

# 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,<sup>1</sup> a very large number of olefin and acetylene complexes have been reported. Reviews in 1941<sup>2</sup> and 1952<sup>3</sup> summarized the early preparative and qualitative stability data. During the early fifties the currently accepted explanation of the bonding was put forward, initially for silver<sup>4</sup> and later for platinum.<sup>5</sup> This stimulated much research on the structure of metal-olefin complexes which was reviewed in 1962.<sup>6,7</sup> 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 bonding<sup>5</sup> and which involve the more recently discovered  $\pi$ -allyl type of bonding.<sup>8</sup> 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,<sup>9,10</sup> 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.<sup>11</sup>

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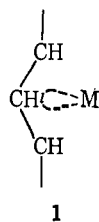
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This review surveys the work on olefin and acetylene complexes of platinum and palladium reported since the previous review in 1962.<sup>6</sup> An attempt has been made to survey all the literature published up to July 1968.

A number of papers published since then have also been included, but a complete coverage was not possible. The closely related field of  $\pi$ -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.<sup>8</sup> In view of the current controversy regarding the nature of the bonding in  $\pi$ -allyl complexes, these have been represented as in 1 to avoid favoring either the  $\pi$ -olefin plus  $\sigma$ -carbon bonded species or the  $\pi$ -allyl species.<sup>12-14</sup>



This review includes only those compounds involving a  $\pi$  bond between the metal ion and the olefin or acetylene; no mention is made of either olefin or acetylene complexes involving a  $\sigma$  bond from carbon to metal; these have been reviewed elsewhere.<sup>15</sup> 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.<sup>16</sup>

## II. Nature of the Bonding

### A. MOLECULAR ORBITAL TREATMENT

The molecular orbital treatment, which was first applied to silver-olefin complexes<sup>4</sup> and later extended to platinum-olefin complexes,<sup>5</sup> gives the currently accepted explanation of the nature of the metal-olefin bond. This essentially involves a  $\sigma$  bond (olefin to metal) and a  $\pi$  bond (metal to olefin) as shown in Figure 1. The  $\sigma$  bond, which in the case of platinum is formed between the filled olefin  $\pi$  orbitals and the empty  $5d_6s_6p^2$  hybrid orbital on platinum, causes an unfavorable distribution of negative charge on the metal ion; however, the  $\pi$  back-donation from the filled  $5d_6p$  hybrid on platinum to the empty olefin  $\pi^*$  (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

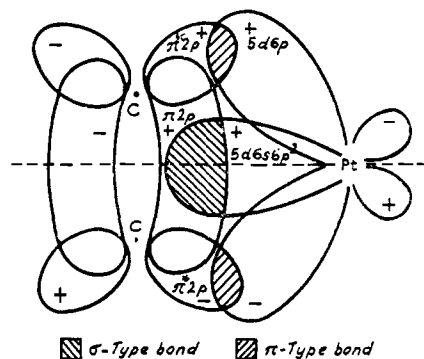


Figure 1. Bonding in metal-olefin complexes (from ref 5).

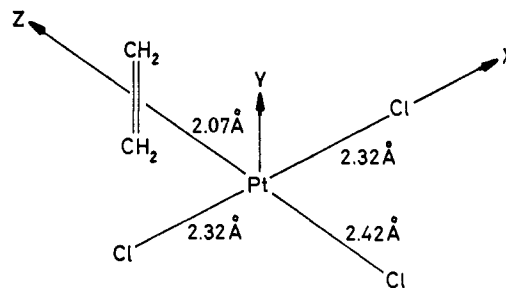


Figure 2. The structure of Zeise's salt. The bond lengths are from ref 18, and the axes are those used throughout this review.

of olefins is lowered by about  $140\text{ cm}^{-1}$  on coordination to platinum,<sup>17</sup> 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 salt<sup>18</sup> (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  $[PtCl_2(\text{dipentene})]^{19}$  in which the ligand is very strained.

The X-ray diffraction pattern of dichloro(*p*-toluidine)-(di-*t*-butylacetylene)platinum(II)<sup>20</sup> 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  $220\text{ cm}^{-1}$  in the infrared stretching frequency of the carbon-carbon triple bond on coordination to platinum(II).<sup>21</sup>

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.<sup>22</sup> The molecular orbital scheme can be made less rigid

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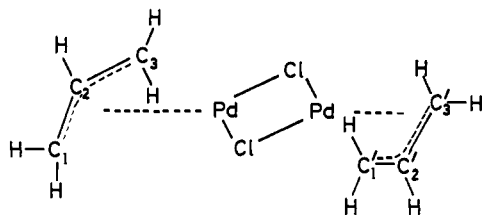


Figure 3. The structure of  $\pi$ -allylpalladium(II) chloride (from ref 26).

if the  $\pi$  back-donation to the olefin  $\pi^*$  (antibonding) orbital can occur from both the metal  $d_{yz}$  and metal  $d_{zx}$  orbitals or any linear combination of these.<sup>23</sup>

In the closely related  $\pi$ -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.<sup>24-26</sup> 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,<sup>18,27</sup> except in special cases where strain exists.<sup>19</sup> 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.<sup>28</sup> 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  $1.52 \pm 0.036$  Å;<sup>29</sup> remeasurement gave a value of  $1.46 \pm 0.037$  Å.<sup>28</sup> A further determination at the temperature of liquid nitrogen gave a value of  $1.366 \pm 0.010$  Å.<sup>30</sup> This value, which is com-

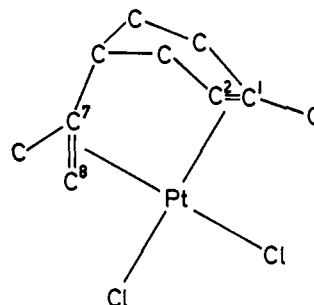


Figure 4. X-Ray structure of dichloro(dipentene)platinum(II) (from ref 19).

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).<sup>31</sup> 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.<sup>32</sup> 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)<sup>19</sup> (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  $62.1^\circ$ .

The complex  $[Pt_3(SnCl_3)_2(cycloocta-1,5-diene)]$  contains a platinum-tin cluster in which the two tin atoms are on each side of the plane containing the three platinum atoms.<sup>33</sup> 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.<sup>20</sup> The bonds joining the *t*-butyl groups to the acetylenic group are bent away from the metal by  $15^\circ$ .

The  $\pi$  back-donation of charge from the metal  $d_{xz}$  orbital to the olefin  $\pi^*$  (antibonding) orbital accounts for the high *trans* effect of olefins. This causes bond weakening if the ligand *trans* to the olefin forms  $\pi$  bonds to the metal, but may even cause a slight strengthening if the *trans* ligand forms pure  $\sigma$  bonds to the metal.<sup>34</sup> 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).<sup>35</sup> Similarly in the complex *cis*-[PtBr<sub>2</sub>(NH<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)] the platinum–bromine bond length *trans* to ethylene was found to be 2.51 Å, whereas the *cis* bond was only 2.40 Å.<sup>36,37</sup> By contrast a very careful determination indicated a value of 2.33 Å for the platinum–chlorine bond length<sup>19</sup> in [PtCl<sub>2</sub>(dipentene)], in close agreement with the platinum–chlorine bond lengths in both *cis*- and *trans*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] (2.33 and 2.32 Å, respectively).<sup>38</sup> Similarly the palladium–chlorine bond lengths in dichloro-(norbondadiene)palladium(II) were found to average 2.316 ± 0.0014 Å,<sup>30</sup> 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.<sup>31</sup>

## 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,<sup>39,40</sup>  $\alpha = 10^\circ$ ,  $\beta = 42^\circ$ ; bis(triphenylphosphine)(diphenylacetylene)platinum,<sup>41</sup>  $\alpha = 14^\circ$ ,  $\beta = 39^\circ$ ; bis(triphenylphosphine)(ethylene)nickel,<sup>42</sup> which is isomorphous with the corresponding platinum complex,<sup>43</sup>  $\alpha = 12^\circ$ ,  $\beta = 42^\circ$ .

The observation that in all three complexes the value of  $\alpha$  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  $\sigma$  bond is formed by donation of olefin or acetylene  $\pi$  electrons to a  $d_{sp^2}$  hybrid orbital on platinum, and the  $\pi$  bond is formed by back-donation from the filled  $d_{yz}$  or  $d_{yz}p_z$  hybrid orbital on platinum to the  $\pi^*$  (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  $\sigma$  bonds to platinum, which is itself in the +2 oxidation state. The small values observed for  $\beta$  (Figure 5) suggest that the three-membered ring would be very strained. However, since the tetracyanoethylene complex melts at 268–270° (with decomposition),<sup>40</sup> the considerable thermal stability of the complex suggests that little strain is present. On the other hand, the finding that the

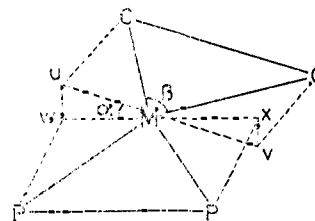


Figure 5. The structure of olefin and acetylene complexes of platinum(0). The plane containing the points u, v, w, and x together with atom M is perpendicular to both the MCC and MPP planes.

fluorine–fluorine coupling constant in the nuclear magnetic resonance spectrum of [Pt(PPh<sub>3</sub>)<sub>2</sub>(hexafluoropropene)] is of the same order as that observed in saturated fluorocarbon systems suggests that the hexafluoropropene moiety is  $\sigma$ -bonded to platinum.<sup>44</sup> In the molecular orbital description a  $\sigma$  bond from the olefin or acetylene  $\pi$  orbital to the platinum  $d_{sp^2}$  hybrid orbital is complemented by back-bonding from the metal  $d_{zz}$  orbital to the olefin  $\pi^*$  (antibonding) orbital. Although these two bonding schemes are essentially equivalent,<sup>40</sup> the molecular orbital description has the advantage of greater flexibility.

Since the  $\sigma$ -donor properties of tetracyanoethylene are negligible, this ligand is virtually “pure  $\pi$ -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  $\pi$ - rather than  $\sigma$ -bonding since the weaker the  $\sigma$ -donor capacity, the more stable the complex.<sup>45</sup>

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.<sup>41</sup> 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.<sup>46</sup> 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.<sup>46</sup> 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<sup>-1</sup> for platinum<sup>17</sup> and 120 cm<sup>-1</sup> for palladium.<sup>47</sup> For acetylenes the carbon–carbon triple-bond stretching frequency is lowered by about 250 cm<sup>-1</sup> on coordination to platinum(II).<sup>48</sup> Acetylenes are polymerized so rapidly by palladium(II) that no comparable figure is available for

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coordination to palladium(II).<sup>48</sup> The infrared spectra of metal-olefin and -acetylene complexes have been widely used to give preliminary evidence for the structure of the complexes.<sup>49</sup> However, infrared studies alone cannot be relied on to distinguish between a normal olefin complex and a  $\pi$ -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  $\pi$ -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.<sup>52,53</sup>

The complex formed between tetramethylbutynediol and  $\text{PdCl}_2$  is a good example where an unexpected structure has been deduced from the infrared spectrum; a band at  $1700\text{ cm}^{-1}$  was assigned to a carbonyl stretching frequency,<sup>54</sup> 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  $2010\text{ cm}^{-1}$  and has the normal divalent metal-acetylene complex structure<sup>21</sup>  $\text{K}^+[\text{PtCl}_3\{(\text{CH}_3)_2(\text{HO})\text{CC}\equiv\text{CC}(\text{OH})(\text{CH}_3)_2\}]^-$ .

The infrared spectra of Zeise's salt, of its dimer, and of the palladium(II) analogs have been studied in detail.<sup>55-61</sup> 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  $427\text{ cm}^{-1}$  (palladium) are due to the metal-ethylene stretching modes.<sup>62,60</sup> An earlier assignment<sup>59</sup> of bands at  $485$  and  $364\text{ cm}^{-1}$  as well as the band at  $408\text{ cm}^{-1}$  to platinum-ethylene stretching modes has been questioned.<sup>60</sup> The band at  $485\text{ cm}^{-1}$ , which was observed at  $490\text{ cm}^{-1}$  in the Raman spectrum of Zeise's salt and assigned to the platinum-olefin asymmetric stretching frequency,<sup>62</sup> was found to be very solvent dependent and was therefore assigned to a combination or overtone band.<sup>60</sup> The band at  $364\text{ cm}^{-1}$  was assigned to the platinum-terminal chlorine stretching mode<sup>60</sup> in agreement with an independent assignment obtained from a number of platinum(II)- and palladium(II)-bridged chloro complexes.<sup>63</sup> 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  $2.14\text{ mdyne/\AA}$  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.<sup>60</sup>

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.<sup>64</sup> This correlation was later withdrawn since the bands assigned to the olefin were found to be due to another ligand present (pyridine N-oxide).<sup>65</sup> 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<sup>67,65,66</sup> 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.<sup>68,67</sup> 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.<sup>68</sup> 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 Substituents<sup>66</sup>

Olefin	$\nu_{\text{C}=\text{C}}$ , $\text{cm}^{-1}$	Olefin	$\nu_{\text{C}=\text{C}}$ , $\text{cm}^{-1}$
$\text{CH}_2=\text{CHCH}_2\text{OH}$	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.<sup>60</sup>

The platinum-chlorine stretching frequencies in the metal-olefin complexes have been well studied.<sup>55-61,63,69</sup> 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.<sup>69</sup> This has been used to confirm the assignment of these bands in dichloro(norbornadiene)platinum(II).<sup>70</sup> The platinum-chlorine stretching frequencies of a series of complexes  $[\text{PtCl}_2\text{L}]^-$  (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.<sup>56,59,61</sup> This has been claimed to be consistent with the high *trans*-effect of olefins.<sup>56</sup> However, as mentioned earlier, ligands which exert a *trans*-effect by a mesomeric or  $\pi$ -acceptor mechanism will only cause bond weakening if the *trans* bond has any  $\pi$ -bonding, and may cause a slight strengthening if the *trans* bond is a pure  $\sigma$  bond.<sup>34</sup> In agreement with this, olefins give a *trans* strengthening of the metal-chlorine stretching frequency relative to phosphines.<sup>61</sup> 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.<sup>63</sup> 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  $\sigma$ -bonded carbon is 0.17 Å longer than that *trans* to the platinum-olefin bond.<sup>71</sup> This is consistent with the *trans*-effect theory cited above.<sup>34</sup>

The platinum-olefin stretching frequencies in  $[\text{PtX}_2(1,5\text{-cyclooctadiene})]$  (X = Cl, Br, I,  $\text{CH}_3$ , and  $\text{C}_6\text{H}_5$ ) and  $[\text{PtX}_2\text{-cyclooctatetraene}]$  (X = Cl, Br, and I) were assigned<sup>72</sup> to bands at about 460  $\text{cm}^{-1}$ . This is similar in frequency to the bands at about 480  $\text{cm}^{-1}$  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.<sup>57</sup> Other workers have assigned a much lower frequency to the platinum-olefin stretching frequency in Zeise's salt.<sup>58,60</sup> 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  $\text{cm}^{-1}$ ), 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  $\sigma$  and  $\pi$  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  $sp^3$ ).<sup>73</sup> 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.<sup>74</sup> 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  $\pi$  back-bonding may be increased by the *trans* ligand before the  $\sigma$  bond from acetylene to platinum is appreciably weakened.

Complexes of platinum(0) with olefins exhibit no infrared bands assignable to the olefinic double bond.<sup>44,75</sup> On coordination to platinum(0) the triple-bond stretching frequency of acetylenes is lowered by 460 to 1705  $\text{cm}^{-1}$ , which is similar to that observed for an uncoordinated double bond.<sup>76</sup> 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  $\pi$ -allylic complexes.<sup>50,51</sup> The details of the application of nuclear magnetic resonance to metal-olefin complexes are given in a recent review.<sup>77</sup>

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.<sup>78</sup> 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.<sup>46</sup>

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.<sup>22</sup> 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.<sup>79,80</sup> Molecular models indicate that the 2- and 6-methyl groups on pyridine maintain the plane of the pyridine molecule perpendicular to the  $\text{PtCl}_2$

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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 *t*-butylethylene only one methyl signal was observed at room temperature although on cooling to  $-50^\circ$  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  $-50^\circ$ . Since at  $-75^\circ$  the rate of exchange of free and coordinated olefins is high<sup>81</sup> ( $>70 \text{ sec}^{-1}$  for ethylene in Zeise's salt),<sup>82</sup> 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.<sup>79</sup>

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.<sup>81,83,84</sup> 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.<sup>83</sup> 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  $20^\circ$  from the perpendicular.<sup>85</sup>

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.<sup>86</sup>

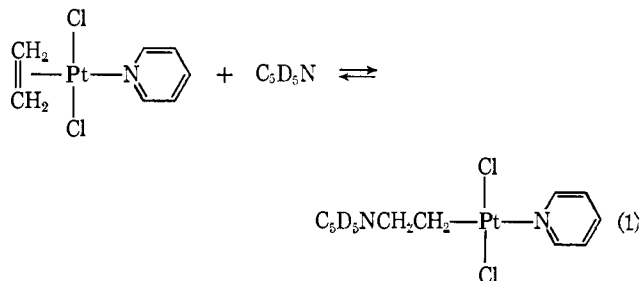
Since the coupling of  $^{195}\text{Pt}$  with the olefinic protons increases with decreasing platinum-hydrogen distance whereas coupling of  $^{195}\text{Pt}$  with the protons on the methylene (or methyl) group adjacent to the double bond decreases with decreasing platinum-hydrogen distance, the coupling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

The chemical shifts of the olefinic protons in a series of *trans*- $[\text{PtCl}_2(\textit{para}$ -substituted pyridine N-oxide)( $\text{C}_2\text{H}_4$ )] complexes were found to move downfield as the electron-withdrawing character of the *para* substituent increased.<sup>80,87</sup> This was ascribed to a reduction in the  $\pi$  back-donation of charge from platinum to ethylene which weakened the ethylene-platinum interaction.<sup>87</sup> 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

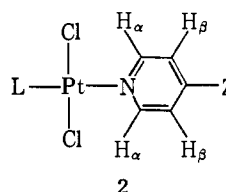
leading to a decrease in the platinum-olefin bond length.<sup>87</sup> However, a simpler explanation, which does not involve a variation in the platinum-ethylene bond length, is that the electron-withdrawing *para* substituent will reduce the pyridine N-oxide to platinum  $\sigma$  bonding and so make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

Nuclear magnetic resonance has indicated that the rate of exchange of free and coordinated ethylene in Zeise's salt is greater than  $70 \text{ sec}^{-1}$  at  $75^\circ$ .<sup>82</sup> 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.<sup>89</sup>

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  $\pi$  bond into a platinum-carbon  $\sigma$  bond (eq 1).<sup>90</sup>



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



coupling of the  $\text{H}_\alpha$  protons to the platinum atom depends on the temperature, the solvent, and the nature of L and Z.<sup>91</sup> 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 Z = 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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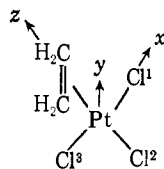
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Table II  
Ultraviolet and Visible Spectra of Zeise's Salt Together with Assignments of the Observed Bands<sup>a</sup>

Obsd bands <sup>b</sup>		Assignment 1 <sup>c</sup>	Assignment 2 <sup>d</sup>	Assignment 3 <sup>e</sup>
$\lambda, \text{cm}^{-1}$	$\epsilon$			
23,900	40,1		{ Pt 5d $\rightarrow$ Pt 5d (unspecified) }	$0.70(\text{Cl}^{1,3} 3p_x) + 0.25(\text{Pt } 5d_{zz}) + 0.04(\text{Cl}^2 3p_x) \rightarrow A$
30,350	340	Pt $5d_{zz} \rightarrow$ Pt $5d_{zz}$	{ Pt 5d $\rightarrow$ Pt 5d (unspecified) }	$0.67(\text{Cl}^{1,3} 3p_y) + 0.33(\text{Pt } 5d_{xy}) \rightarrow B$
33,450	605	Pt $5d_{x^2-y^2} \rightarrow$ Pt $5d_{x^2-y^2}$	Pt $5d_{x^2-y^2} \rightarrow$ C <sub>2</sub> H <sub>4</sub> $\pi^*$	$0.70(\text{Cl}^{1,3} 3p_x) + 0.25(\text{Pt } 5d_{zz}) + 0.04(\text{Cl}^2 3p_x) \rightarrow A$
37,450	3100	{ Pt $5d_{xy} \rightarrow$ Pt $5d_{x^2-y^2}$ } (augmented by charge transfer)	Pt $5d_{xy} \rightarrow$ C <sub>2</sub> H <sub>4</sub> $\pi^*$	{ $0.70(\text{Cl}^{1,3} 3p_x) + 0.25(\text{Pt } 5d_{zz}) + 0.04(\text{Cl}^2 3p_x) \rightarrow B$ } { $0.67(\text{Cl}^{1,3} 3p_y) + 0.33(\text{Pt } 5d_{xy}) \rightarrow A$ }
40,700	3260	Charge transfer	Pt $5d_{yz} \rightarrow$ C <sub>2</sub> H <sub>4</sub> $\pi^*$	$0.64(\text{Cl}^2 3p_x) + 0.19(\text{Cl}^{1,3} 3p_x) + 0.16(\text{Pt } 5d_{zz}) \rightarrow B$

<sup>a</sup> The axes and numbers of the chlorine atoms are as shown



<sup>b</sup> Reference 96, <sup>c</sup> Reference 95, <sup>d</sup> Reference 97, <sup>e</sup>  $A = 0.51(\text{C}_2\text{H}_4 \pi^*) + 0.28(\text{Pt } 6p_y) + 0.14(\text{Pt } 5d_{yz}) + 0.06(\text{Cl}^2 3p_y)$ ,  $B = 0.24(\text{Pt } 5d_{zz}) + 0.20(\text{Cl}^2 3p_x) + 0.17(\text{Cl}^{1,3} 3p_x) + 0.10(\text{Pt } 5d_{x^2-y^2}) + 0.10(\text{C}_2\text{H}_4 \pi^b) + 0.09(\text{Pt } 6p) + 0.04(\text{Pt } 6s) + 0.03(\text{Cl}^{1,3} 3p_x) + 0.01(\text{Cl}^2 3s)$ .

that rotation about the platinum-acetylene bond was slow relative to the nuclear magnetic resonance time scale (*i.e.*, less than  $1.2 \text{ sec}^{-1}$ ) indicating a high activation energy for rotation.<sup>92</sup> 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.<sup>41</sup>

## E. ULTRAVIOLET AND VISIBLE SPECTRA

Ultraviolet and visible spectra have been recorded for Zeise's salt<sup>93-96</sup> and a number of its analogs containing different olefins.<sup>94,97</sup> 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  $\text{PtCl}_4^{2-}$  except for removal of the degeneracy of the  $d_{yz}$  and  $d_{xy}$  orbitals.<sup>95</sup> Although this assumption is open to a number of criticisms, one of which is that the relative energies of the d orbitals in  $\text{PtCl}_4^{2-}$  are uncertain,<sup>98</sup> the values coincide with the relative energies of the d orbitals deduced from the ultraviolet spectra of the platinum(II)-olefin complexes.<sup>97</sup> However, the assignment of the bands at 33,450 and 37,450  $\text{cm}^{-1}$  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.<sup>97</sup> 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.<sup>96</sup> 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  $\pi^*$  (antibonding) orbitals.<sup>97</sup> 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  $d_{z^2} > d_{zz} > d_{x^2-y^2} > d_{xy} > d_{yz}$ , using the axes of Figure 2.<sup>97</sup>

The circular dichroism of optically active olefins is instrumentally difficult to observe since olefins absorb at about 50,000  $\text{cm}^{-1}$ . 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  $\text{cm}^{-1}$ , 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  $\beta$ -pinene and (+)-limonene.<sup>99</sup> 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  $[\text{PtCl}_2(\text{RNH}_2)\text{(olefin)}]$ .<sup>100</sup>

## 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.<sup>101</sup> The results indicate that the magnetic susceptibility of the platinum(II)-olefin bond is approximately twice that of the olefin itself.<sup>102</sup> A similar result was found for other ligands such as carbon monoxide which are known to be  $\pi$ -bonded to the metal. In contrast,  $\sigma$ -bonded complexes gave smaller differences between the magnetic susceptibility of the platinum(II)-ligand bond and

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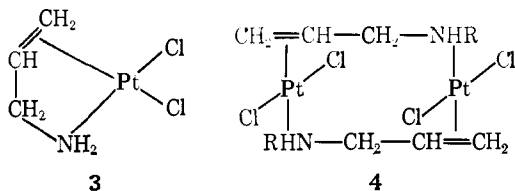
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that of the ligand itself. Until these results are confirmed they should be treated with caution since the compound dichloro(allylamine)platinum(II) was assumed to have structure 3. It has since been shown that secondary allylamines form complexes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

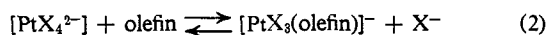


not considered in the magnetic susceptibility calculations.

## G. STABILITY CONSTANT STUDIES

Qualitative information about the relative stabilities of the platinum(II)-olefin complexes was first obtained in 1936.<sup>104</sup> 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,<sup>105</sup> indicating that when  $\pi$  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  $\sigma$  bond between the olefin and platinum(II).<sup>106</sup>

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

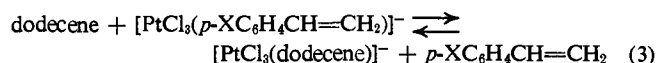


indicated that the olefins gave higher stability constants than water, lower than amines, and comparable with the heavier halides.<sup>107</sup> The stability constants for a series of olefins<sup>107-112</sup> (Table III) indicated that the stabilities of the complexes increased as the structure of the olefin was modified in such a way as to decrease the electron density at the olefin bond. Thus the strength of the  $\pi$  back-bond from platinum(II) to olefin would appear to be more important than that of the  $\sigma$  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  $\text{PtBr}_3^-$  group is a poorer  $\sigma$  acceptor and a better  $\pi$  donor than the  $\text{PtCl}_3^-$  group.<sup>111</sup> It was also found that in addition to electronic

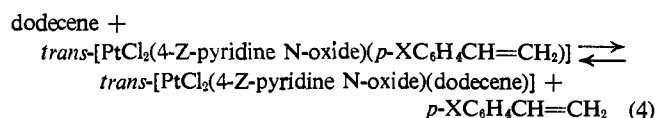
factors, steric factors were important in determining the strength of the platinum(II)-olefin bond.

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.<sup>112</sup> 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.<sup>113</sup> On treating Zeise's salt with 4-substituted pyridine N-oxides, the chloride ligand *trans* to ethylene is displaced by the pyridine N-oxide<sup>114</sup> giving a series of complexes containing a platinum(II)-oxygen bond. The insensitivity of the platinum-oxygen stretching frequency at  $323\text{ cm}^{-1}$  in the infrared spectrum to changes in the 4-substituent suggests that this is essentially a  $\sigma$  bond.<sup>115</sup> Since the donor strengths of the substituted pyridine N-oxide ligands correlate well with the Taft  $\sigma$  values of the substituents,<sup>116</sup> 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.<sup>95</sup> 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  $\sigma$  bond (styrene to platinum(II)) and the  $\pi$  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<sup>a</sup>

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

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

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

<sup>a</sup> Determined in a medium of 1.9 M KX + 0.1 M HX using a spectrophotometric technique, <sup>b</sup> all = CH<sub>2</sub>=CHCH<sub>2</sub>-; but = CH<sub>2</sub>=CH-(CH<sub>2</sub>)<sub>2</sub>-; pent = CH<sub>2</sub>=CH(CH<sub>2</sub>)<sub>3</sub>-.

Table IV  
Stability Constants of Palladium-Olefin Complexes<sup>a</sup>

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

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

Olefin (L)	Temp, °C	Ionic strength, M	Stability constant	$\Delta H_f$ , kcal/mole	$\Delta S$ , eu	Ref
C <sub>2</sub> H <sub>4</sub>	15.0	2	18.7			117
	25.0		17.4			
	35.0		9.7			
C <sub>2</sub> H <sub>4</sub>	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 <sub>2</sub> H <sub>4</sub>	14.8	2	18.7			122
		2.1-2.2	15.5			
		3.1-3.2	15.9			
		4, 5	16.3			
C <sub>3</sub> H <sub>6</sub>	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			

<sup>a</sup> All constants were obtained by measuring the solubility of olefins in aqueous palladium chloride solutions.

IV).<sup>117-122</sup> The results indicated that  $[\text{PdCl}_3(\text{olefin})]^-$  and *trans*- $[\text{PdCl}_2(\text{H}_2\text{O})(\text{olefin})]$  were present in solution as is found with the corresponding platinum(II) complexes.<sup>123</sup> 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,<sup>107</sup> 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 observation<sup>107</sup> that the strength of the  $\pi$  back-bond from metal to olefin is more important than that of the  $\sigma$  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 constants<sup>60</sup> 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 complexes<sup>97</sup> 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 ( $\Delta E$ ). Since the value of  $\Delta E$  increases on going from palladium(II) to platinum(II) (for example, for  $[\text{PdCl}_4]^{2-}$  and  $[\text{PtCl}_4]^{2-}$   $\Delta E$  has the values<sup>124</sup> 19,150 and 23,450  $\text{cm}^{-1}$  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)<sup>30</sup> and dichloro(cyclooctatetraene)palladium(II) (2.08 Å)<sup>32</sup> are, within experimental error, equal to the 2.07 Å found for the platinum(II)-olefin bond length in Zeise's salt.<sup>18</sup>

The observation that *cis* olefins form complexes with higher stability constants than *trans* olefins<sup>125</sup> 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.<sup>126</sup> It has been suggested<sup>127</sup> 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 suggested<sup>66</sup> that whereas in Zeise's salt the mean position of the plane of the ethylene molecule is perpendicular to the

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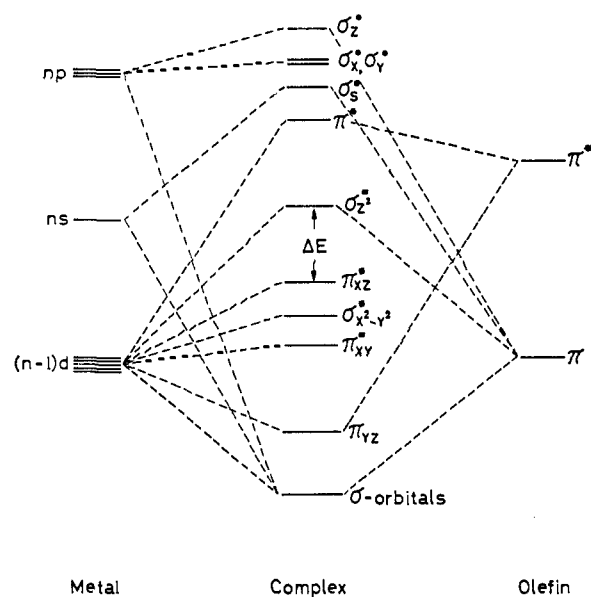


Figure 6. Molecular orbital scheme for platinum(II)- and palladium(II)-olefin complexes. For simplicity the ligand orbitals associated with the ligands other than the olefin have been excluded.



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

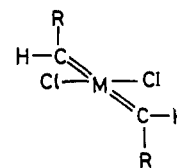
platinum(II)-ethylene bond and parallel to the *cis*-chlorine-platinum(II) bond, in the complex of a *cis*-disubstituted olefin the plane of the olefin would twist about the double-bond axis in such a way as to reduce the steric interference between the substituents and the *cis*-chlorine ligands. This 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.<sup>81,83,84,91</sup> 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  $\sigma$  bond, this will markedly reduce the overlap between the filled d orbitals of the metal and the empty  $\pi^*$  (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.<sup>22</sup>

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.<sup>128-130</sup>

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View along metal-olefin bond

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

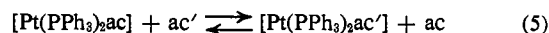


L does not form  $\pi$ -bonds      L forms  $\pi$ -bonds

Figure 9. Schematic representation of the  $\pi$ -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*-[PtCl<sub>2</sub>(EtOH)(C<sub>2</sub>H<sub>4</sub>)]. 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 [PtCl<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)]<sup>-</sup> and [PtCl<sub>2</sub>(EtOH)(C<sub>2</sub>H<sub>4</sub>)]. A mechanism for this exchange involving a dimeric chloro-bridged intermediate was suggested.<sup>130</sup>

Both kinetic and equilibrium measurements have been made for the replacement of one acetylene (ac) coordinated to platinum(0) by another (ac') (eq 5).<sup>131,132</sup> 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 acetylenes<sup>133</sup> indicate that the  $\pi$ -acceptor capacity of the acetylene is more important than its  $\sigma$ -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 review<sup>134</sup> of the *trans*-effect written in 1962 favored the  $\pi$ -bonding mechanism for the *trans*-effect of olefins<sup>135</sup> in which a ligand L (Figure 9) which can form  $\pi$  bonds will withdraw some of the electron density of the  $d_{yz}$  orbital from the ligand (X) in the *trans* position.

(131) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **41**, 1235 (1963).

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(134) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

(135) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955).

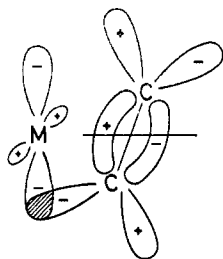


Figure 10. Distortion of the metal-olefin bonding arising from interaction of the metal  $d_{x^2-y^2}$  and olefin  $\pi^*$  (antibonding) orbitals.

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  $\pi^*$  (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  $\pi^*$  (antibonding) orbital. Thus the availability of the  $\pi^*$  (antibonding) orbitals distorts the olefin out of the plane, facilitating the approach of the entering group.<sup>136</sup>

(2) The withdrawal of charge from the metal to the olefin  $\pi^*$  (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.<sup>136</sup> The excess negative charge on the electron-withdrawing ligand will repel the other ligands, the strongest repulsions being with those ligands bonded at  $90^\circ$  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.<sup>137</sup> Thus in Zeise's salt, ethylene labilizes the *trans*-chloride ligand<sup>93,138</sup> but reduces the rate of exchange of *cis*-chloride ligands<sup>138</sup> and also reduces the acid hydrolysis of the *cis*-chloride ligand by a factor of 0.15.<sup>93</sup>

(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.<sup>136</sup>

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.<sup>139,140</sup> Ligands which exert their *trans*-effect by a  $\pi$ -acceptor mechanism will only cause *trans*-bond weakening if the *trans* bond contains  $\pi$ -bonding. If there is only weak  $\pi$ -bonding in the *trans* bond, that bond may either not be

weakened, or may even be strengthened.<sup>34</sup> 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.<sup>141</sup> 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.<sup>19,30,38</sup> In the complex  $[\text{PtCl}(\text{MeO}dicyclopentadiene)]_2$  the platinum-chlorine bond *trans* to the  $\sigma$ -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.<sup>71</sup>

The infrared data have shown that the platinum-chlorine stretching frequency *trans* to an olefin is lower than that *cis* to an olefin.<sup>56,59,61</sup> However, it has also been found, in agreement with the  $\pi$ -acceptor mechanism for the *trans*-effect of olefins,<sup>34</sup> that olefins give a *trans* strengthening of the metal-chlorine stretching frequency relative to phosphines.<sup>61</sup> 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.<sup>142</sup>

Evidence that olefins may actually cause *trans* bond strengthening if the *trans* bond is a pure  $\sigma$  bond is provided by the acid strengths of the two complexes<sup>143</sup>  $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]^{2+}$  ( $pK_a = 5.6$ ) and *trans*- $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})(\text{C}_2\text{H}_4)]^{2+}$  ( $pK_a = 3.5$ ). 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  $\pi$  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  $\sigma$ -bonded ligands bound *trans* to an olefin.  $\sigma$ -Bonded ligands include oxygen, nitrogen, and even chlorine which nuclear quadrupole resonance studies have shown to be an essentially  $\sigma$ -bonded ligand.<sup>144</sup> 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 $\sigma$ AND $\pi$ COMPONENTS OF THE METAL-OLEFIN BOND

The present discussion is limited to a consideration of the relative strengths of the  $\sigma$  and  $\pi$  components of the platinum-olefin bond, since no data have been obtained for the palladium-olefin bond. Historically the  $\sigma$  bond from metal to ligand was introduced before  $\pi$  back-bonding from metal to ligand. As a result in metal-olefin complexes the  $\sigma$  component has tended to be considered as the main component with the  $\pi$  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  $\sigma$  component of the platinum(II)-olefin bond was stronger than the  $\pi$  component.<sup>5,145</sup> This conclusion has been questioned<sup>66</sup> on the grounds that it was based on the doubtful value of 6 D for the nitrogen-aluminum  $\sigma$  bond. This value was obtained by considering the complex  $C_2H_5NH_2AlCl_3$ , which has a dipole moment of 6.9 D.<sup>146</sup> Since the dipole moment of the pyramidal  $AlCl_3$  group, which is present in  $C_2H_5NH_2AlCl_3$ , is about 4 D,<sup>147</sup> a value of 6 D for the nitrogen-aluminum  $\sigma$  bond would seem excessive. There is therefore doubt as to whether the dipole moment studies support a stronger  $\sigma$  than  $\pi$  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.<sup>105</sup> This indicates that when  $\pi$  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  $\sigma$  bonding. More recently studies of the stability constants of both platinum(II)-olefin<sup>107-111</sup> and platinum(0)-acetylene<sup>132</sup> complexes have suggested that the  $\pi$  component of the platinum-olefin or -acetylene bond is more important for the stability of that bond than the  $\sigma$  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  $\pi$  component is stronger than the  $\sigma$  component, there will be less weakening of the  $\pi$  (bonding) component of the olefin bond than if the reverse is true. However, the greater buildup of electron density in the  $\pi^*$  (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  $\pi$  than  $\sigma$  component in the platinum-olefin bond.

The decrease in the platinum-olefin stretching frequency on changing the ligand X in [(cyclooctadiene)PtX<sub>2</sub>] from chloride to bromide to iodide to methyl to phenyl has been interpreted by assuming that the  $\pi$  component of the platinum(II)-olefin bond is greater than the  $\sigma$  component.<sup>148</sup> The constancy of the <sup>198</sup>Pt-<sup>1</sup>H coupling constant, as observed

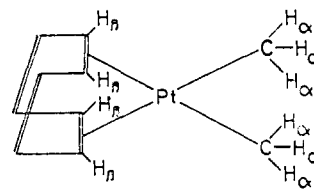


Figure 11. Labeling of the hydrogen atoms in  $[Pt(CH_3)_2(COT)]$ .

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

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

The results discussed so far have either suggested that the  $\pi$  component of the platinum-olefin bond is stronger than the  $\sigma$  component, or have been consistent with this concept. However, the nuclear magnetic resonance<sup>150</sup> and infrared data<sup>148</sup> obtained for a series of cyclooctatetraene (COT) complexes,  $[PtX_2(COT)]$ , have been used to deduce that the percentage contributions of the  $\pi$  components to the platinum(II)-cyclooctatetraene bond were 35, 33, 30, and 56% for X equal to chloride, bromide, iodide, and methyl, respectively.<sup>150</sup> 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  $\sigma$  bond. In view of the very different nature of the  $\sigma$  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  $\sigma$  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  $\pi$  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  $\sigma$  and  $\pi$  components of the metal-olefin bond. Both components are undoubtedly very important, although on balance it appears that the  $\pi$  component may be slightly more important than the  $\sigma$  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<sup>94,103,107</sup> (e.g., allylamine), where it was a liquid but insoluble in water (e.g., cyclooctatetraene<sup>151</sup> or butadiene<sup>152</sup>), and also with gaseous olefins, such as ethylene, where the use of pressure was necessary.<sup>153</sup> 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.<sup>153</sup> 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  $\text{PdCl}_2$  in benzene with ethylene,<sup>154</sup> and also to prepare dichloro(norbornadiene)palladium(II) by treating  $\text{Na}_2\text{PdCl}_4$  with norbornadiene in methanol.<sup>155</sup>

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

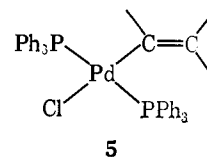
##### 2. Complexes of Zerovalent Platinum and Palladium

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

1. Reduction of *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;<sup>157</sup> ethylene, butadiene, hex-1-ene, cyclohexene, allyl alcohol, styrene, and tetraphenylethylene did not react.<sup>157</sup>

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

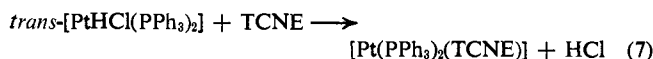
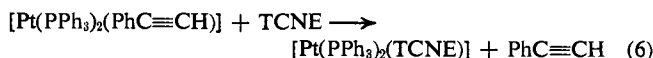
with chloroolefins gives complexes containing palladium-carbon  $\sigma$  bonds (5), although olefins such as maleic anhydride,



ethyl fumarate, and tetracyanoethylene react to give normal olefin complexes of zerovalent palladium.<sup>162-164</sup> 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  $\sigma$  bond.<sup>165</sup>

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,<sup>166</sup> as well as acrylonitrile, vinyl acetate, and maleic anhydride.<sup>167</sup>  $\text{Pt}(\text{PPh}_3)_2$  is formed initially during the preparation of ethylene<sup>168</sup> and tetracyanoethylene<sup>161</sup> 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  $[\text{PtH}(\text{PPh}_3)_3]^+\text{BF}_4^-$  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.<sup>169</sup>

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



prepare tetracyanoethylene (TCNE) complexes.<sup>170</sup> A kinetic investigation of reaction 7 suggested that the most likely mechanism involved the rapid reversible uptake of tetracyanoethylene 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.<sup>171</sup> The octahedral hydrido olefinic complex  $[\text{PtHCN}(\text{PEt}_3)_2(\text{TCNE})]$  was isolated during the reaction of the corresponding cyano complex.<sup>171,172</sup>

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.<sup>173</sup> Attempts to prepare the norbornadiene analog failed.

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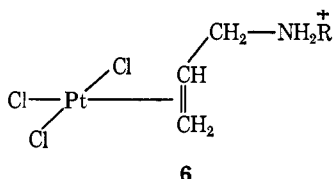


## B. PROPERTIES OF OLEFIN COMPLEXES

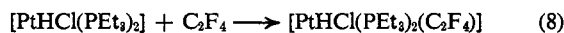
### 1. Complexes of Monoolefins

#### a. Complexes of Divalent Platinum and Palladium

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



both olefin and nitrogen are coordinated to platinum(II) is formed.<sup>94,103</sup> 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.<sup>179</sup> 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,<sup>180</sup> whereas carbon monoxide displaces ethylene from Zeise's salt to give the carbonyl complex<sup>181</sup>  $\text{K}^+[\text{PtCl}_3\text{CO}]^-$ . Although a  $\pi$ -olefin complex of tetrafluoroethylene with platinum(II) was postulated, on the basis of infrared evidence,<sup>182,183</sup> to be formed in eq 8, the claim was withdrawn<sup>184</sup> 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  $\sigma$ -bonded complex formed (Figure 12).<sup>185</sup> A series of platinum(II)-olefin complexes containing the oxygen-bonded ligands pyridine N-oxide<sup>114</sup> and diphenylcyclopropenone<sup>186</sup> *trans* to the olefin have been prepared. A number of stable nonionic platinum(II)-olefin complexes containing amino acids have been prepared. Infrared and

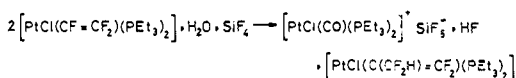
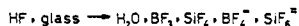
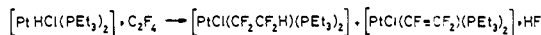
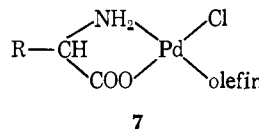


Figure 12. Mechanism for the interaction of platinum(II) complexes with tetrafluoroethylene.

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



Monomeric monoolefin complexes of palladium(II) have been detected in solution.<sup>117-122</sup> The only examples of such complexes that have been isolated are those with pyridine N-oxide *trans* to the olefin.<sup>188</sup> 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.<sup>188</sup> When pure  $\text{PdCl}_2$  is treated with oct-1-ene or dec-1-ene, it is probable that the initial product is a  $\pi$ -olefin complex which rapidly forms the  $\pi$ -allyl complex with liberation of hydrogen chloride. The  $\pi$ -allyl complex adds a further mole of  $\text{PdCl}_2$  giving the  $\pi$ -allyl complex,  $[\text{Pd}_3\text{Cl}_4(\text{C}_n\text{H}_{2n-1})_2]$ , as the final product.<sup>189</sup> With lower olefins (*e.g.*, ethylene,<sup>190</sup> propylene,<sup>190</sup> butene,<sup>190</sup> pentene,<sup>190</sup> cycloheptene,<sup>191</sup> and cyclooctene<sup>191</sup>) dimeric  $\pi$ -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  $\pi$ -allyl complex on heating.<sup>191</sup> But-1-ene, pent-1-ene, hex-1-ene, and oct-1-ene all react with  $\text{PdCl}_2$  in dimethylformamide to give  $\pi$ -allylpalladium(II) complexes.<sup>192</sup> The isolation of  $[(\text{dimethylformamide})_2\text{H}]_2[\text{Pd}_2\text{Cl}_4]$  from the reaction mixture suggests that dimethylformamide promotes  $\pi$ -allyl complex formation by withdrawing protons from the olefin. In agreement with this, sodium carbonate in chloroform will convert  $\pi$ -olefin-palladium(II) complexes of propene and butene into  $\pi$ -allyl complexes.<sup>193</sup> Tertiary allylamines react with  $\text{Li}_2\text{PdCl}_4$  in methanol at room temperature to give complexes such as **8** which contain a palladium(II)-carbon  $\sigma$  bond.<sup>184</sup>

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

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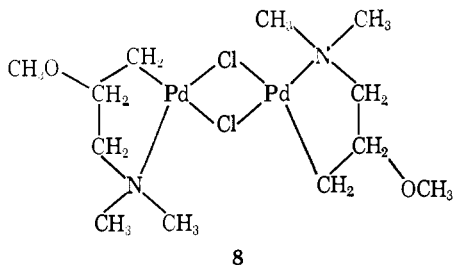
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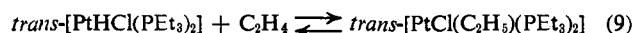
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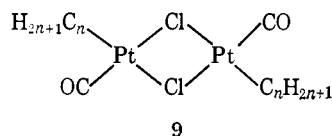
the olefin.<sup>195</sup> Palladium(II) complexes have been used in gas-liquid chromatography columns for the separation of olefins.<sup>196</sup> Platinum(II) complexes have also been examined, but they react too strongly with olefins giving excessively broad peaks.<sup>196</sup>

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



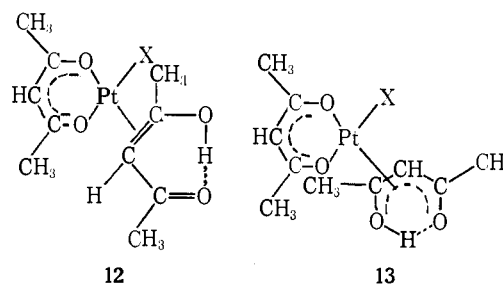
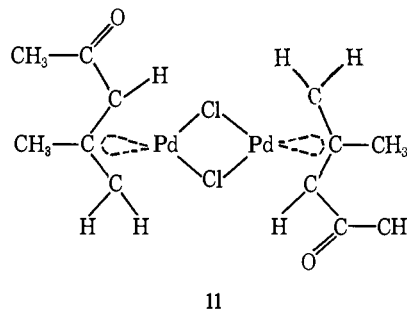
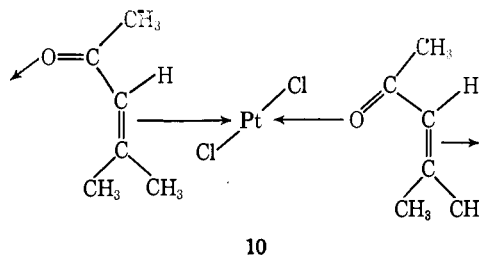
*trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>] + C<sub>2</sub>H<sub>4</sub> ⇌ *trans*-[PtCl(C<sub>2</sub>H<sub>5</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (9) deuterium-labeled complexes, it was shown that the hydrogen atoms attached to either of the carbon atoms of the ethyl group can provide the hydrido ligand.<sup>198</sup> 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.<sup>199</sup>

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

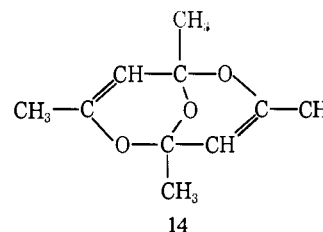


acid, were obtained.<sup>200,201</sup> Mesityl oxide complexes of platinum(II) and palladium(II) differ markedly in structure. While platinum(II) forms a polymeric olefin complex **10**, palladium(II) forms a  $\pi$ -allyl complex (**11**),<sup>202,203</sup> This reflects the relative tendencies of the two metals to form olefin and  $\pi$ -allyl complexes.

On acidifying the complexes K<sup>+</sup>[PtX(acac)<sub>2</sub>]<sup>-</sup> where acac = acetylacetonate and X = Cl or Br, a complex originally thought to be **12** was isolated.<sup>204</sup> However, a reexamination of the data found that the  $\pi$ -allyl structure **13** fitted better.<sup>205</sup> On



acidification of the tris(acetylacetonato)platinum(II) complex which contains one conventional oxygen-bonded acetylacetonate ligand and two  $\gamma$ -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.<sup>206</sup> 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.<sup>166</sup> The presence of electronegative substituents seems to be important for the formation of a stable metal(0)-olefin bond,<sup>157,168,167</sup> suggesting that  $\pi$  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 [Pt(PPh<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)] decomposes at<sup>168</sup> 122–125°, whereas the tetracyanoethylene analog decomposes at<sup>40</sup> 268–270°. A detailed dis-

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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.<sup>207</sup> 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.<sup>207</sup>

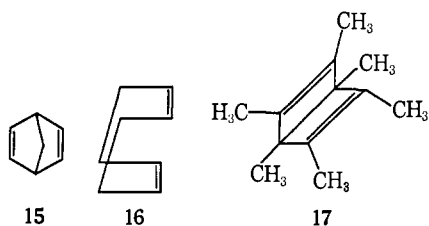
Platinum(0)-olefin complexes of chloroolefins rearrange on heating to give platinum(II) complexes containing platinum-carbon  $\sigma$  bonds (eq 10 where  $X = \text{F}$  or  $\text{Cl}$ ).<sup>44,159</sup> This rearrangement occurs in polar solvents such as ethanol,



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

## 2. Complexes of Nonconjugated Polyolefins

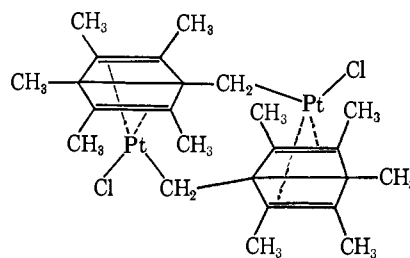
A number of nonconjugated diolefins and higher polyolefins exist in conformations which present the olefinic bonds in ideal arrangements for coordination to metal atoms. Examples of such ligands are norbornadiene (15), 1,5-cyclooctadiene (16), and Dewar hexamethylbenzene (17). Both norbornadiene and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



type  $[\text{PtX}_2(\text{diolefin})]$ , where  $X = \text{halogen}$  or  $\text{alkyl}$ .<sup>208-210</sup> 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,<sup>211,212</sup> whereas under different conditions phosphine complexes of both palladium(II)<sup>213</sup> and platinum(II)<sup>214</sup> isomerize the nonconjugated cyclooctadienes to the 1,3 isomer. The norbornadienepalladium(II) complexes are useful as antiknock additives for fuels.<sup>215</sup>

Dewar hexamethylbenzene (17) displaces benzonitrile from

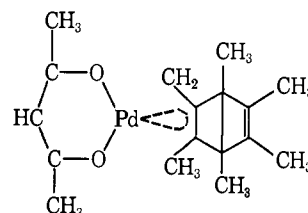
$[\text{PdCl}_2(\text{PhCN})_2]$  to give a monomeric chelate complex which is unstable even in the solid. On adding triphenylphosphine to a solution of the complex, Dewar hexamethylbenzene is liberated, whereas on standing in chloroform solution Kekulé hexamethylbenzene is formed.<sup>216</sup> A monomeric Dewar hexamethylbenzene complex,  $[\text{PtCl}_2(\text{C}_{12}\text{H}_{18})]$ , is formed by reaction of Dewar hexamethylbenzene with  $\text{Na}_2\text{PtCl}_4$  in ethanol.<sup>217</sup> 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



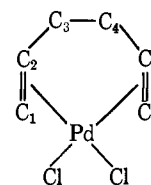
18

is 0.19 Å shorter than that *trans* to the methylene group. This is reflected<sup>217</sup> 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  $\text{cm}^{-1}$ . The iodo analog of  $[\text{PtCl}_2(\text{C}_{12}\text{H}_{18})]$  has a  $\pi$ -allylic structure analogous to that of (acetylacetonato)-(Dewar hexamethylbenzene)palladium(II) (19),<sup>218</sup>

An X-ray structural investigation<sup>219</sup> 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  $\text{C}_3$ - $\text{C}_4$  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 salt<sup>151</sup> 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.<sup>220</sup> This, together with the observation that pyridine

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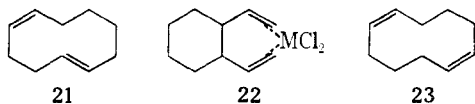
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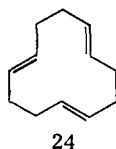
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N-oxide is inert toward complex formation with [PtCl<sub>2</sub>(hexa-1,5-diene)] may be due to the structure of [PtCl<sub>2</sub>(hexa-1,5-diene)], making it impossible to form a trigonal-bipyramidal intermediate.<sup>220</sup>

4-Vinylcyclohexene gives monomeric chelate complexes with platinum(II),<sup>221</sup> whereas in the presence of [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] it rearranges to give [PdCl<sub>2</sub>(1,5-cyclooctadiene)].<sup>222</sup> 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-

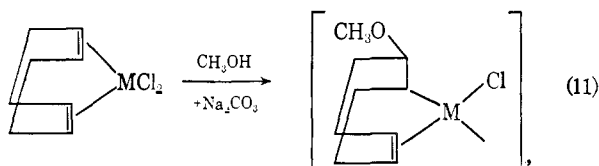


arranges during complex formation to give both platinum(II) and palladium(II) complexes of 1,2-divinylcyclohexane (**22**). It has been suggested that rearrangement occurs *via* a closed-ring  $\pi$ -allyl intermediate.<sup>223,224</sup> By contrast 1,6-cyclodecadiene (**23**) gave a palladium(II) complex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



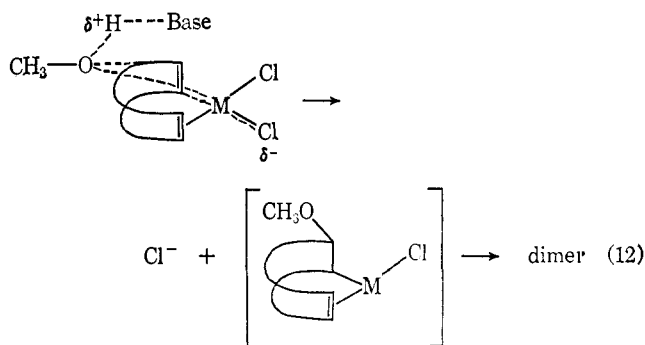
(II).<sup>225,227</sup> Although the complexes are stable crystalline solids, there must be a certain amount of strain because in solution the platinum(II) complex forms [Pt<sub>6</sub>Cl<sub>12</sub>(CDT)<sub>4</sub>] in which each olefin molecule is bound to three platinum atoms.<sup>228</sup>

Diolen complexes of platinum(II)<sup>228</sup> and palladium(II)<sup>229</sup> react with alkaline methanol to give complexes containing a metal-olefin  $\pi$  bond and a metal-carbon  $\sigma$  bond (eq 11). In hot methanol some decomposition to palladium metal is



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

ture of the dimeric methoxydicyclopentadiene-platinum(II) complex has confirmed the presence of a metal-olefin  $\pi$  bond and a metal-carbon  $\sigma$  bond and excluded the possibility of a  $\pi$ -allyl structure.<sup>71</sup> 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).<sup>231-236</sup> 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



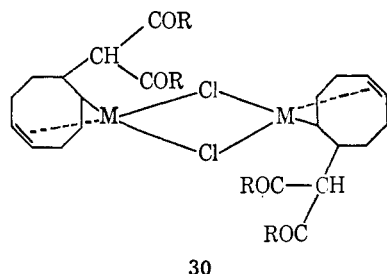
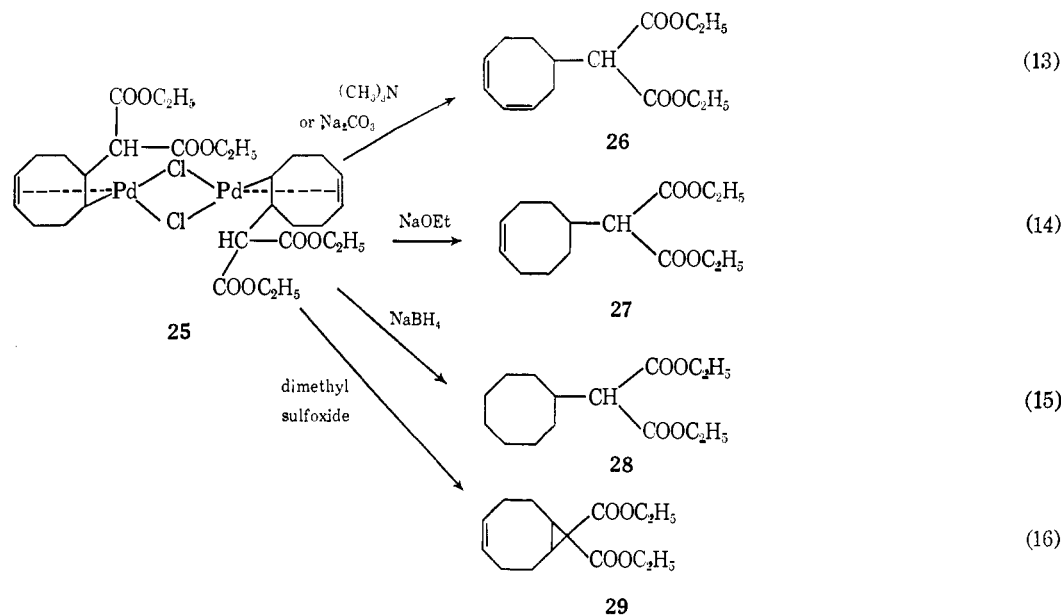
in the dimeric methoxydicyclopentadiene-platinum(II) complex can be split using sodium cyclopentadienide to give  $\pi$ -cyclopentadienyl(methoxydicyclopentadiene)platinum(II).<sup>236</sup>

Nucleophiles such as amines and carboxylate ions react with diolefin complexes in a similar manner to alkoxides.<sup>237</sup> The products obtained by the addition of carbanions such as ethyl malonate to [PdCl<sub>2</sub>(cycloocta-1,5-diene)] (**25**) undergo interesting decomposition reactions in the presence of bases.<sup>238,239</sup> Thus with trimethylamine or sodium carbonate the conjugated diolefin **26** is formed (eq 13), with sodium ethoxide the monoolefin **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  $\sigma$  bonds and metal-olefin  $\pi$  bonds of the general formula [(diene-diketone)M(diketone)] (where M = Pt or Pd and diene = cycloocta-1,5-diene, norbornadiene, or dicyclopentadiene) have been prepared.<sup>240</sup> With halogen acids these give dimeric complexes such as **30**. When dimeric complexes containing a metal-carbon  $\sigma$  bond and a metal-olefin  $\pi$  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  $\sigma$  bond is formed.<sup>240</sup>

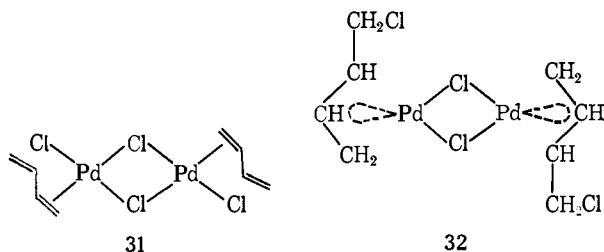
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### 3. Complexes of Conjugated Polyolefins

Conjugated diolefins generally form  $\pi$ -allylic complexes with palladium(II), although platinum(II) forms true olefin complexes with these ligands.<sup>241</sup> 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.<sup>242</sup> At  $-40^\circ$  1,3-butadiene gives quantitative displacement of pentene from  $[\text{PdCl}_2(\text{pentene})]_2$  to give the olefin complex **31**.<sup>243</sup> Above  $-20^\circ$  this complex is unstable, and at room temperature it isomerizes to give the  $\pi$ -allylic complex **32**, which is the normal product obtained at room temperature.<sup>50</sup> By contrast 1,3-cyclooctadiene displaced pentene to give an olefin complex that was stable up to its melting point ( $110^\circ$ ).<sup>248</sup> The infrared spectra of **31** and its 1,3-cyclooctadiene analog both



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

olefin ( $1500\text{ cm}^{-1}$ ) stretching frequency, indicating that the ligands were truly monodentate. Although 1,3- and 1,5-cyclooctadiene gave two distinct complexes with palladium(II),<sup>191,212,244</sup> displacement of benzonitrile from  $[\text{PdCl}_2(\text{PhCN})_2]$  by 1,3-cyclooctadiene led exclusively to the formation of  $[\text{PdCl}_2(1,5\text{-cyclooctadiene})]$ .<sup>245</sup> Spectroscopic studies indicated that the complex  $[\text{Pt}(\text{CH}_3)_2(\text{cyclopentadiene})]$  was a diolefin rather than  $\pi$ -allylic complex.<sup>246</sup> 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.<sup>209,247</sup>

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.<sup>156</sup> 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.<sup>248</sup> This together with the weak band at  $1635\text{ cm}^{-1}$  observed subsequently in the platinum complex suggests that the cyclooctatetraene exists in the tub conformation.<sup>210</sup>  $[\text{PtI}_2(\text{C}_8\text{H}_8)]$  reacts with Grignard reagents to form both mononuclear (**33**) and binuclear (**34**) cyclooctatetraene alkyls and aryls, which are thermally very stable.<sup>210,249</sup> The mononuclear complexes exhibit a weak band at about  $1635\text{ cm}^{-1}$  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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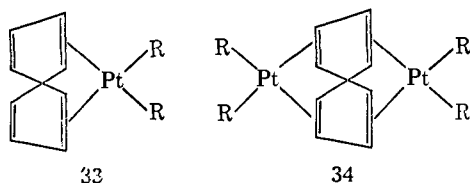
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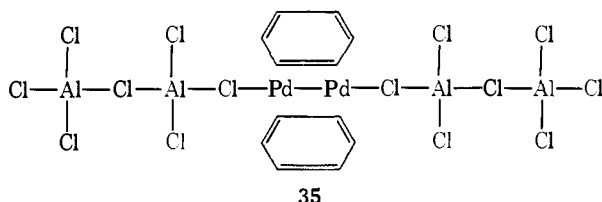
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from  $\text{Na}_2\text{PdBr}_4$ , it has been prepared from  $[\text{PdBr}_2(\text{PhCN})_2]$ .<sup>250</sup>

The "conjugated polyolefin" benzene gives an interesting bisarene complex of palladium(II) (35). The palladium-palladium bond length<sup>251</sup> is 2.58 Å, which is the shortest distance found so far for this metal-metal bond.<sup>252</sup>



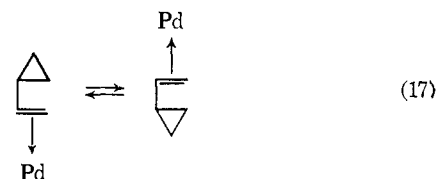
#### 4. Complexes of Three-Membered Ring Systems

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

Cyclopropane reacts with platinum(IV) complexes to give a polymeric complex<sup>255</sup>  $[\text{PtCl}_2(\text{C}_3\text{H}_6)]_n$ . 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.<sup>256</sup> 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.<sup>257</sup> This is surprising since allyl chloride reacts with  $\text{PdCl}_2$  in 50% acetic acid,<sup>258</sup> or in methanol in the presence of carbon monoxide,<sup>259</sup> to give the  $\pi$ -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.<sup>260</sup> 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  $\pi$ -allyl complexes of 1,3-



pentadiene,<sup>260</sup>  $[\text{PdCl}(\pi\text{-CH}_2\text{CHClCHCH}_2)]_2$  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,<sup>261</sup> 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).<sup>94,103</sup> The ligands analogous to 2-allylpyridine with *n* = 2 give insoluble polymeric materials.<sup>103</sup> 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.<sup>262,263</sup> With palladium dimeric complexes are formed in which the olefinic double bond is not coordinated to palladium.<sup>263</sup> 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.<sup>264-266</sup> 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  $\text{cm}^{-1}$ ; Pd(II), 1530  $\text{cm}^{-1}$ ), suggested that the platinum(II)-olefin bond is stronger than the palladium(II)-olefin bond.<sup>266</sup>

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).<sup>267</sup> 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.<sup>267</sup> A study of the platinum(II) and

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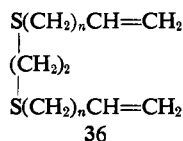
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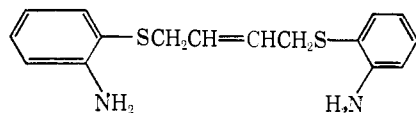
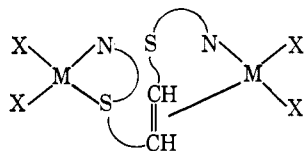
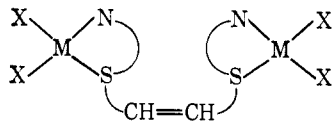
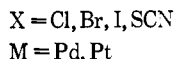
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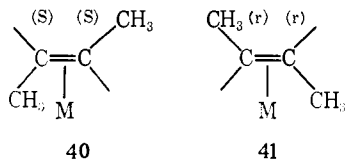
palladium(II) complexes of **37** has shown that the two metal atoms present in each complex are in different environments. This is consistent with structure **38** but not **39** and indicates

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

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

### 6. Complexes of Optically Active Olefins

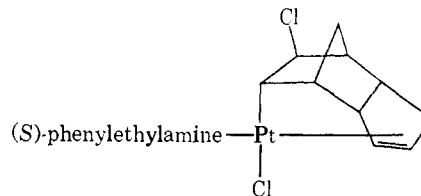
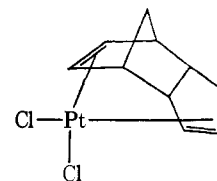
Olefins which have no symmetry planes perpendicular to the plane of the double bond (*e.g.*, *trans*-but-2-ene or propene) can coordinate to a metal in two enantiomorphous ways (**40** and **41**). If an optically active ligand (*e.g.*, 1-phenylethylamine) is also incorporated in the complex, then two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

**40****41**

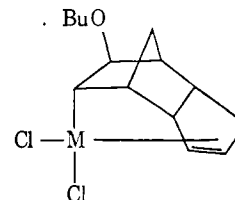
isomers are formed, which can be separated by fractional crystallization. The two diastereoisomers of [PtCl<sub>2</sub>{(-)-(*S*)-1-phenylethylamine}(olefin)], where olefin = *trans*-but-2-ene, propylene, and styrene, have been observed in solution,<sup>269</sup> although with propylene and styrene only one diastereoisomer can be obtained as a crystalline product.<sup>270</sup> 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.<sup>270</sup> Preliminary X-ray analyses have been commenced to determine the absolute configuration of these complexes.<sup>271, 272</sup> 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  $\alpha$  or  $\beta$  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.<sup>273</sup>

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.<sup>274, 275</sup> The enantiomeric [MCl<sub>2</sub>(*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.<sup>275</sup>

*cis,trans*-1,5-Cyclooctadiene was partially resolved into its two enantiomorphs using 1-methylphenylethylamine as the optically active ligand<sup>276</sup> and completely resolved using 1-methylbenzylamine,<sup>277</sup> which was also used to resolve *trans*-cyclooctene.<sup>278</sup> 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.<sup>279</sup> Equilibrium constants for reaction 18 were found to be unity for *trans* complexes,<sup>280</sup> but

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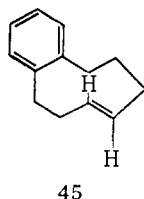
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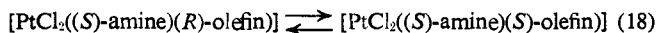
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45



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.<sup>281</sup> As a result of this when *cis*-[PtCl<sub>2</sub>(1-phenylethylamine)(C<sub>2</sub>H<sub>4</sub>)] 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.<sup>282</sup>

#### IV. Preparation and Properties of Acetylene Complexes

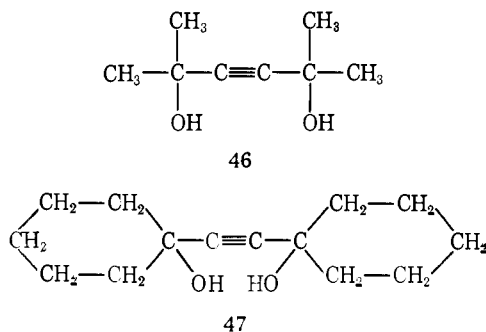
##### A. PREPARATION OF ACETYLENE COMPLEXES

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



47

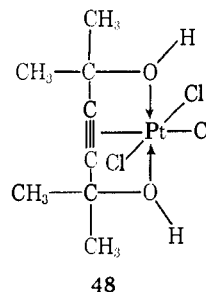
to platinum(II) than ethylene or styrene to form stable complexes of the type [PtCl<sub>2</sub>(ac)]<sup>−</sup> where ac = acetylene.<sup>283–285</sup> On coordination to platinum(II) the triple-bond stretching frequency in the infrared is lowered by about 200 cm<sup>−1</sup>, which is consistent with the formation of a platinum(II)-acetylene π bond.<sup>21</sup> In addition the O–H stretching frequency is lowered by about 125 cm<sup>−1</sup> on coordination.<sup>21, 286, 287</sup> 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.<sup>21</sup> However, more recent work has shown that intermolecular hydrogen bonding can be observed if either higher concentrations of dioxane or stronger bases are used.<sup>286, 287</sup> 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.<sup>288</sup>

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.<sup>21</sup> 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<sup>+</sup>[PtCl<sub>2</sub>{(CH<sub>3</sub>)<sub>2</sub>(HO)CC≡CC(OH)(CH<sub>3</sub>)<sub>2</sub>}]<sup>−</sup> was considered the most likely explanation on the grounds that the platinum(0) complex [Pt(PPh<sub>3</sub>)<sub>2</sub>{(CH<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)(HO)CC≡CC(OH)(C<sub>2</sub>H<sub>5</sub>)(CH<sub>3</sub>)}], which contains no chlorine atoms, has an O–H stretching frequency identical with that of the free ligand.<sup>21</sup> 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.<sup>286, 287</sup> 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.<sup>286, 287</sup> 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.<sup>289</sup>

A series of cationic platinum(II) complexes of the general formula [PtX(en)(ac)]<sub>n</sub><sup>+</sup>, where *n* = 1 or 2, X = Cl, Br, and I, ac = **46**, and en = ethylenediamine, have been prepared.<sup>290</sup> In contrast to the cationic olefin complexes, which are unstable,<sup>291</sup> 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*-[PtX<sub>2</sub>(en)].

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

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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).

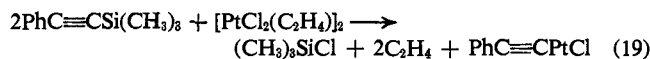
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(289) S. V. Bukhovets, USSR Patent 105,486 (1965); *Chem. Abstr.*, **64**, 16700c (1966).

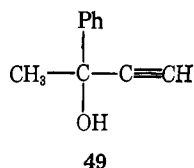
(290) P. Kong and T. Theophanides, *Can. J. Chem.*, **45**, 3193 (1967).

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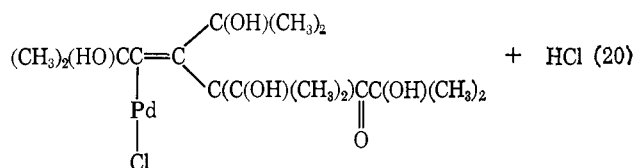
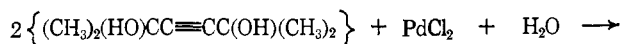
(292) J. E. Poist and C. S. Kraihanzel, *Chem. Commun.*, 607 (1968).



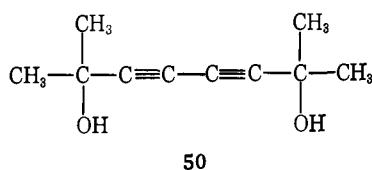
The palladium(II) complexes of acetylenes are more complex and less well understood than the platinum(II) complexes because of the fact that acetylenes are very rapidly polymerized by palladium(II) compounds.<sup>48</sup> Thus **49** forms complexes of the type  $[\text{PdX}(\text{ac})_2]$ ,<sup>293</sup> where X = Cl, Br, I, and SCN, and ac = **49**, in which weak bands at about 1540  $\text{cm}^{-1}$  in the



infrared spectra have been assigned to olefinic double bonds coordinated to palladium(II).<sup>294</sup> **46** when treated with  $\text{PdCl}_2$  in the ratios 1:1, 2:1, and 4:1 always gives the complex  $[\text{PdCl}(\text{ac})_2]$ .<sup>295</sup> This complex shows no infrared bands that can be identified with the triple bond. However, bands at about 1700 and 1630  $\text{cm}^{-1}$  have been assigned to carbonyl and double-bond stretching frequencies, respectively.<sup>294</sup> Equation 20 has been suggested to account for these observations.<sup>54</sup> The formation of a carbonyl group is consistent



with the ability of palladium(II) salts to oxidize acetylenes to carbonyl compounds.<sup>296</sup> **50** gives stable complexes<sup>297</sup> 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  $\text{PdCl}_2$  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  $\text{cm}^{-1}$ . When the reaction is carried out in methanol,  $[\text{PdCl}_2(\text{C}_{14}\text{H}_{32}\text{O})]$  is formed.<sup>298</sup> Both these complexes have been assigned cyclobutadiene-type structures (**52**).<sup>299</sup> On

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

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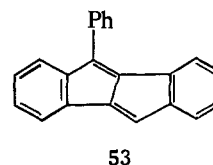
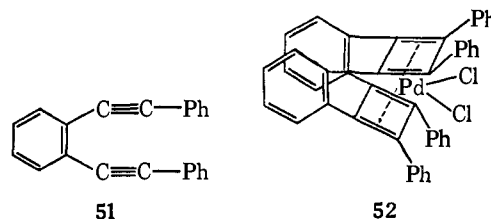
(295) A. V. Babaeva and T. I. Beresneva, *Zh. Neorgan. Khim.*, **11**, 1966 (1966); *Chem. Abstr.*, **65**, 16477b (1966).

(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).

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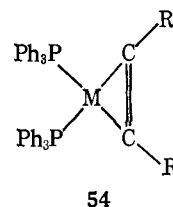


addition of triphenylphosphine to  $[\text{PdCl}_2(\text{C}_{14}\text{H}_{28})]$ , palladium metal and five hydrocarbons, one of which was shown to be **53**, are formed.<sup>298</sup>

The complexes formed between palladium(II) and either isopropenylacetylene or ethynylbenzene have been used in the photometric determination of palladium.<sup>300</sup> 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.<sup>48</sup> 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.<sup>48</sup> Other preparative routes to these complexes that have been used are reaction of the acetylene with  $[\text{Pt}(\text{PPh}_3)_2]$ <sup>166</sup> and exchange of one acetylene with another.<sup>166, 301</sup> 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.<sup>181, 182</sup> 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 benzyne complex of nickel has recently been reported.<sup>302</sup> 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,

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(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 <sup>a</sup>	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
$\text{CH}_3\text{OOC}\equiv\text{CCOOC}\text{CH}_3$	2150	55
$(\text{Ph}_3\text{P})_2\text{Pd}(\text{CCOOMe})_2$	1845, 1830 <sup>b</sup>	d
$(\text{Ph}_3\text{P})_2\text{Pt}(\text{CCOOMe})_2$	1782, 1765 <sup>b</sup>	48

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

although interesting cyclic azo complexes of platinum have been isolated.<sup>303</sup> 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  $[\text{Pt}(\text{PPh}_3)_4]$ .<sup>304</sup>

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

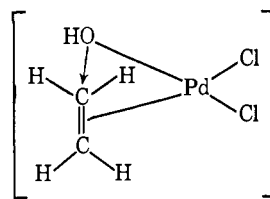
## V. Nucleophilic Attack on Coordinated Olefins

### A. INTRODUCTION

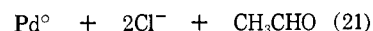
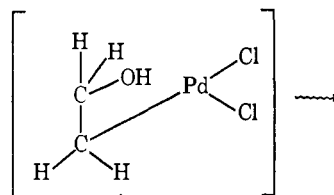
A number of examples of nucleophilic attack on olefins coordinated to metal ions are known. Complex formation reduces the electron density between the carbon atoms, rendering the double bond more susceptible to nucleophilic attack. An interesting difference occurs between the stereochemistry of nucleophilic attack on coordinated chelating diolefins and on monoolefins, since the former give *trans* addition of nucleophiles across the double bond (eq 12),<sup>281-284</sup> whereas the kinetic results for the oxidative hydrolysis of monoolefins coordinated to palladium(II) are only consistent with *cis* addition.<sup>117,305</sup> Although at low temperature (25°) diolefins give *trans* addition of methoxide ion to the double bond and no reduction to the metal,<sup>280</sup> at higher temperatures reduction to palladium metal is observed<sup>229</sup> and vinyl ethers, which are the normal oxidative addition products,<sup>306</sup> are isolated.<sup>280</sup> 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.<sup>307</sup>

It has been suggested<sup>308</sup> 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



$\pi^*$  (antibonding) olefin orbitals to the nucleophile. The observation that for the formation of a stable olefin-platinum(II) bond the  $\pi$  bond from metal to olefin is more important than the  $\sigma$  bond from olefin to metal<sup>107</sup> implies that there will be a considerable buildup of negative charge in the olefin  $\pi^*$  (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<sup>308,309</sup> for the nucleophilic attack of coordinated monoolefins unlikely.<sup>149</sup> 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.<sup>288</sup> 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,<sup>117,305</sup> 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.<sup>98</sup>

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°,<sup>122</sup> whereas equilibria between platinum(II) salts and olefins require 14 days at 30°.<sup>107</sup>

2. While the  $\pi$  back-donation of charge from metal to olefin is known to be considerable in the platinum(II)-olefin complexes,<sup>107</sup> it is possible that it is less in the palladium(II)-olefin complexes since the ionization potentials of palladium are greater than those of platinum<sup>310</sup> 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 bond<sup>60</sup> 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).<sup>311-313</sup> This allows the incoming nucleophile to coordinate to palladium(II) before attacking the olefin, thus lowering the activation energy of the nucleophilic attack.

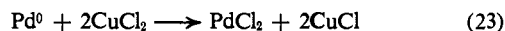
## B. OXIDATION

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 Na<sub>2</sub>PtF<sub>6</sub> solution.<sup>314</sup> Although platinum(II) salts do not oxidize olefins rapidly, Zeise's salt is hydrolyzed slowly on heating in water to give some acetaldehyde.<sup>315</sup>

The oxidation of olefins to carbonyl compounds in the presence of palladium(II) salts, which has been developed commercially into the Wacker process,<sup>9,10,316-318</sup> 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.<sup>9</sup> 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.<sup>9</sup>

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.<sup>319-327</sup> 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.<sup>327</sup> The presence of at least one hydrogen atom on each of the carbon atoms of the double bond is essential.<sup>9</sup> Higher olefins often yield a number of products due to isomerization of the olefin.<sup>328</sup>

2. One mole of olefin is absorbed and reacted for each mole of PdCl<sub>2</sub>,<sup>10</sup> so that the stoichiometry of eq 22 is followed. This together with the fact that the excess solubility of ethylene in PdCl<sub>2</sub> 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).<sup>117,119,305,339</sup>



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,<sup>9</sup> since for platinum this equilibrium lies further to the left as the atomic weight of the halogen increases.<sup>111</sup>

4. The plots of the concentration of olefin absorbed by PdCl<sub>2</sub> solutions against time for a series of temperatures intersect.<sup>9</sup> 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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(333) S. V. Pestrikov and B. L. Kozik, *Neftepererab. Neftekhim., Nauchn-Tekhn. Sb.*, 39 (1965); *Chem. Abstr.*, 63, 16161c (1965).

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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,<sup>9, 317</sup>

6. Ethyl alcohol is not an intermediate oxidation product since ethyl alcohol reacts more slowly than ethylene with  $\text{PdCl}_2$ .<sup>9, 317</sup>

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)<sup>10, 117, 305, 340-349</sup> and olefin,<sup>10, 117, 305, 340-350</sup> In the absence of chloride the reaction is second order in palladium(II).<sup>342</sup> The reaction is inhibited by protons (first order)<sup>117, 305, 342, 348</sup> and chloride ions (second order).<sup>117, 305, 344, 345</sup> 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.<sup>351</sup> The oxidation of styrene gave two possible products, acetophenone and phenylacetaldehyde, whose formation followed different rate laws,<sup>349</sup> *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  $\text{D}_2\text{O}$ , 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.<sup>10</sup> An isotope effect  $K_B/K_D$  of 4.05 was observed in  $\text{D}_2\text{O}$ .<sup>352</sup>

9. Using water and fully deuterated ethylene a very small isotope effect ( $K_B/K_D = 1.07$ ) is observed indicating that no carbon-hydrogen bond is broken during the rate-determining step.<sup>117</sup>

A number of mechanisms have been put forward to explain

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(341) K. I. Matveev, A. M. Osipov, V. F. Odyakov, Yu. V. Suzdal'nitskaya, I. F. Bukhtoyarov, and O. A. Emel'yanova, *Kinetika i Kataliz*, 3, 661 (1962); *Chem. Abstr.*, 59, 5836e (1963).

(342) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Syrkin, *Dokl. Akad. Nauk. SSSR*, 147, 399 (1962); *Chem. Abstr.*, 58, 13740c (1963).

(343) T. Dozono and T. Shiba, *Bull. Japan. Petrol. Inst.*, 5, 8 (1963).

(344) K. Teramoto, T. Oga, S. Kikuchi, and M. Ito, *Yuki Gosei Kagaku Kyokai Shi*, 21, 298 (1963); *Chem. Abstr.*, 59, 7339g (1963).

(345) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Syrkin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1147 (1963); *Chem. Abstr.*, 59, 5830c (1963).

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(347) H. Liu, C.-C. Ts'ui, and H.-M. Wang, *Hua Hsueh Tung Pao*, 415 (1965); *Chem. Abstr.*, 64, 7989e (1966).

(348) I. I. Moiseev, M. N. Vargaftik, S. V. Pestrikov, O. G. Levanda, T. N. Romanova, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, 171, 1365 (1966); *Chem. Abstr.*, 67, 32131 (1967).

(349) H. Okada and H. Hashimoto, *Kogyo Kagaku Zasshi*, 69, 2137 (1966); *Chem. Abstr.*, 66, 85242 (1967).

(350) S. B. Chandalia, *Indian J. Technol.*, 4, 260 (1966).

(351) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, 139, 1396 (1961); *Chem. Abstr.*, 56, 14976h (1962).

(352) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1144 (1963); *Chem. Abstr.*, 59, 5837g (1963).

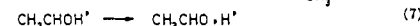
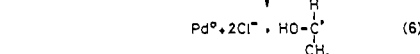
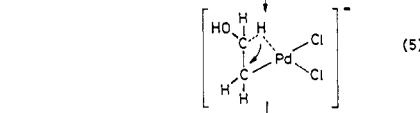
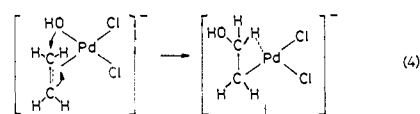
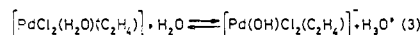
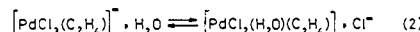
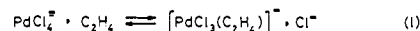


Figure 13. Mechanism for the oxidation of ethylene by aqueous palladium(II) chloride solutions.

the observed kinetic data.<sup>10, 117, 340, 341, 343, 344, 346, 353-359</sup> A recent review of these<sup>309</sup> 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.<sup>117, 305, 343-345, 355, 360</sup> The third stage<sup>117, 305, 355, 360</sup> accounts for the proton inhibition as well as the deuterium isotope effect in  $\text{D}_2\text{O}$ . The last four stages<sup>309</sup> were put forward to avoid the necessity of postulating a two-coordinate  $\sigma$ -bonded complex of palladium suggested earlier.<sup>117</sup> 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.<sup>308, 309</sup> This rotation is known from nuclear magnetic resonance studies to occur in both platinum(II)-olefin and rhodium(I)-olefin complexes.<sup>22, 361</sup> However, such a rotation would present the olefin  $\pi^*$  (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,<sup>107</sup> 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.<sup>149</sup> 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.<sup>362</sup> This has been accounted for by

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(354) M. N. Vargaftik, I. I. Moiseev, Ya. K. Syrkin, and V. V. Yakshin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 930 (1962); *Chem. Abstr.*, 57, 12308e (1962).

(355) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, 153, 140 (1963); *Chem. Abstr.*, 60, 6714c (1964).

(356) J. Chatt, private communication to N. R. Davies, *Nature*, 201, 490 (1964).

(357) S. V. Pestrikov, *Zh. Fiz. Khim.*, 39, 428 (1965); *Chem. Abstr.*, 63, 4117c (1965).

(358) I. I. Moiseev and M. N. Vargaftik, *Dokl. Akad. Nauk SSSR*, 166, 370 (1966); *Chem. Abstr.*, 64, 11248f (1966).

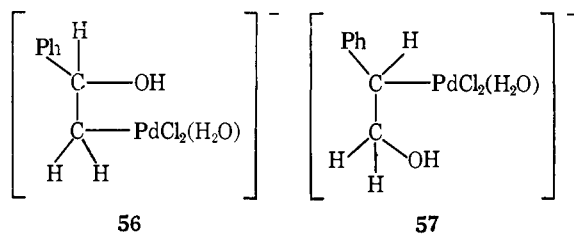
(359) M. Orchin, *Advan. Catalysis*, 16, 1 (1966).

(360) R. Jira, J. Sedlmeier, and J. Smidt, *Ann. Chem.*, 693, 99 (1966).

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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  $\alpha$ -carbon atom, give rise to **56**, whereas electron-withdrawing substituents, by withdrawing charge from the



$\alpha$ -carbon atom, give rise to **57**.<sup>362</sup> The formation of a carbanion ion, as in stage 6, had been suggested previously.<sup>10,363</sup> 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,<sup>296</sup> probably due to the ability of palladium(II) salts to polymerize acetylenes.<sup>48</sup> Thus formaldehyde, acetaldehyde, propionaldehyde, and acraldehyde are formed. A mechanism has been suggested for this reaction,<sup>296</sup> 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.<sup>364</sup>

A solution of  $\text{PdCl}_2$  and cupric acetate in acetic acid catalyzes the direct oxidation of unsaturated aldehydes to unsaturated acids.<sup>365</sup>

## C. ACETYLATION

When ethylene is passed into a solution of  $\text{PdCl}_2$  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.<sup>366-388</sup>

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,<sup>368,369</sup> 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.<sup>369</sup>

3. Kinetic studies have shown that the reaction rate is first order with respect to both olefin and  $\text{Pd}(\text{OAc})_2$ .<sup>390-392</sup> 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.<sup>391</sup>

4. The ethylidene diacetate obtained in the presence of  $\text{CH}_3\text{COOD}$  contained virtually no deuterium, indicating that it is not formed by addition of acetic acid to vinyl acetate,<sup>368</sup> so that at some stage in the reaction a hydride shift must have occurred. Similarly the vinyl acetate does not contain any deuterium.<sup>368</sup>

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.<sup>393</sup> 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.<sup>393</sup> 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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(375) Imperial Chemical Industries Ltd., Netherlands Patent 6,501,827 (1965); *Chem. Abstr.*, 64, 4949g (1966).

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(380) A. Aguiló, Belgian Patent 668,284 (1966); *Chem. Abstr.*, 65, 15236h (1966).

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(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).

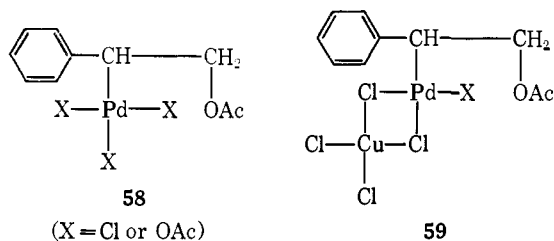
(391) A. P. Belov, I. I. Moiseev, and N. G. Uvarova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1642 (1966); *Chem. Abstr.*, 66, 64832 (1967).

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

from the adjacent carbon atom must be fast.<sup>309</sup> 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.<sup>309</sup>

6. The acetylation of higher olefins has been studied,<sup>306, 307, 354, 394-400</sup> 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 PdCl<sub>2</sub>. 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.<sup>400</sup> 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,<sup>401</sup> *cis*-pent-2-ene,<sup>401</sup> and cyclohexene<sup>285</sup> gives mainly allylic acetate. Propene, however, appears to be an exception to this rule, since it gives quite high yields of allyl acetate.<sup>402</sup>

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

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(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).

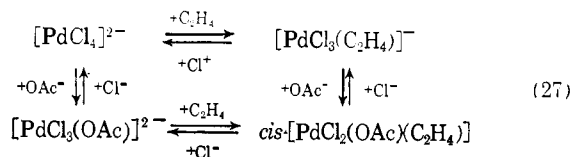
(401) W. Kitching, Z. Rappoport, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, 88, 2054 (1966).

(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).

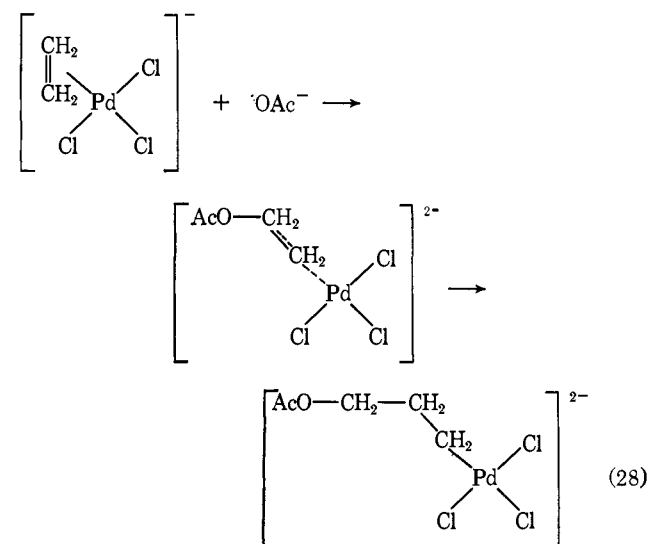
(404) I. I. Moiseev, A. P. Belov, V. A. Igoshin, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, 173, 863 (1967); *Chem. Abstr.*, 67, 53332 (1967).

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

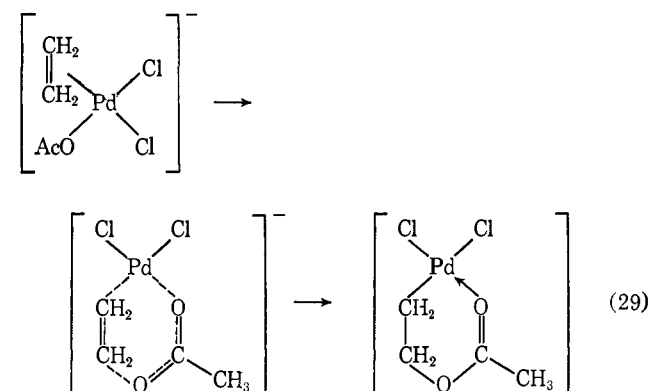


tions of acetate ions has been ascribed to competition between acetate ions and the olefin for coordination to palladium-(II).<sup>404</sup>

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<sup>307, 309, 353</sup> (eq 28), whereas at low chloride or high acetate concentrations an intramolecular attack of the coordinated acetate ion on the olefin to give a

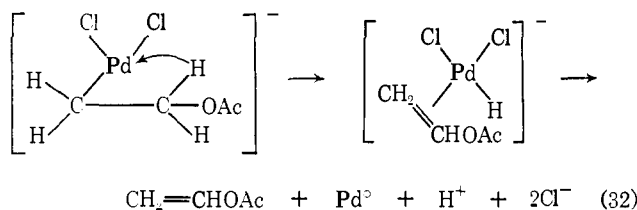
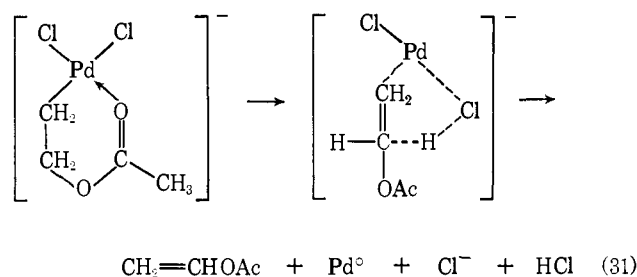
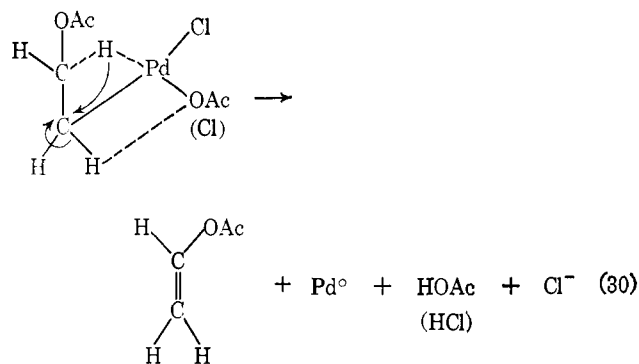


six-membered ring has been suggested (eq 29).<sup>307</sup>

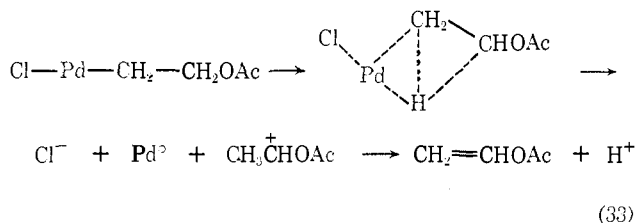


The decomposition of the  $\sigma$ -bonded palladium-alkyl complex has caused controversy. The deuterium labeling studies<sup>317, 368, 393</sup> have been used to support a palladium-assisted hydride transfer mechanism. Two distinct routes have been suggested for this. In the first (eq 30), which does 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





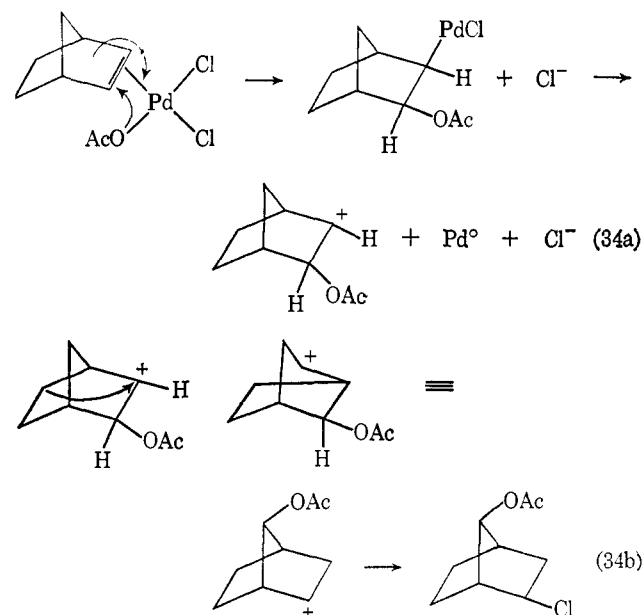
atom from the 1-carbon atom by reaction with a coordinated acetate or chloride ligand.<sup>9,117,309,398</sup> A slight variation of this in which no 1,2-hydride shift is invoked involves a 2-hydrogen elimination mechanism, which may either occur with the formation of hydrogen chloride<sup>307</sup> (eq 31) or may occur with the formation of a palladium-hydrogen bond<sup>405</sup> (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,<sup>368</sup> but has been criticized<sup>307</sup> because,



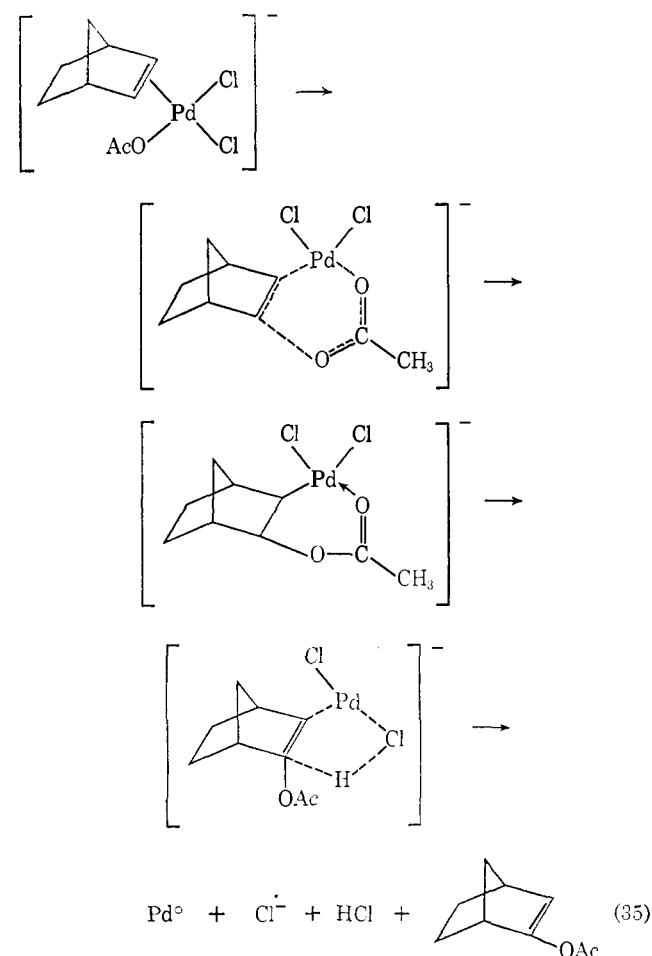
although it accounts well for the absence of deuterium in ethylidene diacetate when the reaction is performed in  $\text{CH}_3\text{COOD}$ , the existence of a free carbonium ion in a highly solvating medium such as acetic acid is unlikely. In addition the carbonium ion would be more likely to react 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  $\beta$ -hydrogen elimination, whether this

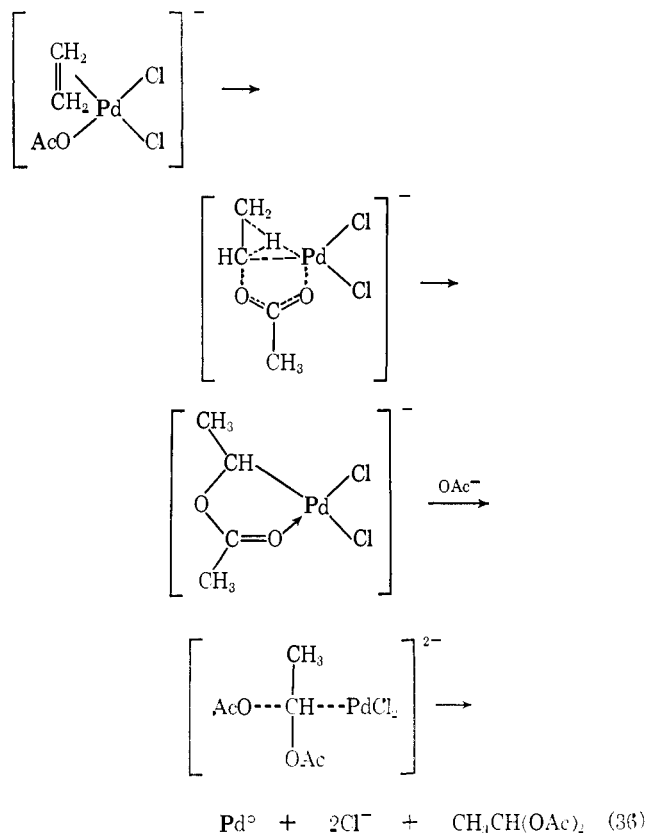


occurs directly or by hydride transfer to the  $\alpha$ -carbon atom, would lead to the formation of 2-acetoxy-2-norbornene (eq 35), which is not observed among the products,<sup>397</sup>

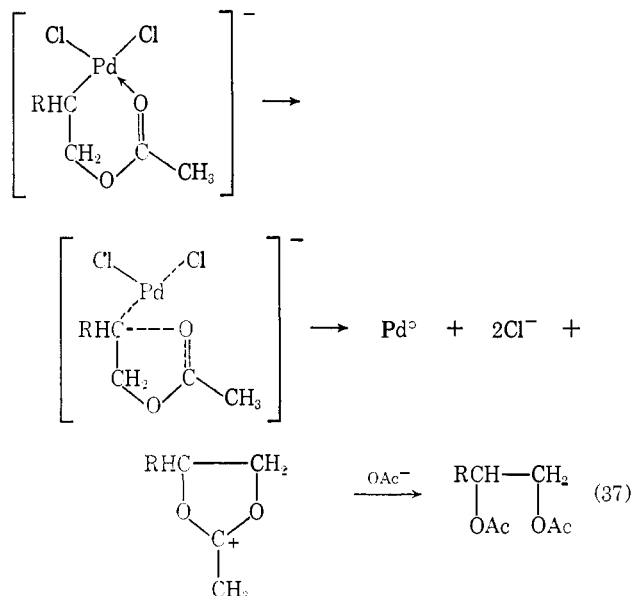


An alternative mechanism which accounts for the formation of ethylidene diacetate without postulating a carbonium ion intermediate involves an acetate displacement of palladium

from the intermediate formed by a 1,2-hydride shift (eq 36),<sup>307</sup> This mechanism still involves a 1,2-hydride shift, the evidence



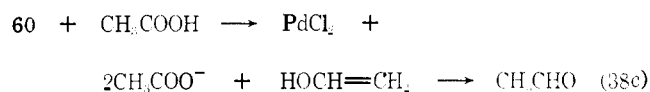
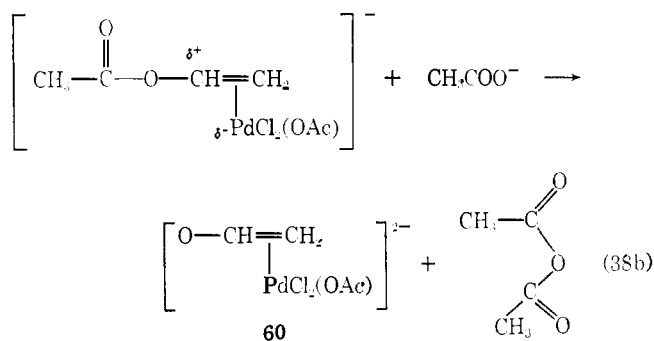
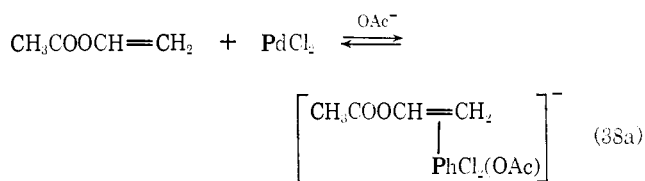
for which has been queried,<sup>309</sup> emphasizing the importance of further work to establish whether or not such a shift does occur. In addition to 1,1-diacetates, 1,2-diacetates have also been found in the reaction products.<sup>307</sup> The formation of 1,2-diacetates has been explained by a neighboring group displacement of palladium by acetate (eq 37),<sup>307</sup> 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  $\text{PdCl}_2$  in acetic acid containing excess sodium acetate, acetaldehyde and acetic anhydride are formed in a 1:1 ratio.<sup>406, 407</sup> It was established that  $\text{PdCl}_2$  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

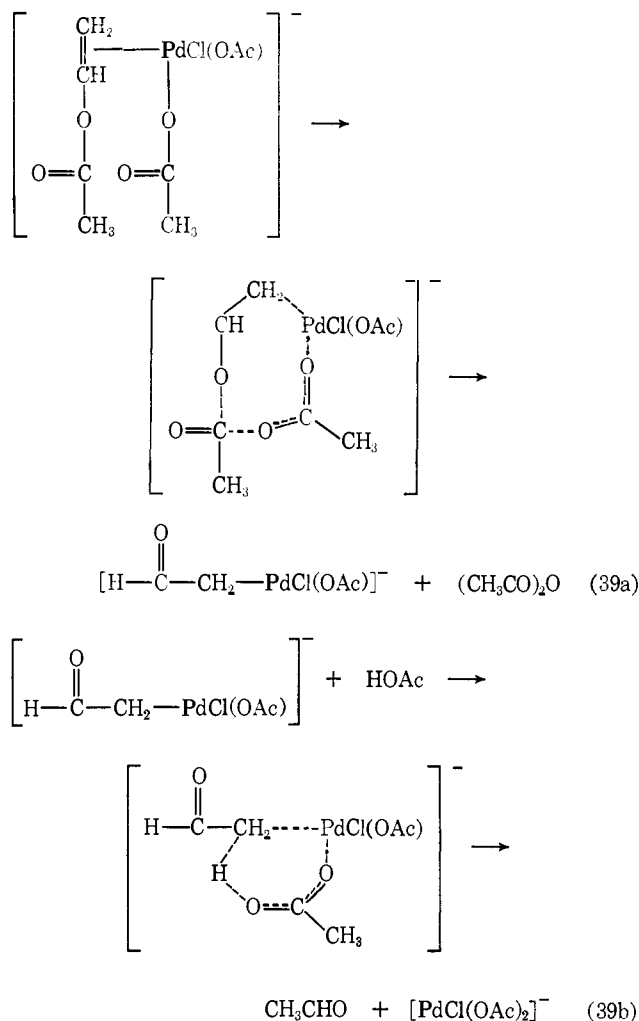


the olefin susceptible to nucleophilic attack by acetate ions giving acetic anhydride and an intermediate, 60, which is then protonated by reaction with acetic acid to give the unstable vinyl alcohol which rearranges to acetaldehyde.<sup>406</sup> An alternative mechanism (eq 39) which involves intramolecular attack by a coordinated acetate ion has been put forward.<sup>389</sup> 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.<sup>389</sup> 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.

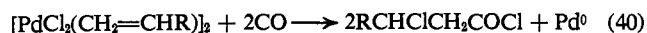
#### D. CARBONYLATION

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.<sup>408</sup> The reaction has been developed commercially to prepare acid chlorides,<sup>409</sup>



carboxylic acids, and esters,<sup>410-418</sup> lactones,<sup>414</sup> and oxo acids.<sup>414</sup>

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)  $\text{PdCl}_2$  in a nonaqueous solvent containing hydrogen chloride;<sup>415</sup> (2) palladium(0) complexes such as  $\text{Pd}(\text{PPh}_3)_4$ .<sup>416-418</sup> 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.<sup>416</sup> The great advantage of complex palladium(II) chloride catalysts over  $\text{PdCl}_2$  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.<sup>418</sup>

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

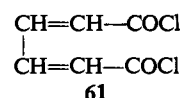
1. Both olefins and acetylenes may be carbonylated in the presence of  $\text{PdCl}_2$ .<sup>408, 419</sup>

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.<sup>408</sup>

4. During carbonylation palladium metal is formed.<sup>420, 421</sup> Palladium on charcoal was found to be as effective a catalyst as  $\text{PdCl}_2$ ,<sup>420-422</sup> which may indicate that metallic palladium rather than  $\text{PdCl}_2$  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.<sup>423</sup> With propargyl alcohol slightly different products were obtained using palladium on charcoal and  $\text{PdCl}_2$ .<sup>424</sup>

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.<sup>419</sup> Using low ratios of acetylene to carbon



monoxide in the presence of  $\text{PdCl}_2$ , maleic acid derivatives are formed.<sup>425</sup> The very small trace of fumaric acid derivative found suggests that the addition of carbon monoxide to acetylene in the presence of  $\text{PdCl}_2$  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).

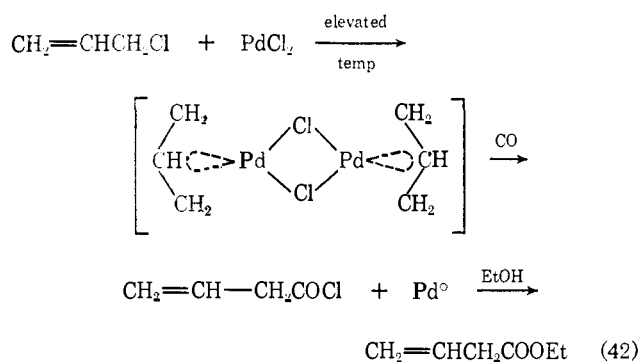
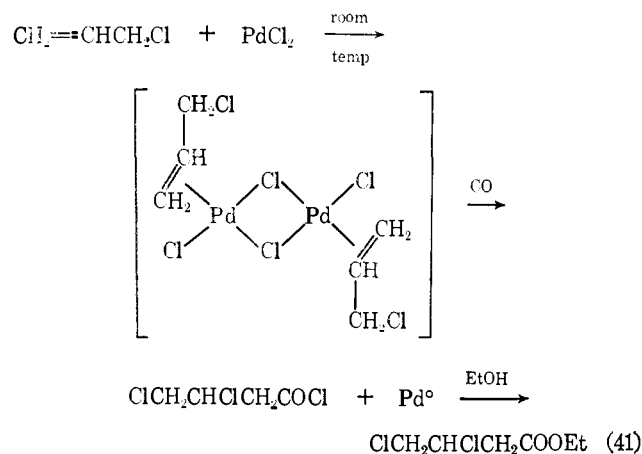
(423) G. C. Bond, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), 63, 42 (1966).

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

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

tive is produced subsequently by an independent isomerization.

6. When allyl compounds are treated in ethanol with carbon monoxide under pressure in the presence of  $\text{PdCl}_2$ , the product obtained depends on the temperature. This was interpreted by assuming that a  $\pi$ -olefin complex was involved as the intermediate at room temperature (eq 41) and a  $\pi$ -allyl complex at higher temperatures (eq 42).<sup>426</sup> The formation of a  $\pi$ -allyl intermediate at higher temperatures is likely



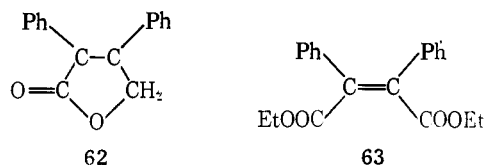
since a number of carbonylations of  $\pi$ -allylpalladium(II) complexes, which give allylic products, have been reported.<sup>416, 426-436</sup> Nonconjugated diolefins which cannot give  $\pi$ -allyl complexes have been studied<sup>437-441</sup> and found to be generally more reactive than conjugated diolefins.<sup>437</sup>

7. The reverse reaction, namely decarbonylation of an acid chloride to give an olefin, was found to be catalyzed by pal-

ladium metal and even more effectively by  $\text{PdCl}_2$ .<sup>442</sup> Aldehydes can be similarly decarbonylated.<sup>442</sup>

8. Carbonylation of ethyl acetylenecarboxylate in ethanolic hydrogen chloride using a  $\text{PdCl}_2$  catalyst gives dicarbonylation as the main reaction, particularly at high hydrogen chloride concentrations.<sup>443</sup>

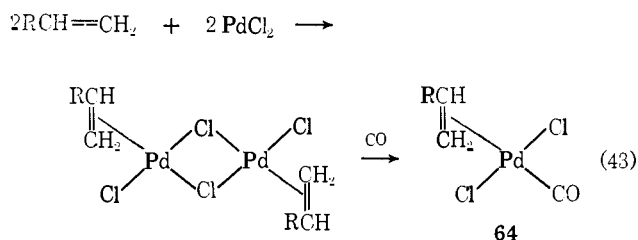
9. The presence of carbon monoxide before the acetylene complex is formed was shown to be important in the carbonylation of diphenylacetylene. When diphenylacetylene was treated with  $\text{PdCl}_2$  in ethanolic hydrogen chloride for an hour followed by introduction of carbon monoxide, tetraphenylfuran and desoxybenzoin were formed, whereas if carbon monoxide was present from the start **62** was formed<sup>444</sup> by *cis* addition of two molecules of carbon monoxide to the



acetylene. This *cis*-addition mechanism was confirmed by the isolation of traces of **63**. Hydrogenolysis of one of the carbonyl groups led to **62**.<sup>444</sup>

10. Carbonylation of cyclopropane in benzene gives a mixture of 1-, 2-, and 3-chlorobutyl chlorides together with *n*-propylbenzene. This latter is the Friedel-Crafts addition product of benzene and cyclopropane and is only formed in the presence of both carbon monoxide and  $\text{PdCl}_2$ .<sup>445</sup>

In discussing the mechanism for the carbonylation of olefins in the presence of  $\text{PdCl}_2$ , it will be assumed that the reaction is homogeneous, although as mentioned above this is not fully established. The first step almost certainly involves the formation of an olefin complex followed by reaction with carbon monoxide to give an olefin carbonyl complex (eq 43).<sup>421</sup> Although the final product **64** has not been isolated with palladium as the metal ion, the corresponding platinum(II)



complex has been prepared by this route with hex-1-ene, oct-1-ene, and styrene.<sup>180</sup> The second stage involves the migration of chloride from palladium to the olefin (eq 44). It has been suggested that the intermediate **65** is less hindered than the alternative **66** so that formation of **65** is favored.<sup>421</sup> However, eq 44 is in effect a nucleophilic attack by a coordinated chloride ion on a coordinated olefin. Since nucleophiles such as hydroxide and acetate ions attack the most substituted carbon atom (*i.e.*, follow Markovnikov's rule), it is unnecessary to invoke steric effects to account for the formation of **65** in preference to **66**. Similarly, it is unnecessary to postu-

(426) J. Tsuji, J. Kiji, S. Imamura, and M. Morikawa, *J. Am. Chem. Soc.*, **86**, 4350 (1964).

(427) J. Tsuji, J. Kiji, and M. Morikawa, *Tetrahedron Lett.*, 1811 (1963).  
(428) J. Tsuji, S. Imamura, and J. Kiji, *J. Am. Chem. Soc.*, **86**, 4491 (1964).

(429) W. T. Dent, R. Long, and G. H. Whitfield, *J. Chem. Soc.*, 1588 (1964).

(430) R. Long and G. H. Whitfield, *ibid.*, 1852 (1964).

(431) S. Brewis and P. R. Hughes, *Chem. Commun.*, 157 (1965).

(432) J. Tsuji and S. Hosaka, *J. Am. Chem. Soc.*, **87**, 4075 (1965).

(433) J. Tsuji and T. Suzuki, *Tetrahedron Lett.*, 3027 (1965).

(434) E. W. Stern and M. L. Spector, *J. Org. Chem.*, **31**, 596 (1966).

(435) J. Tsuji and N. Iwamoto, *Chem. Commun.*, 828 (1966).

(436) C. Bordenca and W. E. Marsico, *Tetrahedron Lett.*, 1541 (1967).

(437) S. Brewis and P. R. Hughes, *Chem. Commun.*, 489 (1965).

(438) S. Brewis and P. R. Hughes, *ibid.*, 6 (1966).

(439) J. Tsuji, S. Hosaka, J. Kiji, and T. Suzuki, *Bull. Chem. Soc. Japan*, **39**, 141 (1966).

(440) J. Tsuji and T. Nogi, *ibid.*, **38**, 146 (1966).

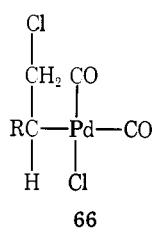
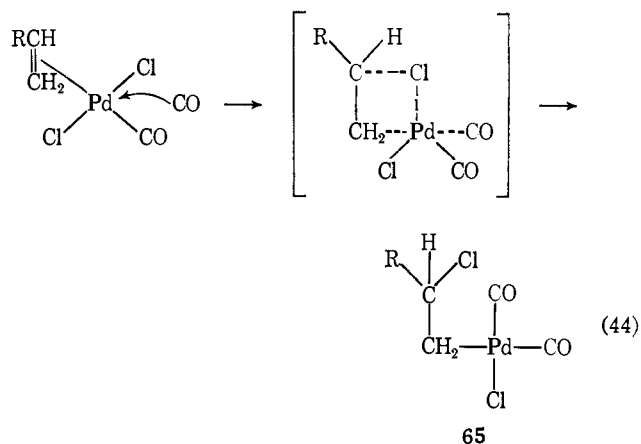
(441) S. Brewis and P. R. Hughes, *Chem. Commun.*, 71 (1967).

(442) J. Tsuji, K. Ohno, and T. Kajimoto, *Tetrahedron Lett.*, 4565 (1965).

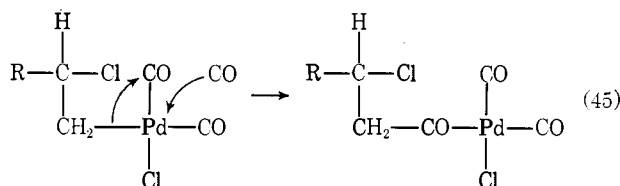
(443) J. Tsuji and T. Nogi, *J. Org. Chem.*, **31**, 2641 (1966).

(444) J. Tsuji and T. Nogi, *J. Am. Chem. Soc.*, **88**, 1289 (1966).

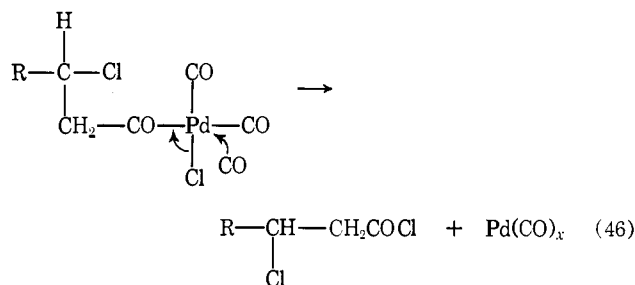
(445) J. Tsuji, M. Morikawa, and J. Kiji, *Tetrahedron Lett.*, 817 (1965).



late the formation of the primary carbanion<sup>180</sup>  $\text{RCHClCH}_2^-$ . The third stage involves the insertion of carbon monoxide into the palladium-carbon  $\sigma$  bond<sup>421,446</sup> (eq 45), which has been shown to occur with both palladium(II) and platinum-



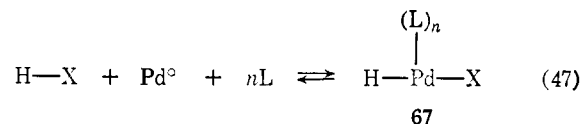
(II) complexes containing phosphine ligands.<sup>312,447</sup> The final stage involves attack of the remaining chloride ligand on the acyl group to give the acyl chloride (eq 46). This mechanism is able to explain the observed data and involves a number of intermediates which are very similar to complexes that have already been prepared. It must, however,<sup>448</sup> be emphasized that



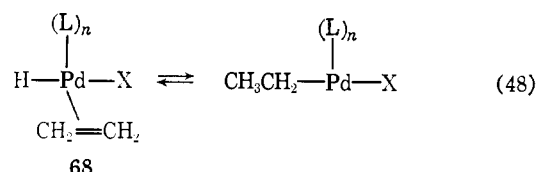
much work remains to be done before this mechanism can be considered to be fully established.

A mechanism, which is similar to that described above for carbonylation in the presence of  $\text{PdCl}_2$ , has been proposed for the carbonylation and decarbonylation of olefins in the

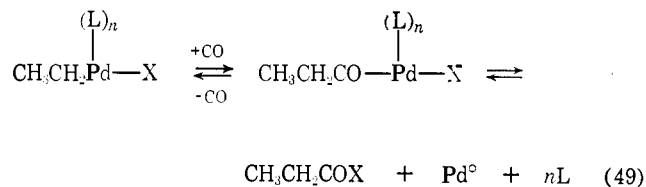
presence of palladium metal.<sup>448</sup> In the first stage (eq 47), which involves the reaction of palladium metal to give a palladium(II) complex, X is a halogen and L is a molecule that can stabilize palladium(II) (either carbon monoxide or solvent). Although no complexes of the type 67 have been 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

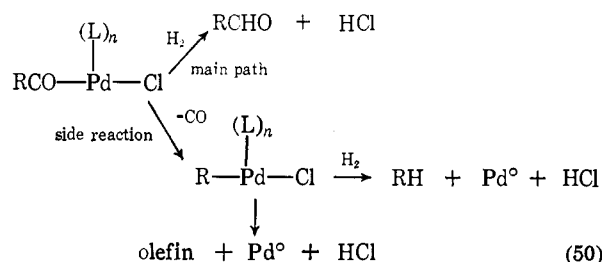
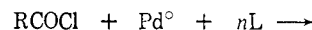


known to occur with platinum(II)-olefin complexes.<sup>197,198</sup> The remaining stages of the reaction (eq 49) parallel those discussed above when  $\text{PdCl}_2$  was the catalyst. In decarbonyla-



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.<sup>448</sup> The transformation of acylpalladium(II) to alkylpalladium(II) complexes on heating in the absence of carbon monoxide is reasonable since acylplatinum(0) complexes on heating in the absence of carbon monoxide give alkylplatinum(0) complexes.<sup>162</sup> The final stage involves decomposition of the alkylpalladium(II) complexes to give the olefin. This reaction has been observed previously.<sup>388</sup>

The study of the carbonylation of olefins and the decarbonylation of acid chlorides has enabled a mechanism for the Rosenmund reduction<sup>449</sup> 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).

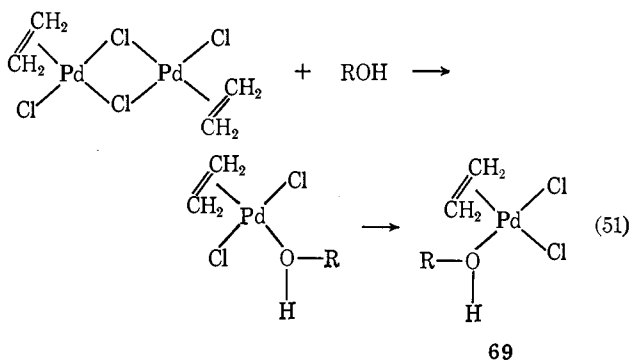
hydrogen in a high-boiling solvent such as xylene in the presence of a palladium metal catalyst. The proposed mechanism (eq 50) involves the formation of an acylpalladium complex which reacts with hydrogen to yield an aldehyde and palladium metal.<sup>448</sup> The decarbonylated by-products that are 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

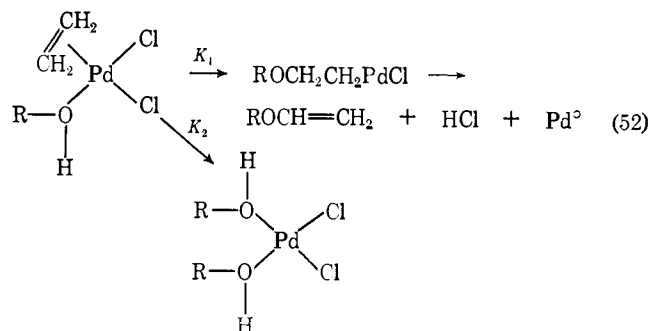
A number of other nucleophiles undergo oxidative addition to olefins that are coordinated to palladium(II).

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<sup>306, 450, 451</sup> or acetals,<sup>886, 452, 453</sup> primary amines give secondary amines,<sup>306</sup> amides give N-alkenylamides,<sup>306</sup> chloride gives vinyl chloride,<sup>451, 454</sup> and cyanide gives vinyl cyanide.<sup>455</sup> Where higher olefins are involved the nucleophilic attack proceeds according to Markovnikov's rule.

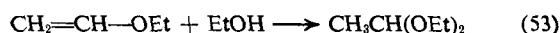
The nucleophilic attack of coordinated olefins by alcohols has been studied in some detail. Methanol and ethanol both react with the coordinated olefin whereas higher alcohols displace the olefin. It has been suggested that the initial reaction of alcohol with  $[\text{PdCl}_2(\text{C}_2\text{H}_4)]_2$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



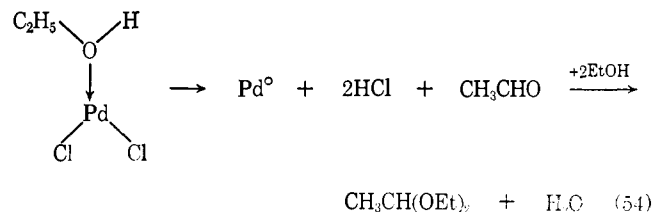
attacks the olefin oxidizing it to an ether or a further molecule of alcohol attacks **69** giving *cis*- $[\text{PdCl}_2(\text{ROH})_2]$  (eq 52).<sup>456</sup> For R = methyl and ethyl,  $K_1 \gg K_2$ , whereas for higher alkyl groups,  $K_2 \gg K_1$ . The acetal formed by reaction of ethanol with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



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

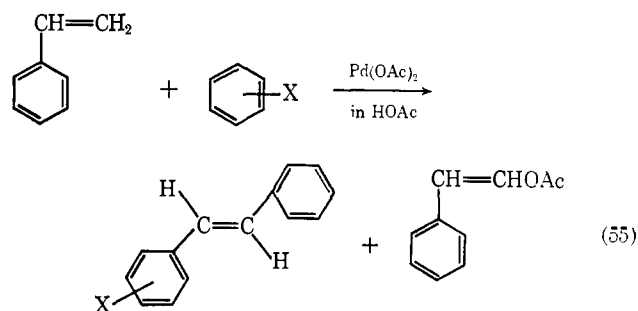


coordinated to palladium(II), to acetaldehyde, which then reacts with further ethanol to give the acetal (eq 54). Using <sup>14</sup>C-



labeled ethylene, it was shown<sup>456</sup> 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.<sup>457</sup> 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  $\text{Pd}(\text{OAc})_2$ .<sup>458</sup> 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  $\text{Pd}(\text{OAc})_2$ .<sup>459</sup>

The  $\text{PdCl}_2$ -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.<sup>460</sup> During the course of the oxidation  $\text{PdCl}_2$  is reduced to

(450) Imperial Chemical Industries Ltd., Netherlands Patent 6,511,468 (1966); *Chem. Abstr.*, 65, 3750d (1966).

(451) S. K. Choi, *Chosun Kwakawan Tongbo*, 30 (1966); *Chem. Abstr.*, 67, 116938 (1967).

(452) I. I. Moiseev and M. N. Vargaftik, USSR Patent 137,508 (1960); *Chem. Abstr.*, 56, 328c (1962).

(453) I. I. Moiseev, A. A. Grigor'ev, and M. Ya. Klimenko, USSR Patent 163,436 (1964); *Chem. Abstr.*, 62, 6396a (1965).

(454) C. W. Capp, G. W. Godin, R. F. Neale, J. B. Williamson, and B. W. Harris, British Patent 918,062 (1963); *Chem. Abstr.*, 59, 5021g (1963).

(455) Y. Odaira, T. Oishi, T. Yukawa, and S. Tsutsumi, *J. Am. Chem. Soc.*, 88, 4105 (1966).

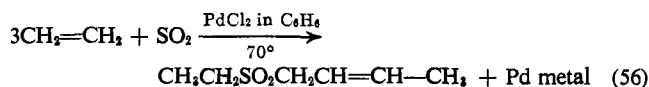
(456) A. D. Ketley and L. P. Fisher, *J. Organometal. Chem.* (Amsterdam), 13, 243 (1968).

(457) I. Moritani and Y. Fujiwara, *Tetrahedron Lett.*, 1119 (1967).

(458) Y. Fujiwara, I. Moritani, M. Matsuda, and S. Teranishi, *ibid.*, 633 (1968).

(459) Y. Fujiwara, I. Moritani, M. Matsuda, and S. Teranishi, *ibid.*, 3863 (1968).

(460) H. S. Klein, *Chem. Commun.*, 377 (1968).



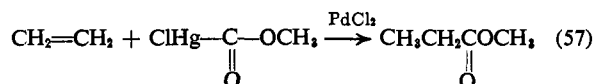
palladium metal.

Although the condensation of olefins with formaldehyde to give a 1,3-dioxane is catalyzed by  $\text{PdCl}_2$ , especially in the presence of cupric chloride, the presence of oxygen is not essential suggesting that the addition follows a different mechanism to that of other nucleophiles such as hydroxide or acetate ions.<sup>461</sup> The addition of 3-butyrolactone to ethylene in the presence of  $\text{PdCl}_2$  is similar.<sup>462</sup> The nonoxidative addition of methoxide ions to diolefin-platinum(II) complexes to give complexes containing a platinum-carbon  $\sigma$  bond and a platinum-olefin  $\pi$  bond has already been discussed in section III.B.2.

Grignard reagents and phenyllithium attack olefins coordinated to palladium(II),<sup>463</sup> With styrene the terminal hydrogen atom is selectively substituted, whereas with propylene, although both vinylic carbon atoms are attacked, there is a marked preference for the nonterminal carbon atom.

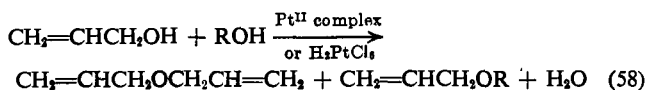
In the presence of  $\text{PdCl}_2$ , nucleophiles such as carboxylic acids and alcohols will displace the chlorine atom on vinyl chloride to give vinyl esters and vinyl ethers, respectively.<sup>464</sup>

Carbomethoxymercuric chloride reacts with palladium(II)-olefin complexes to give alkanolic esters (eq 57).<sup>465</sup> Further work is required to determine the mechanism of this reaction



and the source of the hydrogen atom that adds across the double bond.

Chloroplatinic acid and platinum(II) complexes catalyze the formation of allyl ethers from allyl alcohol by eq 58,<sup>466, 467</sup>



The original authors suggested a cyclic mechanism (Figure 14)

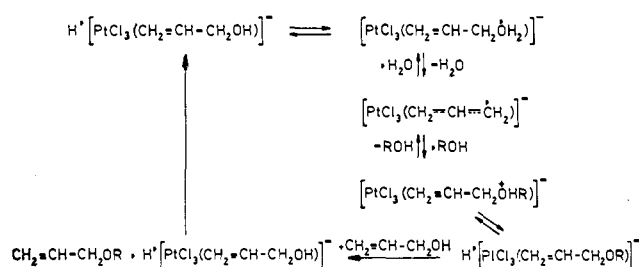


Figure 14. Possible mechanism for the platinum(II)-catalyzed etherification of allyl alcohol.<sup>468</sup>

(461) S. Sakai, Y. Kawashima, Y. Takahashi, and Y. Ishii, *Tetrahedron Lett.*, 1073 (1967).

(462) T. Saegusa, T. Tsuda, and K. Isayama, *ibid.*, 3599 (1967).

(463) H. Okada and H. Hashimoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 70, 2152 (1967).

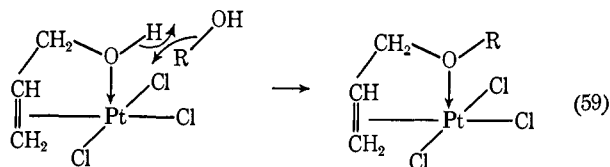
(464) E. W. Stern, M. L. Spector, and H. P. Leftin, *J. Catalysis*, 6, 152 (1966).

(465) T. Saegusa, T. Tsuda, and K. Nishijima, *Tetrahedron Lett.*, 4255 (1967).

(466) J. Milgrom and W. H. Urry, Proceedings of the 7th International Conference on Coordination Chemistry, Stockholm and Uppsala, 1962, p 264.

(467) J. Milgrom and W. H. Urry, U. S. Patent 3,173,958 (1965); *Chem. Abstr.*, 62, 16058h (1965).

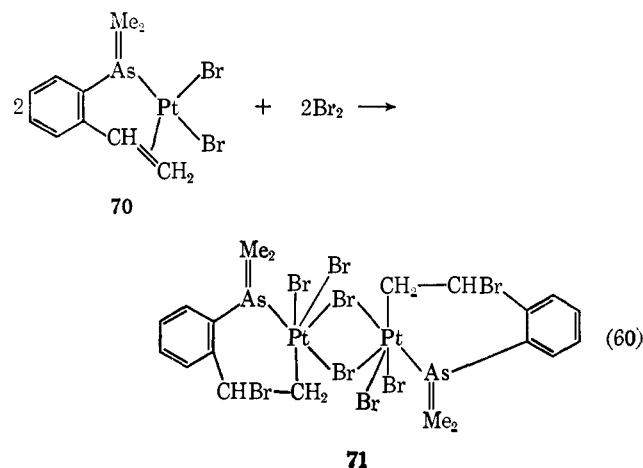
to account for the formation of  $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{OR}$  as the major product from methylallyl alcohol in the presence of platinum(II) salts, in contrast to the acid-catalyzed etherification which yields  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OR}$  as the major product.<sup>15</sup> However, a simpler mechanism involves displacement of the alcoholic hydrogen by an alkyl group and simultaneous formation of water (eq 59). Such a reaction would be facilitated by oxygen-platinum interaction, which has been shown



to occur in solvents such as benzene and carbon tetrachloride.<sup>287</sup> The electron-releasing alkyl group should strengthen the oxygen-platinum interaction providing the driving force for the reaction.

## VI. Electrophilic Attack on Coordinated Olefins

Although free olefins are generally attacked by electrophilic reagents and unaffected by nucleophilic reagents, the reverse is true of coordinated olefins. Electrophilic attack on olefins coordinated to platinum and palladium is rare and limited to one tentative case. This is the bromination of the platinum(II) complex **70** to give the platinum(IV) complex **71** (eq 60).<sup>468</sup> It has been suggested<sup>469</sup> that this bromination occurs by synchronous *cis* addition of a polarized bromine molecule



with the negative end attacking the platinum and the positive end attacking the double bond. Recent studies have indicated that the olefinic double bond coordinated to platinum(II) is electron deficient between the carbon atoms in the region of the  $\pi$ -bonding orbital and electron rich on the side of the olefinic carbon atom that is remote from the double bond in the region of the  $\pi^*$  (antibonding) orbital.<sup>107</sup> Electrophilic attack would therefore be expected to occur on the side of the carbon atom that is remote from the double bond. No stereochemical investigations of this reaction have yet been undertaken.

(468) M. A. Bennett, G. J. Erskine, and R. S. Nyholm, *J. Chem. Soc., A*, 1260 (1967).

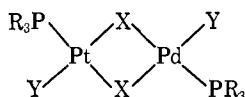
(469) M. A. Bennett, Symposium on Metal-Olefin and  $\pi$ -Allyl Complexes, Sheffield, England, April 1967.



## 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.<sup>470</sup> This work was later repeated,<sup>199, 471, 472</sup> and it was shown that if care was taken to avoid a rise in temperature the reaction was homogeneous, but if the temperature rose,<sup>471</sup> or an excess of hydrogen was used,<sup>472</sup> platinum metal was deposited and the reaction became heterogeneous.

Palladium(II) is generally unstable in the presence of hydrogen,<sup>473, 474</sup> so that until recently it was rarely used as a homogeneous catalyst although it has often been used as a heterogeneous catalyst.<sup>16, 475</sup> However,  $\text{PdCl}_2$  in dimethylformamide or dimethylacetamide does catalyze the homogeneous hydrogenation of dicyclopentadiene.<sup>471</sup> Aqueous solutions of  $\text{PdCl}_2$  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.<sup>476</sup> 1-Olefins have been homogeneously hydrogenated in the presence of both  $[\text{PdCl}_2(\text{PR}_3)_2]$  complexes<sup>477</sup> and binuclear platinum(II)-palladium(II) complexes of type 72.<sup>478</sup> It has recently been shown that palladium(II)



72, R = Bu, Pr; X = Cl, Br, PPh<sub>2</sub>; Y = Cl, Br

complexes containing tin(II) ligands are effective catalysts for the homogeneous hydrogenation of olefins.<sup>11, 479, 480</sup>

Although platinum(II) complexes that do not contain tin(II) ligands have been used as homogeneous hydrogenation catalysts,<sup>481</sup> 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.<sup>168</sup> Higher olefins were hydrogenated more slowly,<sup>163, 482</sup> which was attributed to the weaker complexes formed between higher olefins and platinum(II).<sup>168</sup> 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 alcohols<sup>483</sup> or carboxylic acids and esters.<sup>484</sup> In general, coordinating solvents decrease the catalytic activity of both platinum(II) and palladium(II) complexes relative to noncoordinating solvents.<sup>485</sup> 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.<sup>482</sup> Platinum(II) complexes containing both  $\text{SnCl}_3^-$  and phosphine ligands catalyze the selective reduction of diolefins and triolefins in soybean oil methyl ester to monoolefins<sup>11, 486-488</sup> and in methyl linolenate to diolefins and monoolefins.<sup>11, 479, 489</sup> 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.<sup>480</sup> 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.<sup>489</sup>

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.<sup>214</sup> *cis-trans* isomerization of the double bond also occurs during the hydrogenation.<sup>479, 486, 488</sup>

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

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.<sup>214</sup>

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.<sup>214</sup>

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.<sup>480</sup>

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.<sup>214, 486, 488, 490</sup> Stannous chloride reacts with chloride ions to give the  $\text{SnCl}_3^-$  ion, which exhibits a high *trans*-effect<sup>491</sup> and which is known to be a good ligand

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(472) K. E. Hayes, *Nature* **210**, 412 (1966).

(473) J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, **86**, 1776 (1964).

(474) R. Cramer and R. V. Lindsey, *ibid.*, **88**, 3534 (1966).

(475) P. N. Rylander, *Ann. N. Y. Acad. Sci.*, **145**, 46 (1967).

(476) E. B. Maxted and S. M. Ismail, *J. Chem. Soc.*, 1750 (1964).

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(478) Imperial Chemical Industries Ltd., Netherlands Patent 6,611,373 (1967); *Chem. Abstr.*, **67**, 54266 (1967).

(479) J. C. Bailar and H. Itatani, *J. Am. Chem. Soc.*, **89**, 1592 (1967).

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(482) G. C. Bond and M. Hellier, *Chem. Ind. (London)*, **35** (1965).

(483) H. Van Bekkum, J. Van Gogh, and G. Van Minnen-Pathuis, *J. Catalysis*, **7**, 292 (1967).

(484) L. P. Van't Hof and B. G. Linsen, *ibid.*, **7**, 295 (1967).

(485) H. A. Tayim, *Dissertation Abstr.*, **B28**, 1407 (1967).

(486) J. C. Bailar and H. Itatani, Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, 1964, p 67; *Chem. Abstr.*, **64**, 20015g (1966).

(487) J. C. Bailar and H. Itatani, *Inorg. Chem.*, **4**, 1618 (1965).

(488) J. C. Bailar and H. Itatani, *J. Am. Oil Chemists' Soc.*, **43**, 337 (1966).

(489) E. N. Frankel, E. A. Emken, H. Itatani, and J. C. Bailar, *J. Org. Chem.*, **32**, 1447 (1967).

(490) I. Jardine and F. J. McQuillin, *Tetrahedron Lett.*, 4871 (1966).

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

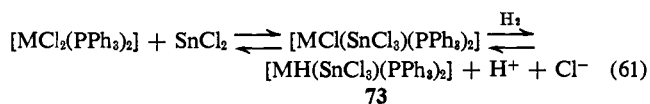
for platinum(II)<sup>491-495</sup> and palladium(II).<sup>496</sup> The  $\text{SnCl}_3^-$  ligand is a weak  $\sigma$  donor and a strong  $\pi$  acceptor because of the presence of vacant 5d orbitals of the right size and energy to accept d electrons from platinum and palladium.<sup>497</sup> This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

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  $\text{SnCl}_3^-$  ligands blocking the sites that would otherwise be available for coordination of hydride ions or olefins.<sup>214</sup> A platinum to tin ratio of 1:5 has been found to give the best results.<sup>483, 484, 500</sup> Below a ratio of 1:3 metallic platinum is formed, and above a ratio of 1:7 the rate of hydrogenation gradually decreases.<sup>484</sup> 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  $\text{SnCl}_3^-$  ions.<sup>484</sup>

8. Hydrogenation by  $\text{H}_2$  in MeOD and  $\text{D}_2$  in MeOH results in all the deuterated ethylenes appearing at the start of the reaction and  $\text{C}_2\text{H}_3\text{D}$  being the basic product obtained from ethylene.<sup>500</sup>

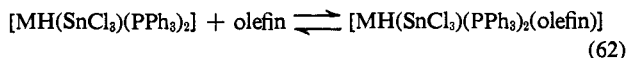
The following mechanism satisfactorily explains all these observations.

*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  $\text{Pd}$ ),<sup>214</sup> **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.<sup>488</sup>

*Stage 2:* The formation of a five-coordinate hydridometal(II)-olefin complex (eq 62). A number of such five-coordinate complexes have been isolated<sup>480</sup> with  $M = \text{Pt}$ . The formation



of such a complex would account for the fact that under

(492) J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 5176 (1964).

(493) D. M. Adams and P. J. Chandler, *Chem. Ind.* (London), 269 (1965).

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(496) M. A. Khattak and R. J. Magee, *Chem. Commun.*, 400 (1965).

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(498) D. A. Brown and N. J. Fitzpatrick, *J. Chem. Soc., A*, 1793 (1967).

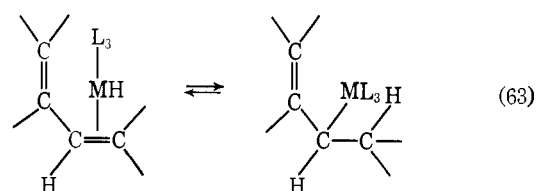
(499) J. Halpern, *Ann. Rev. Phys. Chem.*, 16, 103 (1965).

(500) A. P. Khrushch, L. A. Tokina, and A. E. Shilov, *Kinetika i Kataliz*, 7, 901 (1966); *Chem. Abstr.*, 66, 37090 (1967).

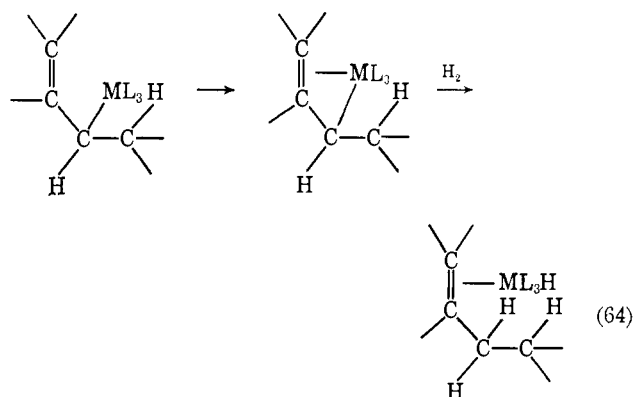
conditions in which palladium(II) complexes are not reduced to palladium metal they are generally better hydrogenation catalysts than platinum(II) complexes,<sup>479</sup> since palladium(II) can more readily expand its coordination sphere than platinum(II).<sup>311-313</sup>

*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.<sup>197,198</sup>



*Stage 5:* Rearrangement of the alkyl complex by attack of the free double bond on the metal to give a  $\sigma$ - $\pi$  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  $\sigma$ - $\pi$  complex could in theory decompose to a



$\pi$ -allyl complex which would then be hydrogenated to give the  $\pi$ -olefin complex, this mechanism is unlikely since no  $\pi$ -allyl complexes could be detected by nuclear magnetic resonance.<sup>480</sup>

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

An alternative mechanism<sup>501</sup> 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,<sup>502</sup> so that heterogeneous hydrogenation can usefully be considered in terms of organometallic

(501) R. S. Nyholm, "Proceedings of the 3rd International Congress on Catalysis," North Holland Publishing Co., Amsterdam, 1965, p 25.

(502) P. B. Wells, *Platinum Metals Rev.*, 7, 18 (1963).

intermediates.<sup>490,503-506</sup> 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.<sup>507-509</sup> 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.<sup>509</sup>

### VIII. Homogeneous Hydrosilation of Olefins

The hydrosilation of olefins catalyzed by platinum complexes closely resembles the catalytic hydrogenation of olefins.<sup>507</sup> Although platinum(II) complexes are effective hydrosilation catalysts,<sup>510</sup> platinum(IV) complexes such as chloroplatinic acid have been more widely studied.<sup>511-514</sup> The reaction, which has been used industrially,<sup>515-520</sup> 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.<sup>510</sup>

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.<sup>521</sup> However, since the solutions have been shown to remain optically clear, platinum complexes are true homogeneous catalysts.<sup>510,514</sup>

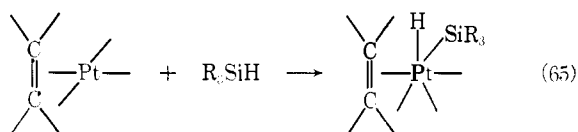
Hydrosilation is often accompanied by considerable isomerization of the olefin, the relative importance of hydrosilation and isomerization being partly determined by the silane present.<sup>510</sup> Terminal olefins give hydrosilation more rapidly than branched olefins.<sup>513</sup> After the addition 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.<sup>513</sup> 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.<sup>473</sup> 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.<sup>510</sup>

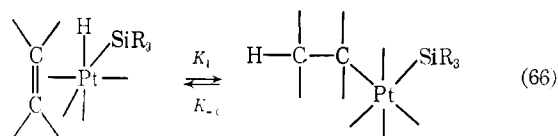
The hydrosilation of acetylenes results in the formation of *trans* products, indicating that *cis* addition of  $R_3Si-H$  across the triple bond has occurred.<sup>521</sup> Similarly the hydrosilation of 1-methylcyclohexene occurs in a stereospecifically *cis* manner<sup>522</sup> and the hydrosilation of bicycloheptadiene catalyzed by chloroplatinic acid gives the only known case of *endo* addition to this olefin.<sup>523</sup>

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.<sup>514</sup> However, there was complete deuterium retention by the olefin during the hydrosilation of 1-methyl-*d*<sub>3</sub>-cyclohexene indicating that in this case intramolecular hydrogen exchange had occurred.<sup>522</sup>

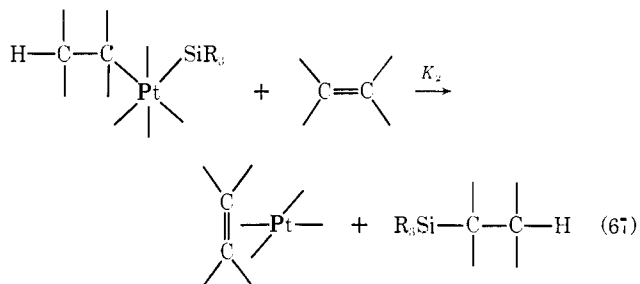
A mechanism for the reaction has been suggested<sup>510,514</sup> which involves the formation of a platinum(II)-olefin complex by reduction of chloroplatinic acid by the olefin. The platinum(II)-olefin complex then forms a platinum(IV) complex by addition of the silane (eq 65). This adduct then rearranges



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

(503) F. J. McQuillin, W. O. Ord, and P. L. Simpson, *J. Chem. Soc.*, 5996 (1963).

(504) D. A. Denton, F. J. McQuillin, and P. L. Simpson, *ibid.*, 5535 (1964).

(505) I. Jardine and F. J. McQuillin, *J. Chem. Soc., C*, 458 (1966).

(506) A. M. Khan, F. J. McQuillin, and I. Jardine, *Tetrahedron Lett.*, 2649 (1966).

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(508) J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968).

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(513) J. C. Saam and J. L. Speier, *ibid.*, 83, 1351 (1961).

(514) J. W. Ryan and J. L. Speier, *ibid.*, 86, 895 (1964).

(515) Imperial Chemical Industries Ltd., Belgian Patent 609,997 (1962); *Chem. Abstr.*, 57, 16657f (1962).

(516) B. A. Ashby, French Patent 1,361,705 (1964); *Chem. Abstr.*, 61, 13451b (1964).

(517) G. Koerner, German Patent 1,210,844 (1966); *Chem. Abstr.*, 64, 15922b (1966).

(518) Imperial Chemical Industries Ltd., Netherlands Patent 6,510,184 (1966); *Chem. Abstr.*, 65, 749a (1966).

(519) H. F. Lamoreaux, U. S. Patent 3,313,773 (1967); *Chem. Abstr.*, 67, 3316 (1967).

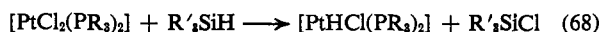
(520) A. J. Chalk, U. S. Patent 3,444,111 (1967); *Chem. Abstr.*, 67, 109343 (1967).

(521) R. A. Benkeser, M. L. Burrows, L. E. Nelson, and J. V. Swisher, *J. Am. Chem. Soc.*, 83, 4385 (1961).

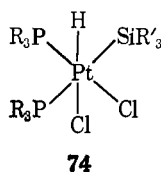
(522) T. G. Selin and R. West, *ibid.*, 84, 1863 (1962).

(523) H. G. Kuivila and C. R. Warner, *J. Org. Chem.*, 29, 2845 (1964).

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.<sup>501</sup> The exceptionally high *trans*-effect of silicon ligands, which is inductive



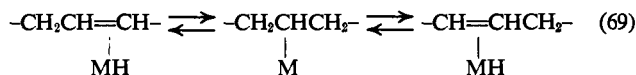
in origin and should therefore be present in octahedral as well as square-planar complexes, indicates that the platinum-silicon  $\sigma$  bond is very strong.<sup>524</sup>

The addition of germanium hydride derivatives across olefinic double bonds is also homogeneously catalyzed by chloroplatinic acid.<sup>525</sup> Extensive isomerization occurs and, as in the homogeneous hydrogenation of olefins,<sup>480</sup> 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.<sup>523,525</sup>

## IX. Catalytic Isomerization of Olefins

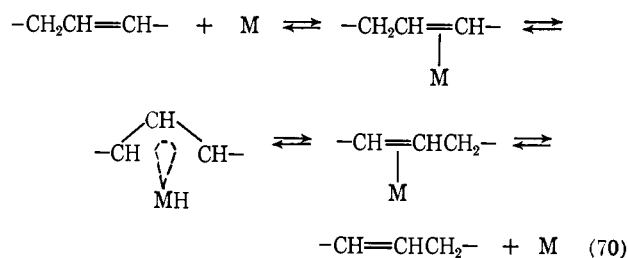
The isomerization of olefins in the presence of palladium(II) and to a lesser extent platinum(II) complexes has been widely observed. For example, the isomerization of unconjugated diolefins to conjugated diolefins is the first stage in the catalytic hydrogenation of polyolefins.<sup>480</sup> Five mechanisms,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

1. *Intermolecular Hydrogen Transfer.*<sup>478</sup> This mechanism, represented schematically by eq 69, involves the following steps: (a) formation of a metal hydride; (b) coordination

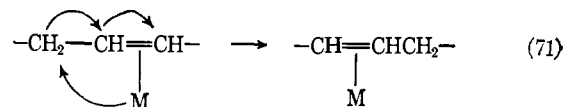


of the olefin to the metal hydride; (c) reversible addition of the metal hydride across the olefin double bond to give a metal alkyl; (d) alkyl complex reverting to a hydrido- $\pi$ -olefin complex containing the isomerized olefin; (e) displacement of the isomerized olefin from the metal by further unisomerized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

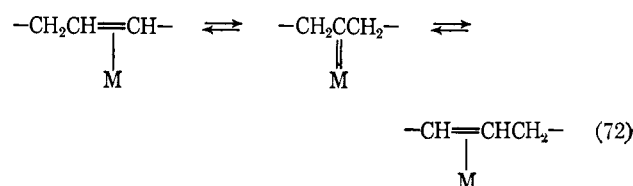
2. *Intramolecular Hydrogen Transfer.* Three possible mechanisms for intramolecular hydrogen transfer have been suggested: (a) formation of an intermediate hydrido- $\pi$ -allylic complex<sup>526</sup> (eq 70); (b) two concerted 1,2 hydrogen shifts accompanied by simultaneous migration of the metal ion<sup>527</sup>



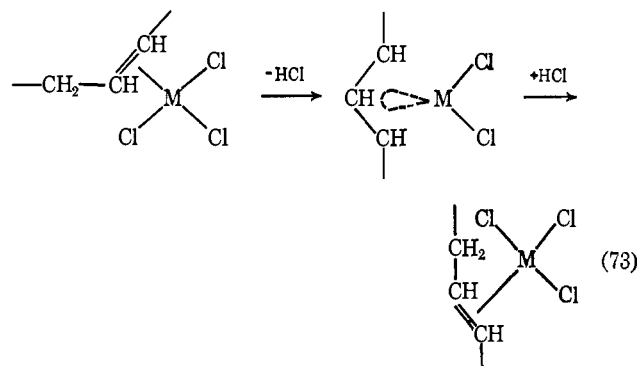
(eq 71); (c) formation of a metal-carbene intermediate<sup>528</sup>



(eq 72).



3. *Reversible  $\pi$ -Allyl Complex Formation.*<sup>528</sup> 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,<sup>528</sup> 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  $\text{PtCl}_2$ ,<sup>526,529</sup> platinum(II)-olefin complexes in chloroform,<sup>530</sup> alcohols,<sup>478</sup> or acetic acid,<sup>466</sup> platinum(II)-phosphine complexes either alone<sup>445</sup> or in the presence of silanes<sup>510</sup> or stannous chloride,<sup>214</sup> mixtures of chloroplatinic acid and stannous chloride,<sup>482,531</sup> and bis(acetylacetonato)-platinum(II).<sup>532</sup> In general platinum(II) complexes are less active than palladium(II) complexes.

(528) N. R. Davies, *Rev. Pure Appl. Chem.*, **17**, 83 (1967).

(529) A. J. M. Wenham and M. B. Sparke, French Patent 1,365,885 (1964); *Chem. Abstr.*, **61**, 13106g (1964).

(530) H. Hogeveen and H. C. Volger, *J. Am. Chem. Soc.*, **89**, 2486 (1967).

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

(532) M. Misono, Y. Saito, and Y. Yoneda, *ibid.*, **10**, 200 (1968).

(524) J. Chatt, C. Eaborn, and S. Ibekwe, *Chem. Commun.*, 700 (1966)

(525) R. H. Fish and H. G. Kuivila, *J. Org. Chem.*, **31**, 2445 (1966).

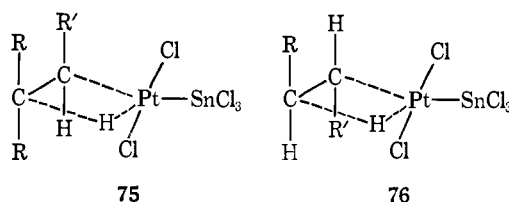
(526) F. Asinger, B. Fell, and P. Krings, *Tetrahedron Lett.*, 633 (1966).

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

The inhibition of isomerization in basic systems,<sup>466</sup> and the fact that the isomerization proceeds more rapidly in the presence than in the absence of molecular hydrogen,<sup>474</sup> 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.<sup>214</sup> The hydrogen in these complexes was shown to originate either from molecular hydrogen or the solvent, but not from the olefin,<sup>214</sup> so that in  $\text{CH}_3\text{OD}$  extensive deuteration of the product was observed.<sup>474</sup>

Of the possible mechanisms the hydrido- $\pi$ -olefin mechanism (eq 69) fits the experimental observations best. The reversible reaction of platinum(II)-olefin complexes with hydrogen to give  $\sigma$ -bonded platinum-alkyl complexes has been studied in detail<sup>197,198</sup> (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- $\pi$ -allylic intermediate (eq 70) may be formed.<sup>526</sup> However, since it has now been shown that the olefin is an insignificant source of hydrogen for hydrido-olefin complex formation,<sup>214</sup> 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.<sup>473,482,581</sup> 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.<sup>581</sup>

## B. ISOMERIZATION OF OLEFINS IN THE PRESENCE OF PALLADIUM COMPLEXES

Palladium complexes that catalyze the isomerization of olefins include  $\text{PdCl}_2$ ,<sup>526,527,529,538-537</sup>  $[\text{PdCl}_2(\text{PhCN})_2]$ ,<sup>222,535,538,539</sup> palladium(II)-olefin<sup>530,535,538,540</sup> and  $-\pi$ -allyl complexes,<sup>530</sup>

(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).

(536) N. R. Davies, *Nature*, **201**, 490 (1964).

(537) I. I. Moiseev, A. A. Grigor'ev, and S. V. Pestrikov, *Zh. Organ. Khim.*, **4**, 354 (1968); *Chem. Abstr.*, **68**, 104357 (1968).

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

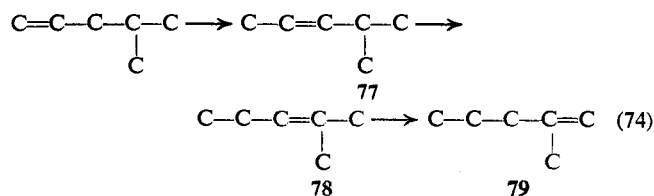
(539) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **88**, 3491 (1966).

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

palladium(II)-phosphine complexes,<sup>213,445,541</sup> bis(acetylacetonato)palladium(II),<sup>532</sup> and palladium(0) complexes.<sup>542-544</sup>

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  $\text{C}_3\text{H}_7\text{CD}_2\text{CH}=\text{CH}_2$  by  $\text{PdCl}_2$  in acetic acid, there is no appreciable migration of deuterium to the terminal carbon atom, suggesting that the migration occurs by a stepwise mechanism.<sup>527</sup> This result, which is in disagreement with the results obtained in the presence of  $[\text{PdCl}_2(\text{PhCN})_2]$ ,<sup>539</sup> is consistent with the hydrido- $\pi$ -olefin mechanism (eq 69) since a relatively high deuterium-hydrogen isotope effect would be expected<sup>545</sup> 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.<sup>527</sup> 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.<sup>197</sup> Instead a hydrido- $\pi$ -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.<sup>539</sup> 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.<sup>585</sup> 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.<sup>546</sup>

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

(541) H. Itatani and J. C. Bailar, *J. Am. Oil, Chemists' Soc.*, **44**, 147 (1967).

(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).

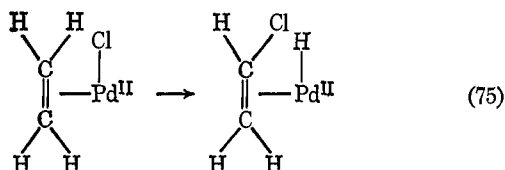
(544) I. I. Moiseev, S. V. Pestrikov, and L. M. Sverzh, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1866 (1966); *Chem. Abstr.*, **66**, 64859 (1967).

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

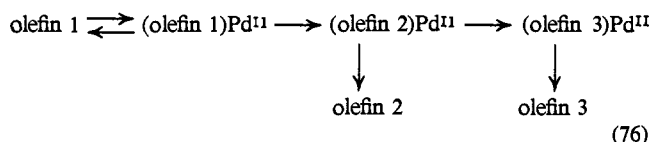
(546) N. R. Davies, A. D. DiMichiel, and V. A. Pickles, *Australian J. Chem.*, **21**, 385 (1968).

multistep isomerization. The possibility that it proceeds by reversible  $\pi$ -allyl complex formation (eq 73) is eliminated by the observation that in  $\text{CH}_3\text{COOD}$  no deuterium is incorporated in the product.<sup>536</sup> In addition it has been shown that  $\pi$ -allyl-palladium(II) complexes do not catalyze olefin isomerization.<sup>534,547</sup> In spite of this observation the hydrido- $\pi$ -allyl mechanism (eq 70) is still possible, because the intermediate in this mechanism contains a hydride ion which is not present in the  $\pi$ -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,<sup>539</sup> which suggests that most of the isomerization occurs by an intramolecular hydrogen migration. The hydrido- $\pi$ -allylic mechanism (eq 70) gives intramolecular hydrogen migration whereas the hydrido- $\pi$ -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- $\pi$ -olefin and the hydrido- $\pi$ -allyl mechanisms, since isomerization can be effected by  $\text{PdCl}_2$  or  $[\text{PdCl}_2(\text{PhCN})_2]$  in the absence of solvent<sup>535,537</sup> or in benzene solution.<sup>473,534,539,547</sup> 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 ethylene<sup>474</sup> 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- $\pi$ -allyl mechanism that will account for multistep migration is a multistep hydrido- $\pi$ -olefin mechanism (eq 76).<sup>528</sup> 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 shown<sup>82</sup> 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.<sup>548</sup> 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.<sup>473,534,535,546</sup> 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.<sup>125</sup> 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.<sup>187,546</sup> This has been ascribed to steric hindrance in *cis*-( $\text{C}_6\text{H}_5\text{C}=\text{CC}-$ ).

In conclusion neither the hydrido- $\pi$ -olefin (eq 69) nor the hydrido- $\pi$ -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,<sup>535</sup> 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,<sup>527</sup> 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,<sup>549</sup> the platinum(II) analog does not catalyze the dimerization of ethylene<sup>549</sup> and decomposes on heating above 180° to give chlorinated  $\text{C}_2$  hydrocarbons.<sup>199</sup> 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.<sup>550–554</sup>

The polymerization of olefins by palladium(II) complexes is very dependent on the nature of both the solvent<sup>555</sup> and the other ligands coordinated to palladium(II).<sup>551,552,556–558</sup> Thus  $\text{PdCl}_2$  catalyzes the polymerization of butadiene to 1,2-polybutadiene whereas both  $\text{PdI}_2$  and  $\text{Pd}(\text{CN})_2$  give very low

(549) J. T. Van Gemert and P. R. Wilkinson, *J. Phys. Chem.*, **68**, 645 (1964).

(550) J. Smidt, W. Hafner, and J. Sedlmeier, British Patent 887,362 (1963); *Chem. Abstr.*, **58**, 3521e (1963).

(551) R. S. Berger and E. A. Youngman, *J. Polymer Sci., Part A*, **2**, 357 (1964).

(552) N. Phung and G. Lefebvre, *Compt. Rend.*, **265**, C519 (1967).

(553) F. N. Jones, *J. Org. Chem.*, **32**, 1667 (1967).

(554) H. C. Volger and K. Vrieze, *J. Organometal. Chem. (Amsterdam)*, **13**, 495 (1968).

(555) Y. Kusunoki, R. Katsuno, N. Hasegawa, S. Kurematsu, Y. Nagao, K. Ishii, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, **39**, 2021 (1966).

(556) A. J. Canale, W. A. Hewett, T. M. Shryne, and E. A. Youngman, *Chem. Ind. (London)*, 1054 (1962).

(557) A. J. Canale and W. A. Hewett, *J. Polymer Sci., Part B*, **2**, 1041 (1964).

(558) A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman, and T. R. Steadman, *Inorg. Chem.*, **6**, 657 (1967).

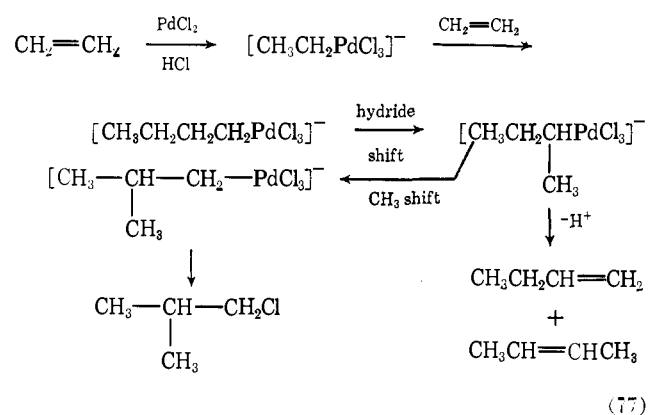
(547) J. F. Harrod and A. J. Chalk, *Nature*, **205**, 280 (1965).

(548) R. Miller, personal communication to ref 474.

yields of predominantly *trans*-1,4-polybutadiene.<sup>557</sup> Palladium(II) complexes have been used both for the dimerization and polymerization of olefins<sup>559-563</sup> and to copolymerize olefins and carbon monoxide.<sup>564,565</sup> While palladium(II) halides react with allene to give  $\pi$ -allylpalladium(II) complexes,<sup>566,567</sup> palladium(II) complexes containing weakly coordinating anions such as acetate, nitrate, or perchlorate catalyze the dimerization of allene.<sup>568</sup> When palladium(0) complexes such as Pd(PPh<sub>3</sub>)<sub>4</sub> are used to polymerize olefins, the final product formed depends on the solvent present.<sup>569,570</sup>

A number of studies of the mechanism of the polymerization of olefins by palladium(II) complexes have been made, but the results are far from complete. During the polymerization palladium(II) is reduced to the metal unless oxidizing agents such as cupric or ferric salts are present.<sup>565,571-573</sup> It was shown that the polymerization of butadienes did not involve classical free radicals since the addition of normal free-radical inhibitors did not affect the rate of the polymerization.<sup>566</sup> By contrast the palladium(II)-catalyzed polymerization of styrene and methyl methacrylate appeared to proceed by a free-radical mechanism.<sup>551</sup> In the dimerization of vinyl acetate a "free-radical scavenger" such as hydroquinone must be added to prevent further polymerization occurring.<sup>571</sup>

A mechanism involving a  $\sigma$ -bonded alkylpalladium(II) intermediate has been proposed for the dimerization of ethylene by PdCl<sub>2</sub> (eq 77).<sup>555</sup> The predominant route is determined by the particular solvent used; for example, methyl



and butyl acrylate give some isobutyl chloride as a by-product

(559) A. U. Blackham, U. S. Patent 3,194,800 (1965); *Chem. Abstr.*, 63, 8518f (1965).

(560) U. S. Rubber Co., Netherlands Patent 6,607,898 (1966); *Chem. Abstr.*, 67, 11922 (1967).

(561) J. E. McKeon and P. S. Starcher, U. S. Patent 3,330,815 (1967); *Chem. Abstr.*, 67, 64884 (1967).

(562) H. S. Klein, U. S. Patent 3,354,236 (1967); *Chem. Abstr.*, 68, 21491 (1968).

(563) A. D. Ketley and J. A. Braatz, *J. Polymer Sci., Part B*, 6, 341 (1968).

(564) J. Tsuji and S. Hosaka, *ibid.*, 3, 703 (1965).

(565) R. G. Schultz, *ibid.*, 4, 541 (1966).

(566) R. G. Schultz, *Tetrahedron*, 20, 2809 (1964).

(567) M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc., A*, 1687 (1966).

(568) G. D. Shier, *J. Organometal. Chem. (Amsterdam)*, 10, P 15 (1967).

(569) S. Takahashi, T. Shibano, and N. Hagihara, *Tetrahedron Lett.*, 2451 (1967).

(570) S. Takahashi, H. Yamazaki, and N. Hagihara, *Bull. Chem. Soc. Japan*, 41, 254 (1968).

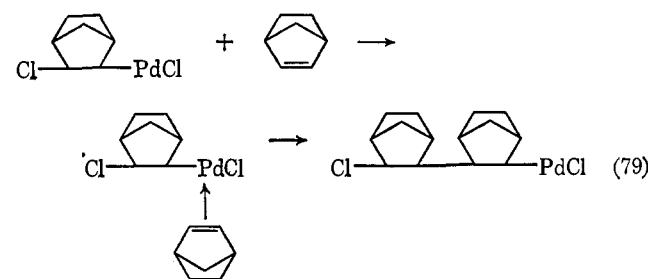
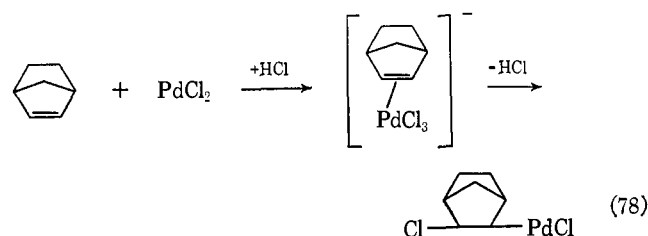
(571) Shell International Research Maatschappij N. V., Netherlands Patent 6,409,545 (1966); *Chem. Abstr.*, 65, 3756e (1966).

(572) C. F. Kohl and R. Van Helden, *Rec. Trav. Chim.*, 86, 193 (1967).

(573) H. C. Volger, *ibid.*, 86, 677 (1967).

whereas acetic acid gives none. Although this mechanism accounts for the products observed, it has a number of unsatisfactory features. The formation of a palladium(II)-carbon  $\sigma$  bond generally requires the presence of a strongly electron-withdrawing ligand which is absent in this case.<sup>574</sup> The mechanism also involves the isomerization of a primary alkyl complex to a secondary alkyl complex which is unlikely to occur, since in the case of platinum(II), primary alkyl complexes are much more stable than secondary alkyl complexes.<sup>198</sup>

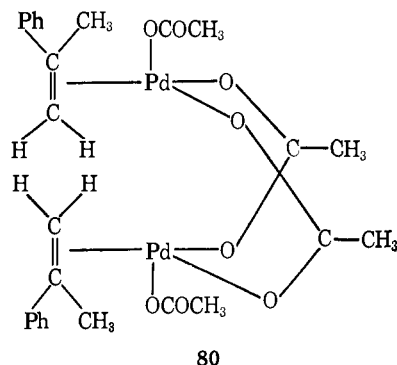
A similar mechanism involving the insertion of an olefin into a palladium-carbon  $\sigma$  bond was put forward to account for the polymerization of norbornene.<sup>565</sup> The initiation stage of the polymerization involves the formation of a palladium-carbon  $\sigma$  bond by decomposition of a palladium-olefin complex (eq 78). The propagation stage of the polymerization involves repeated formation of a palladium-olefin complex and insertion of the olefin into the palladium-carbon  $\sigma$  bond (eq 79). The polymerization is terminated by decomposition



of the palladium-carbon  $\sigma$  bond to give palladium metal.

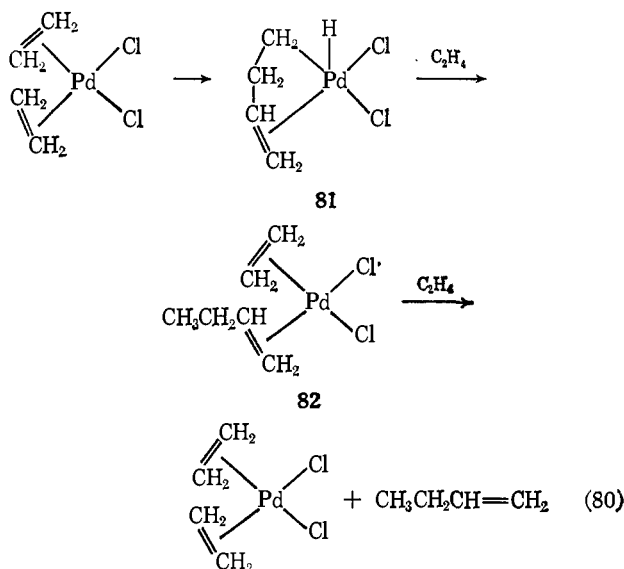
Since olefins such as 1,1-diphenylethylene and 2-phenylpropene can be polymerized, the hydrogen abstraction must occur from the terminal carbon atom, which excludes the possibility of a  $\pi$ -allyl-palladium complex being an intermediate.<sup>573</sup> The difference in the palladium-palladium bond lengths is probably responsible for the fact that vinyl acetate is dimerized in the presence of palladium(II) acetate but oxidized to acetaldehyde and acetic anhydride by PdCl<sub>2</sub> in the presence of cupric acetate.<sup>572</sup> In the  $\pi$ -allylpalladium(II) complexes the distances between the palladium atoms that could promote dimerization are 7.7 Å for the chloride and 2.9 Å for the acetate.<sup>572</sup> The dimerization of olefins in the presence of palladium(II) acetate probably involves a binuclear  $\pi$ -olefin palladium(II) acetate complex 80.<sup>572,573</sup> The approach of a nucleophilic acetate ion, which may be inter- or intramolecular, to one of the olefin molecules facilitates the abstraction of a hydride ion by palladium. This hydride ion is then oxidized to a proton and released while the two electrons gained by the palladium atom are transferred to the olefin to give a vinylic carbanion.<sup>573</sup> This vinylic carbanion, which is held very close to the olefin coordinated to the other palladium

(574) G. Calvin and G. E. Coates, *J. Chem. Soc.*, 2008 (1960).



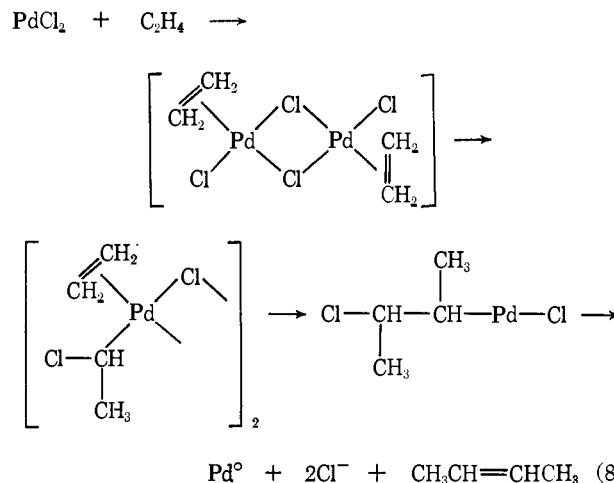
atom can then attack the other olefin by an intramolecular nucleophilic mechanism similar to that already discussed for the acetylation of olefins (eq 29).

A mechanism involving the initial formation of *cis*-[PdCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] has been suggested to account for the PdCl<sub>2</sub>-catalyzed dimerization of ethylene (eq 80).<sup>568</sup> 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).<sup>120</sup> Although *cis*-[PdCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] 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*-[PtCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>],<sup>575</sup> and *cis* complexes of palladium(II) containing chelating diolefins are known.<sup>219</sup> The complex *trans*-[PdCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>], which would be expected to be formed before the *cis* complex,<sup>575</sup> was in fact isolated from the reaction mixture and shown to be stable up to -40°. <sup>568</sup>

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 [PdCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] (eq 81).<sup>307</sup> 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.<sup>576</sup> The degree of polymerization, which depends on the solvent, decreases as the temperature increases.<sup>577</sup> On treating acetylene with PdCl<sub>2</sub> the principle product is *trans*-polyacetylene although a number of side products including benzene are formed.<sup>578</sup> The only report of a platinum-catalyzed polymerization involved the use of PtCl<sub>4</sub> in the presence of a hydridic reducing agent.<sup>579</sup>

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,<sup>580</sup> no platinum complexes have been described. The first palladium complex was prepared by the reaction of PdCl<sub>2</sub> and diphenylacetylene in ethanol to give hexaphenylbenzene and the dimeric complex [PdCl{C<sub>6</sub>H<sub>4</sub>(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>. This complex reacts with hydrochloric acid to give [PdCl<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>].<sup>581,582</sup> The intermediate dimer [PdCl{C<sub>6</sub>H<sub>4</sub>(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub> can be prepared in better yields by the action of diphenylacetylene on [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] in ethanol-chloroform<sup>583-586</sup> or from Na<sub>2</sub>PdCl<sub>4</sub> and diphenylacetylene in

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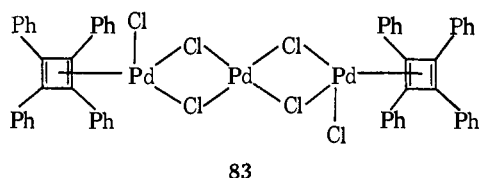
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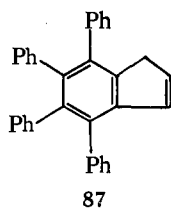
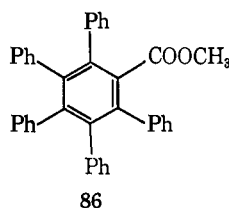
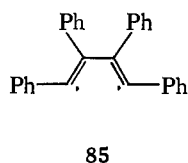
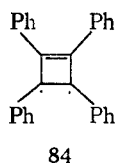
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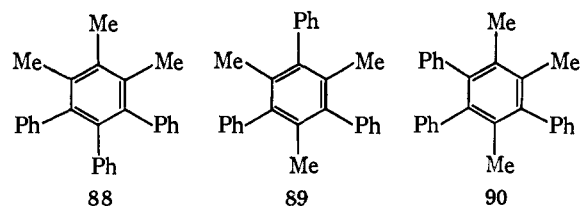
aqueous ethanol.<sup>587</sup> This intermediate exists in two isomeric forms, one of which was originally thought to contain a palladium-carbon  $\sigma$  bond and a palladium-olefin  $\pi$  bond, and the other was thought to be a  $\pi$ -cyclobutenyl complex.<sup>584,588</sup> An X-ray structure determination has shown that both isomers are  $\pi$ -allyl complexes, one of which has the ethoxy group in an *endo* position with respect to palladium and the other in an *exo* position.<sup>589,590</sup> In a 3:1 chloroform-ethanol solvent  $[\text{PdCl}_2(\text{PhCN})_2]$  reacts with diphenylacetylene to give  $[(\text{PdCl}_2)_3(\text{C}_6\text{Ph}_4)_2]$ ,<sup>585</sup> whereas in benzene polymeric  $[(\text{C}_6\text{Ph}_4)\text{PdCl}_2(\text{PdCl}_2)_n\text{PdCl}_2(\text{C}_6\text{Ph}_4)]$  is formed.<sup>586</sup> The spectroscopic data indicate that these complexes have structure **83**. These complexes react with hydrochloric acid to give  $[\text{PdCl}_2(\text{C}_6\text{Ph}_4)]$ .



$[\text{PdCl}_2(\text{C}_6\text{Ph}_4)]$  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.<sup>584</sup> It reacts with phosphines in boiling benzene in the absence of air to give octaphenylcyclooctatetraene and  $[\text{PdCl}_2(\text{PR}_3)_2]$ .<sup>586,591</sup> During the reaction a green intermediate, which is probably either **84** or **85**, is formed.<sup>582,592</sup> Treatment of  $[\text{PdCl}_2(\text{C}_6\text{Ph}_4)]$  in the absence of air with methyl phenylacetylene-carboxylate and cyclopentadiene gives **86** and **87**, respec-



tively.<sup>582</sup> When  $[\text{PdCl}_2(\text{C}_6\text{Ph}_4)]$  is treated with phosphines or pyridine in the presence of air, tetraphenylfuran is formed.<sup>582,585</sup> The formation of hexaphenylbenzene during the preparation of  $[\text{PdCl}_2(\text{C}_6\text{Ph}_4)]$  probably occurs as a result of the addition of one of the diradicals **84** or **85** to unreacted diphenylacetylene,<sup>444,581,593</sup> although the formation of **88** as well as **89** and **90** during the trimerization of methylphenylacetylene in the presence of  $\text{PdCl}_2$  indicates that the reaction may well



be more complex.<sup>576</sup> The dimer  $[\text{PdCl}_2(\text{C}_6\text{Ph}_4)]_2$  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.<sup>594</sup>

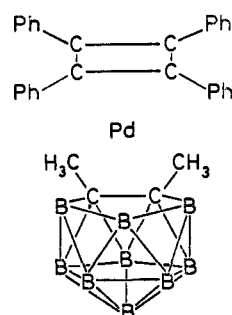
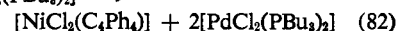
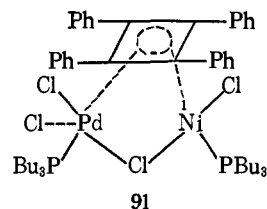


Figure 15. Structure of  $[\text{Pd}(\pi\text{-}(\text{C}_6\text{H}_5)_4\text{C}_4)(\pi\text{-B}_9\text{C}_2\text{H}_{11}(\text{CH}_3)_2)]$  (from ref 594).

Tetraphenylcyclobutadiene complexes of molybdenum,<sup>595,596</sup> tungsten,<sup>596</sup> iron,<sup>597</sup> cobalt,<sup>597-599</sup> and nickel<sup>597,600</sup> have been prepared by ligand exchange with the palladium(II) complex.<sup>601</sup> The formation of the nickel complex by eq 82 has been studied in some detail.<sup>600</sup> The first step involves dissociation of one molecule of phosphine from the nickel  $[\text{PdCl}_2(\text{C}_6\text{Ph}_4)]_2 + 2[\text{NiCl}_2(\text{PBu}_3)_2] \rightarrow$



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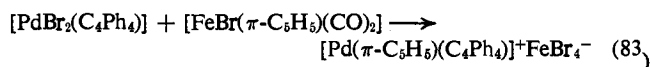
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since in the presence of dienophiles no tetraphenylcyclobutadiene-dienophile adducts were detected.

Although  $\pi$ -cyclopentadienylcobalt complexes react with  $[\text{PdCl}_2(\text{C}_6\text{H}_4)]$  to give the expected complex  $[\text{Co}(\pi\text{-C}_5\text{H}_5)(\text{C}_6\text{H}_4)]$ ,<sup>597,602</sup> with  $\pi$ -cyclopentadienyliron complexes transfer of cyclopentadiene from iron to palladium is observed (eq 83).<sup>603-605</sup> 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.<sup>605</sup>

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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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