tritium exchange is observed, a hydridoplatinum(II)-olefin intermediate cannot be formed although a hydrido- π -allylic intermediate (eq 70) may be formed.⁵²⁶ However, since it has now been shown that the olefin is an insignificant source of hydrogen for hydrido-olefin complex formation,²¹⁴ this observation is consistent with a hydridoplatinum(II)-olefin mechanism (*i.e.*, eq 69).

In the isomerization of terminal olefins, an abnormally high proportion of the *trans* isomer is formed.^{473,482,531} This observation, which is in direct contrast to the result obtained using palladium(II) complexes, can be understood if it is assumed that in the alkyl complex the atoms C, C, H, and Pt are approximately in a plane. This leads to two possible intermediates **75** and **76**, which, ignoring the interactions with platinum which are identical in **75** and **76**, only differ



in the nonbonded repulsions between hydrogen atoms. These interactions lead to **76** being of lower energy than **75** and hence *trans* olefins being preferentially formed.⁵³¹

B. ISOMERIZATION OF OLEFINS IN THE PRESENCE OF PALLADIUM COMPLEXES

Palladium complexes that catalyze the isomerization of olefins include PdCl_2 ,^{526,527,529,533-537} $[\text{PdCl}_2(\text{PhCN})_2]$,^{222,525,528,539} palladium(II)-olefin^{530,535,538,540} and π -allyl complexes,⁵³⁰

(533) N. R. Davies and B. Cruikshank, *Australian J. Chem.*, **19**, 815 (1966).

(534) G. C. Bond and M. Hellier, *J. Catalysis*, **4**, 1 (1965).

(535) M. B. Sparke, L. Turner, and A. J. M. Wenham, *ibid.*, **4**, 332 (1965).

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(538) M. B. Sparke, L. Turner, and A. J. M. Wenham, IUPAC Abstracts, Division A, A B4-30, 1963, p 175.

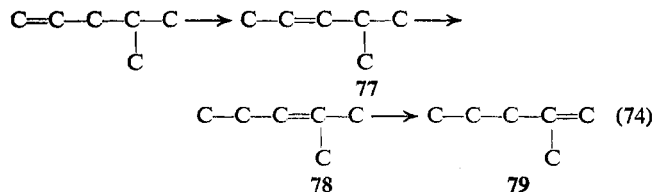
(539) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **88**, 3491 (1966).

(540) G. Pregaglia, M. Donati, and F. Conti, *Chim. Ind. (Milan)*, **49**, 1277 (1967).

palladium(II)-phosphine complexes,^{213,445,541} bis(acetylacetonato)palladium(II),⁵³² and palladium(0) complexes.⁵⁴²⁻⁵⁴⁴

There is some dispute as to whether the isomerization of olefins by palladium(II) complexes occurs by a stepwise or multistep migration of hydrogen. During the isomerization of $\text{C}_6\text{H}_{11}\text{CD}_2\text{CH}=\text{CH}_2$ by PdCl_2 in acetic acid, there is no appreciable migration of deuterium to the terminal carbon atom, suggesting that the migration occurs by a stepwise mechanism.⁵²⁷ This result, which is in disagreement with the results obtained in the presence of $[\text{PdCl}_2(\text{PhCN})_2]$,⁵³⁹ is consistent with the hydrido- π -olefin mechanism (eq 69) since a relatively high deuterium-hydrogen isotope effect would be expected⁵⁴⁵ whereby carbon-hydrogen bond rupture would be strongly favored relative to carbon-deuterium bond rupture. The failure of 2-methylpent-1-ene to isomerize was advanced as evidence for the stepwise migration of atoms in eq 71, due to the absence of hydrogen on the 2-carbon atom of this olefin.⁵²⁷ However, it has since been found that 2-methylallylbenzene, which also has no hydrogen attached to the 2-carbon atom, is isomerized, suggesting that a stepwise migration of hydrogen by reaction 71 is not responsible for isomerization.¹⁹⁷ Instead a hydrido- π -olefin mechanism (eq 70) was postulated. It was suggested that 2-methylallylbenzene isomerizes because it yields the conjugated 2-methylstyrene, which is an energetically favorable process, whereas the energy difference between 2-methylpent-1-ene and 2-methylpent-2-ene is not sufficiently favorable to enable the isomerization of 2-methylpent-1-ene to proceed.

There is a considerable amount of evidence that multistep migration of hydrogen does occur. The isomerization of $\text{RCD}_2\text{CH}=\text{CH}_2$ in the presence of $[\text{PdCl}_2(\text{PhCN})_2]$ gives a C-3 to C-1 deuterium shift.⁵³⁹ In the isomerization of 4-methylpent-1-ene it was found that the ratio of 2-methylpent-1-ene to 2-methylpent-2-ene exceeded the equilibrium ratio.⁵³⁵ This isomerization could not proceed by a stepwise mechanism (eq 74), since it is thermodynamically impossible for the



yield of **79** to exceed that of **78** by this route. The observation of all three products (**77**, **78**, and **79**) in the reaction mixture suggests that some stepwise and some multistep isomerization occurs. A similar observation was made in the isomerization of 4-phenylbut-1-ene in the presence of $[\text{PdCl}_2(\text{PhCN})_2]$, where some stepwise and some multistep migration occurred.⁵⁴⁶

The most probable mechanism for the stepwise migration of hydrogen is the hydrido- π -olefin mechanism (eq 69). There is some controversy about the mechanism of the

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(542) I. I. Moiseev and S. V. Pestrikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1717 (1965); *Chem. Abstr.*, **63**, 17835b (1965).

(543) I. I. Moiseev and S. V. Pestrikov, *Dokl. Akad. Nauk SSSR*, **171**, 151 (1966); *Chem. Abstr.*, **66**, 37112 (1967).

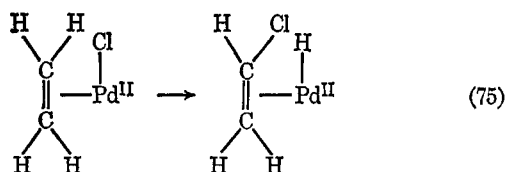
(544) I. I. Moiseev, S. V. Pestrikov, and L. M. Sverzh, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1866 (1966); *Chem. Abstr.*, **66**, 64859 (1967).

(545) W. H. Saunders, *Chem. Ind. (London)*, 663 (1966).

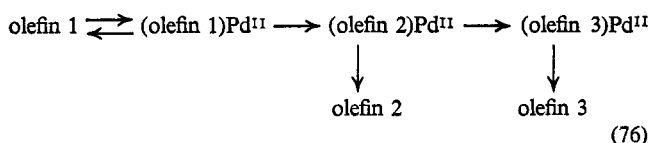
(546) N. R. Davies, A. D. DiMichiel, and V. A. Pickles, *Australian J. Chem.*, **21**, 385 (1968).

multistep isomerization. The possibility that it proceeds by reversible π -allyl complex formation (eq 73) is eliminated by the observation that in CH_3COOD no deuterium is incorporated in the product.⁵³⁶ In addition it has been shown that π -allyl-palladium(II) complexes do not catalyze olefin isomerization.^{534,547} In spite of this observation the hydrido- π -allyl mechanism (eq 70) is still possible, because the intermediate in this mechanism contains a hydride ion which is not present in the π -allylpalladium(II) complexes. The simultaneous isomerization of pent-1-ene and deuterium-labeled hept-1-ene ($\text{C}_4\text{H}_9\text{CD}_2\text{CH}=\text{CH}_2$) by $[\text{PdCl}_2(\text{PhCN})_2]$ results in very little transfer of deuterium to the pent-1-ene,⁵³⁹ which suggests that most of the isomerization occurs by an intramolecular hydrogen migration. The hydrido- π -allylic mechanism (eq 70) gives intramolecular hydrogen migration whereas the hydrido- π -olefin mechanism (eq 69) gives intermolecular hydrogen migration.

In contrast to platinum, when isomerization is catalyzed by palladium(II) complexes the olefin being isomerized must be the source of hydrogen for both the hydrido- π -olefin and the hydrido- π -allyl mechanisms, since isomerization can be effected by PdCl_2 or $[\text{PdCl}_2(\text{PhCN})_2]$ in the absence of solvent^{535,537} or in benzene solution.^{473,534,539,547} Under these conditions hydrido-palladium(II) complexes would not be formed unless an olefin were present. The isolation of a trace of vinyl chloride during the isomerization of *cis*-but-2-ene in the presence of ethylene⁴⁷⁴ suggests that the hydride is displaced from the olefin to the palladium by nucleophilic attack of the olefin by chloride ion or other nucleophiles present (eq 75).



An alternative to the hydrido- π -allyl mechanism that will account for multistep migration is a multistep hydrido- π -olefin mechanism (eq 76).⁵²⁸ Multistep migration would occur



if the liberation of olefin 2 from its complex were slow relative to the isomerization of this complex to the complex of olefin 3. This mechanism is unlikely because the rate of exchange of free olefin with olefin coordinated to palladium(II) is expected to be very rapid, since nuclear magnetic resonance studies have shown⁵² that for platinum(II)-olefin complexes this exchange is very rapid.

A further mechanism that would explain multistep migration involves a combination of a stepwise migration of the double bond associated with cleavage of the olefin and rearrangement of the fragments.⁵⁴⁸ This mechanism is, however, unlikely since no skeletal rearrangements of olefins in the presence of palladium(II) complexes have been observed.

Where quantitative studies of the relative amounts of *cis*

and *trans* isomers formed during the isomerization of terminal olefins have been made, it has generally been found that the amount of the *cis* isomer formed, at least in the early stages of the reaction, is greater than would be present in an equilibrium mixture of *cis* and *trans* isomers.^{473,534,535,546} This result, which is in contrast to that found in the presence of platinum(II) complexes, is consistent with the greater stability of *cis*-olefin complexes.¹²⁵ The only exception to this has been observed in the isomerization of $\text{C}_6\text{H}_5\text{CC}=\text{C}-$ to $\text{C}_6\text{H}_5\text{C}=\text{CC}-$ where the product formed is mainly the *trans* isomer.^{187,546} This has been ascribed to steric hindrance in *cis*-($\text{C}_6\text{H}_5\text{C}=\text{CC}-$).

In conclusion neither the hydrido- π -olefin (eq 69) nor the hydrido- π -allylic mechanism (eq 70) can satisfactorily explain all the experimental observations, and a great deal of work remains to be done to distinguish between these two possible mechanisms. At present it appears likely that both mechanisms can occur, depending on the precise experimental conditions. It is possible that both temperature and the solvent have an important bearing on the actual mechanism of isomerization. The solvent may be particularly important since both the isomerization of 2-methylpent-1-ene, which appeared to proceed *via* a C-3 to C-1 hydrogen shift,⁵³⁵ and the isomerization of $\text{C}_5\text{H}_{11}\text{CD}_2\text{CH}=\text{CH}_2$, which appeared to proceed *via* a C-2 to C-1 hydrogen shift,⁵²⁷ were carried out at 62–65°. However, the former was carried out in the olefin itself, whereas the latter was carried out in acetic acid.

X. Polymerization

A. POLYMERIZATION OF OLEFINS

Although palladium(II) complexes are effective homogeneous catalysts for the polymerization of olefins, only a few examples of the polymerization of olefins catalyzed by platinum(II) complexes have been reported. Thus while $[\text{PdCl}_2(\text{C}_2\text{H}_4)_2]$ catalyzes the dimerization of ethylene and also decomposes on heating to give butenes,⁵⁴⁹ the platinum(II) analog does not catalyze the dimerization of ethylene⁵⁴⁹ and decomposes on heating above 180° to give chlorinated C_2 hydrocarbons.¹⁹⁹ In the few cases where platinum(II) complexes have been found to catalyze the dimerization or further polymerization of olefins, the accounts are descriptive and no mechanistic studies have been reported.^{550–554}

The polymerization of olefins by palladium(II) complexes is very dependent on the nature of both the solvent⁵⁵⁵ and the other ligands coordinated to palladium(II).^{551,552,556–558} Thus PdCl_2 catalyzes the polymerization of butadiene to 1,2-polybutadiene whereas both PdI_2 and $\text{Pd}(\text{CN})_2$ give very low

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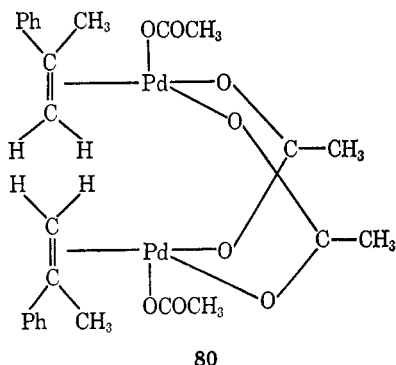
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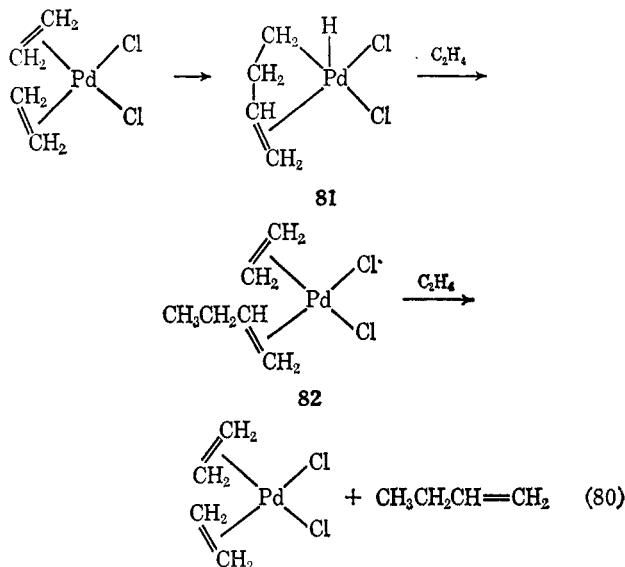
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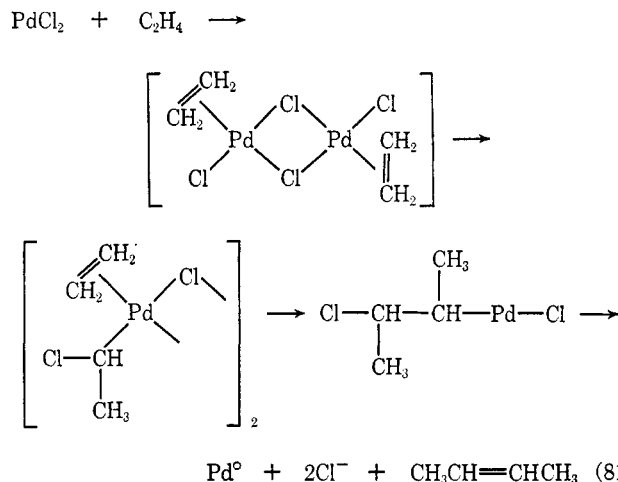
atom can then attack the other olefin by an intramolecular nucleophilic mechanism similar to that already discussed for the acetylation of olefins (eq 29).

A mechanism involving the initial formation of *cis*-[PdCl₂(C₂H₄)₂] has been suggested to account for the PdCl₂-catalyzed dimerization of ethylene (eq 80).⁵⁵⁸ One of the coordinated ethylene molecules attacks the other by an intramolecular



nucleophilic mechanism, displacing hydride ion on to the palladium. A molecule of ethylene then reacts with the intermediate (81) to give the *cis*-bis(olefin) complex 82. The butene formed is readily displaced by ethylene since the latter coordinates more strongly to palladium(II).¹²⁰ Although *cis*-[PdCl₂(C₂H₄)₂] has not been isolated, it may well be formed under the conditions of the reaction, which include 10 atm of ethylene, since evidence has been obtained for the formation of *cis*-[PtCl₂(C₂H₄)₂],⁵⁷⁵ and *cis* complexes of palladium(II) containing chelating diolefins are known.²¹⁹ The complex *trans*-[PdCl₂(C₂H₄)₂], which would be expected to be formed before the *cis* complex,⁵⁷⁵ was in fact isolated from the reaction mixture and shown to be stable up to -40°.⁵⁵⁸

A further mechanism put forward to account for the dimerization of ethylene and propylene by palladium(II) salts involves insertion of one carbon atom of ethylene into the palladium(II)-chlorine bond of [PdCl₂(C₂H₄)₂] (eq 81).³⁰⁷ This reaction, which is analogous to eq 36 discussed above in connection with the acetylation of olefins, is followed by an intramolecular insertion of ethylene into the palladium-



carbon σ bond. Decomposition of this complex yields the observed butene.

At present there is insufficient experimental data on the polymerization of olefins to distinguish between the reaction mechanisms suggested, and a great deal more experimental work is needed.

B. POLYMERIZATION OF ACETYLENES

Acetylene and monosubstituted acetylenes readily form complexes with palladium(II) which are labile and polymeric.⁵⁷⁶ The degree of polymerization, which depends on the solvent, decreases as the temperature increases.⁵⁷⁷ On treating acetylene with PdCl₂ the principle product is *trans*-polyacetylene although a number of side products including benzene are formed.⁵⁷⁸ The only report of a platinum-catalyzed polymerization involved the use of PtCl₄ in the presence of a hydridic reducing agent.⁵⁷⁹

The most widely investigated acetylene polymerization reaction catalyzed by palladium(II) complexes is the dimerization of disubstituted acetylenes to give cyclobutadienes. Although a number of palladium-cyclobutadiene complexes have been prepared since they were predicted on theoretical grounds to be stable,⁵⁸⁰ no platinum complexes have been described. The first palladium complex was prepared by the reaction of PdCl₂ and diphenylacetylene in ethanol to give hexaphenylbenzene and the dimeric complex [PdCl{C₆H₄(OC₆H₅)₂]₂. This complex reacts with hydrochloric acid to give [PdCl₂(C₆H₄)₂].^{581,582} The intermediate dimer [PdCl{C₆H₄(OC₆H₅)₂]₂ can be prepared in better yields by the action of diphenylacetylene on [PdCl₂(PhCN)₂] in ethanol-chloroform⁵⁸³⁻⁵⁸⁵ or from Na₂PdCl₄ and diphenylacetylene in

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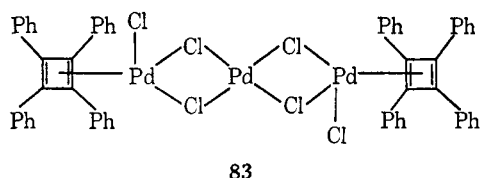
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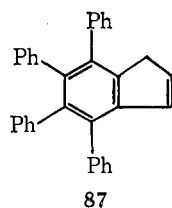
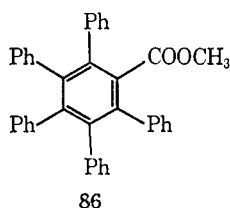
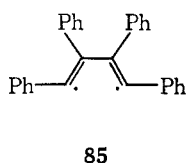
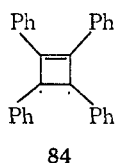
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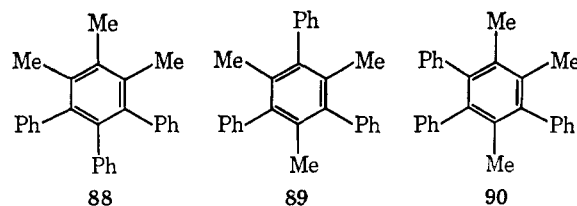
aqueous ethanol.⁵⁸⁷ This intermediate exists in two isomeric forms, one of which was originally thought to contain a palladium-carbon σ bond and a palladium-olefin π bond, and the other was thought to be a π -cyclobutenyl complex.^{584,588} An X-ray structure determination has shown that both isomers are π -allyl complexes, one of which has the ethoxy group in an *endo* position with respect to palladium and the other in an *exo* position.^{589,590} In a 3:1 chloroform-ethanol solvent $[\text{PdCl}_2(\text{PhCN})_2]$ reacts with diphenylacetylene to give $[(\text{PdCl}_2)_3(\text{C}_4\text{Ph}_4)_2]$,⁵⁸⁵ whereas in benzene polymeric $[(\text{C}_4\text{Ph}_4)\text{PdCl}_2(\text{PdCl}_2)_n\text{PdCl}_2(\text{C}_4\text{Ph}_4)]$ is formed.⁵⁸⁶ The spectroscopic data indicate that these complexes have structure **83**. These complexes react with hydrochloric acid to give $[\text{PdCl}_2(\text{C}_4\text{Ph}_4)]$.



$[\text{PdCl}_2(\text{C}_4\text{Ph}_4)]$ is thermally stable and resistant to oxidizing agents. It undergoes a number of interesting reactions which may also be preparatively important. On heating *in vacuo* it gives 1,4-dichloro-1,2,3,4-tetraphenyl-1,3-butadiene.⁵⁸⁴ It reacts with phosphines in boiling benzene in the absence of air to give octaphenylcyclooctatetraene and $[\text{PdCl}_2(\text{PR}_3)_2]$.^{586,591} During the reaction a green intermediate, which is probably either **84** or **85**, is formed.^{582,592} Treatment of $[\text{PdCl}_2(\text{C}_4\text{Ph}_4)]$ in the absence of air with methyl phenylacetylene-carboxylate and cyclopentadiene gives **86** and **87**, respec-



tively.⁵⁸² When $[\text{PdCl}_2(\text{C}_4\text{Ph}_4)]$ is treated with phosphines or pyridine in the presence of air, tetraphenylfuran is formed.^{582,585} The formation of hexaphenylbenzene during the preparation of $[\text{PdCl}_2(\text{C}_4\text{Ph}_4)]$ probably occurs as a result of the addition of one of the diradicals **84** or **85** to unreacted diphenylacetylene,^{444,581,593} although the formation of **88** as well as **89** and **90** during the trimerization of methylphenylacetylene in the presence of PdCl_2 indicates that the reaction may well



be more complex.⁵⁷⁶ The dimer $[\text{PdCl}_2(\text{C}_4\text{Ph}_4)]_2$ reacts with disodium dicarbollide splitting the chlorine bridge to give a monomeric complex which X-ray diffraction indicated to have the sandwich structure shown in Figure 15.⁵⁹⁴

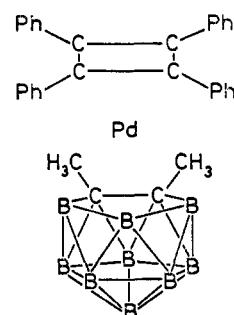
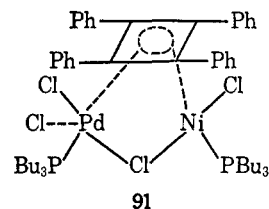


Figure 15. Structure of $[\text{Pd}(\pi\text{-C}_6\text{H}_5)_4\text{C}_4]$ ($\pi\text{-B}_9\text{C}_2\text{H}_{11}(\text{CH}_3)_2$) (from ref 594).

Tetraphenylcyclobutadiene complexes of molybdenum,^{595,596} tungsten,⁵⁹⁶ iron,⁵⁹⁷ cobalt,⁵⁹⁷⁻⁵⁹⁹ and nickel^{597,600} have been prepared by ligand exchange with the palladium(II) complex.⁶⁰¹ The formation of the nickel complex by eq 82 has been studied in some detail.⁶⁰⁰ The first step involves dissociation of one molecule of phosphine from the nickel $[\text{PdCl}_2(\text{C}_4\text{Ph}_4)]_2 + 2[\text{NiCl}_2(\text{PBu}_3)_2] \rightarrow$
 $[\text{NiCl}_2(\text{C}_4\text{Ph}_4)] + 2[\text{PdCl}_2(\text{PBu}_3)_2]$ (82)

complex. This phosphine molecule then coordinates to palladium(II), which probably weakens the palladium(II)-cyclobutadiene bond since no cyclobutadiene complexes of palladium(II) containing phosphine ligands have been prepared despite a number of attempts. The final stage, which involves the transfer of cyclobutadiene from palladium(II) to nickel(II), probably involves a bridged intermediate such as **91** rather than formation of free tetraphenylcyclobutadiene,



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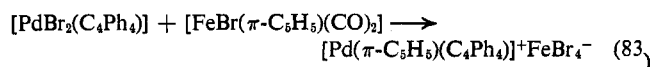
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since in the presence of dienophiles no tetraphenylcyclobutadiene-dienophile adducts were detected.

Although π -cyclopentadienylcobalt complexes react with $[\text{PdCl}_2(\text{C}_6\text{H}_4)]$ to give the expected complex $[\text{Co}(\pi\text{-C}_5\text{H}_5)(\text{C}_6\text{H}_4)]$,^{607,602} with π -cyclopentadienyliron complexes transfer of cyclopentadiene from iron to palladium is observed (eq 83).⁶⁰⁸⁻⁶⁰⁵ This reaction is also thought to proceed *via*



a bridged intermediate in which the transition state involves the cyclopentadienyl group bound to both metal atoms.⁶⁰⁵

(602) P. M. Maitlis, Symposium on Current Trends in Organometallic Chemistry, Cincinnati, Ohio, June 1963, Abstract 58.

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XI. Conclusion

Although a number of advances have been made in the understanding of the bonding in metal-olefin and -acetylene complexes since 1962, the most spectacular advances have been made in studying the chemistry of olefins and acetylenes coordinated to platinum and palladium. This work in turn has demonstrated further gaps in the present understanding of the nature of the bonding in these complexes, so that in the next few years there are likely to be considerable advances both in the fundamental understanding of the nature of the metal-olefin bond and in the reactions of olefins coordinated to metal.

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