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CATALYSIS BY PALLADIUM SALTS

II. THE PREPARATION AND PROPERTIES OF SOME OLEFIN COMPLEXES OF PALLADIUM(II)

G. F. PREGAGLIA, F. CONTI and B. MINASSO*
Montecatini Edison S.p.A., Centro di Ricerche Bollate, via S. Pietro 50, 20021 Bollate, Milan (Italy)
R. UGO
Istituto di Chimica Generale ed Inorganica e Centro C.N.R. via Venezian 21, 20133 Milan (Italy)

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SUMMARY

Some geometric isomers of the complexes $[PdCl_2(olefin)]_2$ (in which the olefin is ethylene, 1-pentene, *cis*-2-, or *trans*-2-pentene) have been isolated, and characterized in the solid state by IR spectroscopy.

The equilibrium constants in chloroform solution of the complexes of various isomeric n-pentenes have been determined, and the nature of the palladium–olefin bonding investigated by IR and NMR spectroscopy.

INTRODUCTION

In the last ten years a large amount of work has been carried out on different aspects of olefin catalysis by palladium(II) complexes[1-5]. Many related mechanisms have been proposed to explain the features of some catalytic reactions such as double bond migration, dimerization, dehydrodimerization, oxidation, carbonylation, etc. In all the mechanisms a π-olefin complex of palladium(II) is generally considered to be involved in the first step of the catalytic process. However, the fact that many different geometric isomers of square planar palladium–olefin complexes can be formed in solution has never been taken seriously into account.

The olefin–Pd^{II} salt system is more complex than was first supposed. Although it is well established that the most stable species in organic solutions is the dimer $[PdX_2(olefin)]_2$, a certain amount of the monomer $PdX_2(olefin)_2$ could, in fact, be present when excess olefin is used as in a catalytic reaction. Not only is there the analogy with Pt^{II} (for which the corresponding monomeric complexes can be easily obtained)[6], but also the probable existence of these monomeric species has been suggested by Ketley and co-workers[7,8] and other authors[6], especially in connection with investigations of ethylene dimerisation by palladium(II) chloride. It is important to note that the monomeric species can exist in both *cis* and *trans* isomers.

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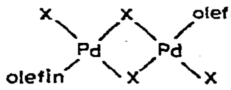
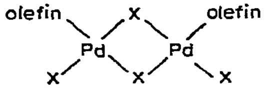
* Now with 3M Italia, 17016 Ferrania (Savona).

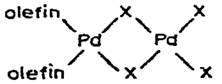
In the case of dimeric species three different geometries (I)–(III) must be considered; these different isomers are denoted:



(I)



(II)



(III)

Moreover, in the case of olefins higher than propylene, the position as well as the geometry of the double bond is involved. It follows that in a reaction such as olefin isomerization the complexity of the mixture of isomeric Pd^{II} complexes can be very great[9,10]. There is no reason in fact, to believe *a priori* that any one of the isomers is more stable than all the others, although, because of the rather high kinetic lability of Pd^{II} complexes, it is possible that only a few of the possible complexes are present in detectable amounts in solution or can be isolated in the solid state. In order to provide greater knowledge of the existence and stability of some of these isomers, we have carefully investigated the nature of the complexes formed when an olefin reacts with palladium(II) chloride.

RESULTS

Synthesis and characterisation of π-olefin complexes of palladium(II)

In order to avoid problems connected with double bond position and geometry in the olefinic moiety we initially studied the ethylene complexes. Only one dimeric ethylene complex, known as the Kharasch complex[11], has been reported. The structure of this complex has been resolved by X-ray crystallography[12], and corresponds to structure(I). A very unstable monomeric species, which probably has a *cis* geometry, has also been described[6].

We have confirmed that the Kharasch complex is the only one which can be isolated from the reaction of ethylene with the benzonitrile palladium complex in chloroform solution, or with a suspension of $PdCl_2$ in chloroform. However, a different compound, analysing as $[PdCl_2(C_2H_4)]_2$, is obtained when ethylene is bubbled through a chloroform or benzene solution of the isomeric mixture of *cis*-2-pentene palladium(II) complexes (see later). This new compound, which is slightly soluble in chloroform or benzene, showed an X-ray powder pattern and an infrared spectrum rather different from those of the Kharasch complex. The differences, which were more apparent in the infrared spectrum, were too large to be ascribed to different crystalline forms of the same complex (see Table 1), and a possible molecular structure of this new isomeric olefin complex was inferred from the infrared absorptions in the Pd–Cl stretching region[13].

In this region, a different pattern of Pd–Cl bands is to be expected for the (I)–(III) isomers, which each have different symmetries. The new material is thought to be very probably the (III) isomer on the basis of the two terminal stretching fre-

TABLE 1

INFRARED AND RAMAN (cm^{-1}) SPECTRA IN NUJOL

Compound	*Isomer*	*ν(C=C)*	*ν(M–Cl)*	*ν(M–Cl)bridge*	*ν(M–C)*	*Other bands*
$[PdCl_2(C_2H_4)]_2$	(I)	1525	357	306, 271	425	1028(sh), 1021
			360 (Raman)	300, 295 (Raman)		
$[PdCl_2(C_2H_4)]_2$	(III)	1520, 1515	361, 352	306, 279	415	1026(sh), 1020, 1007(sh), 1004
			362, 357, 353(sh) (Raman)	306, 265 (Raman)		1268 (Raman)
$[RhCl(C_2H_4)_2]_2$		1516, 1502		273, 259, 250		1231, 1228, 1216, 995, 830
$[PdCl_2($*cis*$\text{-}2\text{-}C_5H_{10})]_2$	(I)	1517	355	305, 276	395	925, 868, 834, 760
			355[a]	298, 283[a]		
$[PdCl_2($*cis*$\text{-}2\text{-}C_5H_{10})]_2$	(II)	1518	354	300, 277	397	1065, 1035, 985, 917, 845
$[PdCl_2($*cis*$\text{-}2\text{-}C_5H_{10})]_2$	(III)	1515	353, 346	288, 255	396	920, 855, 845, 832, 750
$[PdCl_2(1\text{-}C_5H_{10})]_2$	(I)	1518	355[b]	300, 283[b]		998, 925, 936, 760[b]
$[PdCl_2(1\text{-}C_5H_{10})]_2$	(III)	1507	356, 343(sh)	302, 280	425, 437	1003, 992
$[PdCl_2($*trans*$\text{-}2\text{-}C_5H_{10})]_2$	(III)	1530	355, 340	303, 274	442, 406	1020, 1000, 938, 888, 864, 764
		1535, 1530[c]	355, 345[c]	296, 284[c]		

[a] In benzene. [b] Liquid. [c] In tetrachloroethane.

quencies (Table 1) which are observed in both the infrared and Raman spectra in accord with the point group symmetry C_{2v}. In the case of the (I) isomer the two terminal Pd–Cl stretching frequencies should be nearly coincident, as the coupling between the two terminal Pd–Cl bonds is probably very low; this expectation is indirectly supported by the presence of coincident terminal Pd–Cl absorptions in both the infrared and Raman spectra of the (I) isomer, despite the C_{2h} point group symmetry. Finally, the coupling through the bridging palladium system is negligible. In the new complex the separation of the two terminal Pd–Cl stretching frequencies is rather high (9 cm^{-1}) and in good agreement with that expected for two Pd–Cl terminal bonds in a *cis* position. The spectra of the two isomers of the ethylene complex in the Pd–Cl stretching region are shown in Fig. 1.

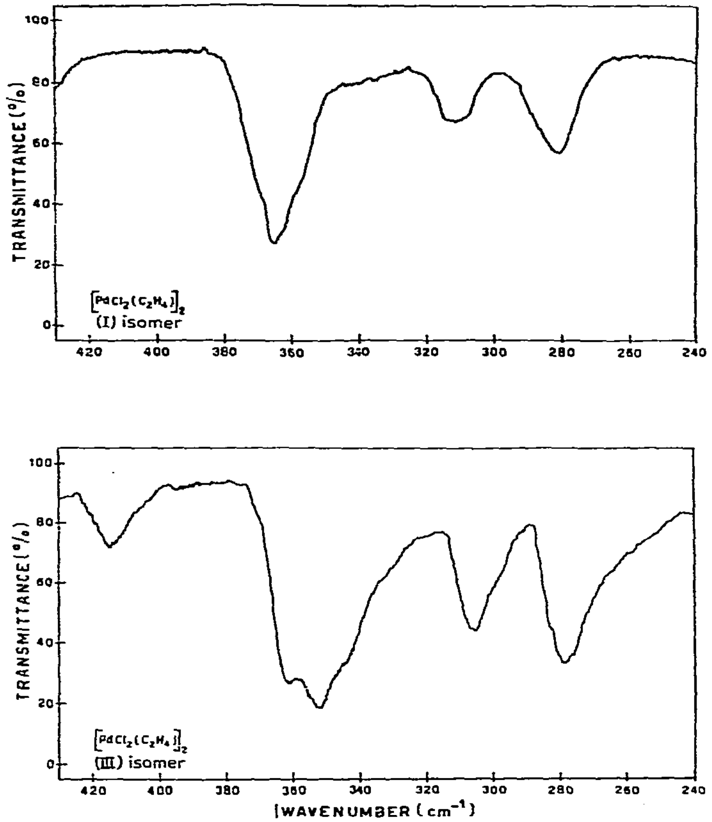


Fig. 1. IR spectra in the 420–240 cm^{-1} region of Nujol mulls of (I) and (III) isomers of the ethylene complex.

The probable (III) structure of the new isomer is confirmed by other infrared evidence. The two doublets (1515–1520 cm^{-1} and 1020–1026 cm^{-1}) can be ascribed to the relative *cis* position of the two ethylene molecules. It is these doublets which make the infrared spectrum of this compound so different from that of the Kharasch complex (Fig. 2); the infrared spectrum of the rhodium complex $[RhCl(C_2H_4)_2]_2$[14], where two ethylene molecules are in a *cis* position, shows a very similar pattern of doublets. Interestingly, isolation of the (III) isomer of the palladium ethylene complex

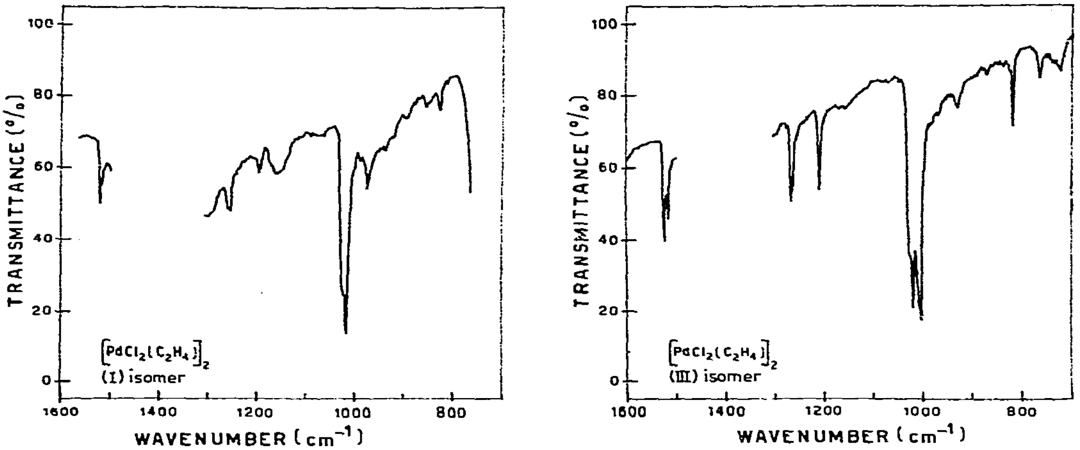


Fig. 2. IR spectra in the 1600–200 cm^{-1} region of Nujol mulls of (I) and (III) isomers of the ethylene complex.

has been achieved only when the *cis*-2-pentene palladium complex was used as starting material. Palladium complexes with different olefins, such as *trans*-2-pentene, *cis*-2-butene or *trans*-2-butene, gave only the (I) isomer.

The (III) isomer is relatively stable in the solid state under an atmosphere of ethylene but it changes slowly at room temperature into a mixture of $PdCl_2$ and π-butene complexes (in which the *cis*-2-butene species is prevalent). The presence of traces of chloroform seems to be necessary for this transformation. The benzene suspension of the compound is not stable indefinitely, for the portion which goes into solution changes very quickly into the (I) isomer. This fast isomerization in solution is not peculiar to ethylene complexes but, as we shall see later, is typical of all the olefin palladium(II) complexes that we have investigated. In this case we failed to reverse the isomerization, *i.e.* (I)→(III).

We have also studied the complexes which can be formed with higher olefins during the isomerisations catalysed by palladium(II) salts. In some previous studies[9] it was established that the rate of double bond isomerisation in *cis*-2-pentene was low enough to be ignored at room temperature and under our standard conditions of synthesis (see Experimental). From this olefin we have isolated three different crystalline compounds of formula $[PdCl_2(C_5H_{10})]_2$ using different methods of synthesis (Table 2). The (III) isomer [characterized by its infrared spectrum in the Pd–Cl stretching region (Table 1)] is the major product formed by the direct interaction of $PdCl_2$ and the olefin in the absence of solvent. Sometimes it is contaminated by small amounts of the (I) isomer (see later). In the presence of a solvent, such as chloroform, two different materials are obtained, one soluble and the other insoluble. The insoluble product is the (III) form isomer, while the soluble product is probably the (I) isomer. The last compound can usually also be obtained by treating either (I) or (III) isomers of the ethylene complex with excess *cis*-2-pentene. However, particularly when the reaction time is long enough, the (I) isomer is always contaminated by the (III) isomer, and sometimes only the (III) isomer is obtained. This is to be expected, because the (I)⇌(III) equilibrium is affected by the different solid state stability of the two forms. Generally the (III) form is the only one obtained by slow formation of

TABLE 2

SUMMARY OF METHODS OF PREPARATION OF PENTENE COMPLEXES

Olefin	*Isomer*	*Method of preparation*
cis-2-Pentene	(I)	(*i*), $PdCl_2$ + *cis*-2-C_5H_{10} + solvent (soluble fraction)
		(*ii*), (I) or (III) $[PdCl_2(C_2H_4)]_2$ + *cis*-2-C_5H_{10} + solvent
cis-2-Pentene	(II)	$[PdCl_2(1\text{-}C_5H_{10})]_2$ + *cis*-2-C_5H_{10} (without solvent)
cis-2-Pentene	(III)	(*i*), $PdCl_2$ + *cis*-2-C_5H_{10} (without solvent)
		(*ii*), $PdCl_2$ + *cis*-2-C_5H_{10} + solvent (insoluble fraction)
trans-2-Pentene	(I)	(III) $[PdCl_2$(*trans*-2-$C_5H_{10})]_2$ quickly isomerizing in solution to (I) isomer
trans-2-Pentene	(III)	(*i*), $PdCl_2$ + *trans*-2-C_5H_{10} (without solvent)
		(*ii*), (I) or (III) $[PdCl_2(C_2H_4)]_2$ + *trans*-2-C_5H_{10} (without solvent)
1-Pentene	(I)	(III) $[PdCl_2(1\text{-}C_5H_{10})]_2$ isomerizing at −78° in $CHCl_3$ to (I) isomer
1-Pentene	(III)	(*i*), $PdCl_2 + 1\text{-}C_5H_{10}$ at 0° (low conversion, without solvent)
		(*ii*), (I) or (III) $[PdCl_2(C_2H_4)]_2 + 1\text{-}C_5H_{10}$ at 0° (without solvent)

the crystals as, for instance, by slow evaporation of a chloroform solution of either the (I) or the (III) form.

A third crystalline material has been obtained by treating with *cis*-2-pentene, in the absence of solvent, the reaction mixture consisting of 1-pentene complexes of formula $[PdCl_2(1\text{-}C_5H_{10})]_2$. This compound shows infrared and X-ray powder spectra different from those of the other two materials. Structure (II) can be proposed in accordance with the infrared spectrum in the Pd–Cl stretching region (Table 1), but a different crystalline form of the (I) isomer cannot be completely ruled out.

The rather easy rearrangement of olefin–palladium complexes from one isomeric form to another seems to be due to the easy dissociation of the complexed olefins. Such dissociation has been confirmed by several experimental observations; for example, when the (III) *cis*-2-pentene complex is dissolved in chloroform or benzene without addition of any excess of the olefin, a palladium chloride adduct of formula $[PdCl_2$(*cis*-2-$C_5H_{10})]_2PdCl_2$ is recovered from the solution in a quantity corresponding to 20% of the palladium chloride. Such adducts are rather common in palladium(II) chemistry, they can, for example, be obtained with π-allylic ligands[15]. The formation of the adduct can be explained only by a dissociation of the complexes; the adduct cannot be obtained in the presence of even a slight excess of free olefin. Partial dissociation is also confirmed by the low molecular weight found in chloroform or benzene for the (III) isomer.

Many other difficulties were found in trying to isolate pure π-complexes of *trans*-2-pentene or 1-pentene, in fact these two olefins, largely isomerize during the synthesis of palladium chloride complexes at room temperature. In the case of *trans*-2-pentene, a yellow insoluble material is obtained by direct interaction of $PdCl_2$ with the liquid olefin in the absence of solvent; the (III) structure can be assigned to this compound from the number of terminal Pd–Cl stretching frequencies (Table 1). The same compound was obtained by interaction of ethylene complexes [either (I) or (III) isomer] with *trans*-2-pentene in the absence of solvent. Strangely enough, the (I) isomer of this olefin was never isolated in a pure form, although it should, by analogy with the *cis*-2-pentene complexes, be present as the major constituent in solutions in organic solvents. In a freshly prepared chloroform solution of the (III) isomer at 30°, it is still possible to detect a doublet at 1534–1530 cm^{-1} which probably corresponds to the (III) isomer. Subsequently a rather fast double bond migration takes place, and a complex of *cis*-2-pentene, in the (I) form, appears.

The isolation and characterisation of the 1-pentene complexes is particularly difficult because of the very fast double bond isomerisation of 1-pentene to 2-pentene. For instance, from the direct reaction of $PdCl_2$ with 1-pentene at 0°, a π-palladium complex of 1-pentene, containing $PdCl_2$ as impurity, was obtained only when the palladium chloride conversion was low. The insoluble yellow compound obtained after total conversion was mainly the (III) form of the *cis*-2-pentene complex. The synthesis of a pure 1-pentene complex was achieved by treating the (I) or (III) isomer of the ethylene complex with 1-pentene at 0°, in the absence of solvent; a light yellow compound melting at around 54° was obtained in this way. Structure (III) can be assigned from the two terminal Pd–Cl stretchings (see Table 1). From a chloroform solution of this complex at −78° in the presence of free 1-pentene, a different compound can be isolated by addition of n-pentane. This low melting compound (~14°) can also be obtained by addition of 1-pentene to chloroform solutions of the (III) or (I) isomers of the *cis*-2-pentene complexes. The characterisation of this isomer by IR spectroscopy is not straight forward because the coordinated 1-pentene is isomerised by the infrared radiation. However, the presence of a broad terminal Pd–Cl stretching frequency agrees with either of structures (I) and (II). Structure (I) is more likely, as this isomer has already been reported to be the more stable in solution.

We were unable to isolate any monomeric palladium complex even when using a great excess of olefin. However, we have some indirect infrared evidence which shows that monomeric species are probably formed in a detectable amount at low temperatures. The infrared spectrum of the (III) or (I) isomer containing *cis*-2-pentene, dissolved in the free olefin, shows the disappearance of the bridging Pd–Cl stretching frequencies on lowering the temperature to −100° (Fig. 3). Obviously these monomeric complexes cannot be isolated pure because of their instability, but they can be present in small amounts, even at room temperature, when a large excess of olefin is used.

Infrared and NMR spectra

The significant infrared and Raman absorptions for all the compounds isola-

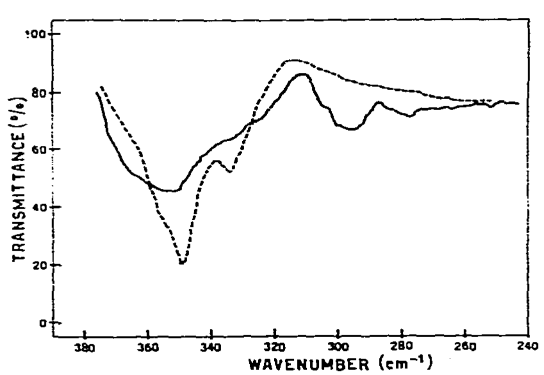


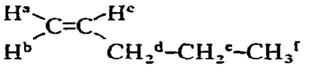
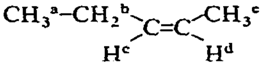
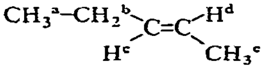
Fig. 3. IR spectra in the 400–240 cm^{-1} region of (III) isomer $[PdCl_2(cis\text{-}2\text{-}C_5H_{10})]_2$ in $1\text{-}C_5H_{10}$ at −40° (----) and at room temperature (—).

ted in the solid state are listed in Table 1. Some comment should be made on the position and Raman intensities of the absorptions in the region 1450–1550 cm^{-1} which are commonly attributed to $\nu(C{=}C)$. As already reported by other authors[16], these absorptions are very weak in the Raman spectra, although they are rather intense in the infrared spectra. The assignment of these IR absorptions is the subject of some disagreement between different authors; in fact Hiraishi[17] suggested, on the basis of the Raman intensities, that the absorptions in the 1500 cm^{-1} region are principally due to $>CH_2$ scissoring while the strong Raman absorption at around 1250 cm^{-1} must be attributed to $\nu(C{=}C)$. We have observed the presence of absorption bands at around 1550 cm^{-1} in some of our complexes in which the $>CH_2$ group is absent. However, this is not an argument against Hiraishi's assignment of the absorption at around 1500 cm^{-1} to a C–H deformation, because such an absorption is present in the spectra of both ethylene and butene oxides. The C=C stretching and the C–H in plane deformations are of the same symmetry, so it is probable that the two absorptions at around 1500 and 1250 cm^{-1} are mixed bands, into which the latter component introduces a high polarisability.

Another interesting point is related to the fact that the (I), (II), and (III) isomers have rather different patterns of absorption in the region of the out-of-plane deformation of ethylenic hydrogens. These bands are usually influenced by small conformational changes, which can be expected in our several isomers.

TABLE 3

^1H NMR SPECTRA

Olefin	$\delta_{free}{}^{a}$	$\delta_{coordinated}{}^{c}$
	a,b: 4.90 (m) c: 5.72 (m) d: 2.00 (m) e: 1.42 (m) f: 0.90 (t) (J 15 Hz)	a,b: 5.21 (q), 4.97 (q) (J_{ab} 2.1, J_{ac} 8.2, J_{bc} 15 Hz) c: 6.32 d,e: 1.97 (m, broad) f: 1.07 (t) (J 14 Hz)
	a: 0.90 (t) (J 15 Hz) b: 1.53 (d) (J 5 Hz) c,d: 5.28 (m) e: 1.95 (m)	a: 1.38 (t) (J 15 Hz) b: 1.66 (d) (J 5 Hz) c,d: 6.16 (m) e: 2.00 (m)
	a: 0.94 (t) (J 15 Hz) b: 1.62 (m) c,d: 5.41 (m) e: 1.97 (m)	a: 1.48 (t) ($J \simeq 15$ Hz) b: 1.82 (m) c,d: 5.85 (m, broad) e: 1.98 (m, broad)

[a] In $CDCl_3$.

The NMR data are reported in Table 3. Two features are apparent: (*a*), the resonances of the olefinic protons shift slightly to low field, as in silver complexes, and in contrast to the behaviour of similar platinum complexes[18]; (*b*), the signal of the methyl group bound to the double bond does not shift, whilst those from the methyl groups bound to the aliphatic chain shift slightly to low field. The latter effect could be associated with some non-bonding interaction with the metal[19].

Equilibrium studies

It is well known from the chemistry of silver–[20], mercury–[21] and platinum–olefin complexes[5] that there is quite a large difference between the stability constants of 1- and 2-olefin complexes and also between those of *cis*- and *trans*-olefin complexes. It is thus probable that 1-pentene and *cis*- and *trans*-2-pentene are bound to palladium with different strengths. In order to provide better knowledge of the palladium complexes which can be formed from a mixture of isomeric pentenes and of the relative amounts of different pentenes bound the palladium under catalytic conditions, we have determined the equilibrium constants for the exchange reaction between a π-complex and free olefin, where the olefins are all the isomers of pentene. All the equilibria must probably be referred to the (I) isomers of palladium complexes, which are the most stable in organic solvents, as already indicated.

The following equilibria were studied:

$$[\mathrm{PdCl_2}(\textit{trans}\text{-}2\text{-}\mathrm{C_5H_{10}})]_2 + 2\ \textit{cis}\text{-}2\text{-}\mathrm{C_5H_{10}} \overset{K_1}{\rightleftarrows} [\mathrm{PdCl_2}(\textit{cis}\text{-}2\text{-}\mathrm{C_5H_{10}})]_2 + 2\ \textit{trans}\text{-}2\text{-}\mathrm{C_4H_{10}}$$

$$[\mathrm{PdCl_2}(1\text{-}\mathrm{C_5H_{10}})]_2 + 2\ \textit{cis}\text{-}2\text{-}\mathrm{C_5H_{10}} \overset{K_2}{\rightleftarrows} [\mathrm{PdCl_2}(\textit{cis}\text{-}2\text{-}\mathrm{C_5H_{10}})]_2 + 2\ 1\text{-}\mathrm{C_5H_{10}}$$

$$[\mathrm{PdCl_2}(\textit{trans}\text{-}2\text{-}\mathrm{C_5H_{10}})]_2 + 2\ 1\text{-}\mathrm{C_5H_{10}} \overset{K_3}{\rightleftarrows} [\mathrm{PdCl_2}(1\text{-}\mathrm{C_5H_{10}})]_2 + 2\textit{trans}\text{-}2\text{-}\mathrm{C_5H_{10}}$$

Two different methods were used (for details see the Experimental section).

(*i*). Nearly quantitative precipitation of the palladium complexes from solution by 20-fold dilution with cooled n-pentane, and analysis of the coordinated olefins displaced with 1,5-cyclooctadiene.

(*ii*). Direct analysis of the solutions, at different temperatures, by infrared spectroscopy in the double bond stretching region.

We first investigated equilibrium 1 by this second method. This equilibrium was only studied from room temperature to −20°, and in this range the equilibrium constants (Table 4) follow the Van t'Hoff equation with a very small ΔH (ca. −2.7 kcal/mole). Below −20° the Van t'Hoff equation is not satisfied and a new ab-

TABLE 4

VALUES OF K_1 AT VARIOUS TEMPERATURES (METHOD *i*)[a]

T(°*C*)	*Compn. of coordinated olefin* (%)			K_1
	1-C_5H_{10}	*trans*-2-C_5H_{10}	*cis*-2-C_5H_{10}	
−17		42.9	57.1	13.0
−30	Traces	43.9	56.1	12.9
−50	Traces	40.8	59.2	15.8
−78		36.6	63.4	19.5
−78[b]		41.5	58.5	21.1

[a] (III) $[\mathrm{PdCl_2}(\textit{cis}\text{-}2\text{-}\mathrm{C_5H_{10}})]_2$ (2.0 mmoles). *trans*-2-$\mathrm{C_5H_{10}}$ (9.3 mmoles); $\mathrm{CHCl_3}$ (2.5 ml). [b] *Trans*-2-$\mathrm{C_5H_{10}}$ (13.9 mmoles) the other concentrations being constant.

TABLE 5

DETERMINATION OF K_2 AT −78° (METHOD *i*)[a]

Complex (mmole)	*Olefin (mmole)*	*Compn. of coordinated olefin (%)*			K_2
		$1\text{-}C_5H_{10}$	*trans*-$2\text{-}C_5H_{10}$	*cis*-$2\text{-}C_5H_{10}$	
2.0	4.6	38.9	1.7	59.4	6.5
2.0	8.7	55.1	Traces	44.9	5.7
2.0	8.7	60.3	Traces	39.7	4.3
2.9[b]	0.88	61.1	Traces	38.9	8.0

[a] In $CHCl_3$ (2.5 ml). [b] Addition of *cis*-$2\text{-}C_5H_{10}$ to (I) $[PdCl_2(1\text{-}C_5H_{10})]_2$.

TABLE 6

K_1 VALUES OBTAINED BY PRECIPITATION, (*i*), AND BY INFRARED ANALYSIS, (*ii*)

T(°C)	*Method (i)*	*Method (ii)*
−6		10.9
−17	13.0	13.8
−24		13.6
−30	12.8	15.1
−37		15.9
−49	15.8	18.3
−53		18.3
−78	19.5; 21.1	

sorption appears at 1545 cm^{-1}, which is probably due to a monomeric species. This new absorption disappears on raising the temperature, and the spectrum returns to the original pattern. It was impossible to obtain K_2 and K_3 by this method, because the absorptions were insufficiently separated.

The precipitation method was used to obtain K_2; the values are subject to a certain error, as is evident from Table 5. The average value at −78° is 6.1. The accuracy could be affected by incomplete precipitation of the palladium complexes or by the change in the molar ratio of the different complexes during the precipitation. The accuracy was checked by comparing K_1 values obtained by both infrared and precipitation methods. The good agreement found (Table 6) gives some indication of the reliability of the K_2 values obtained by the precipitation method. Because of the isomerisation of 1-pentene, it was impossible to obtain a value for K_3 directly. Its value at −78°, derived, as the ratio of K_1 to K_2; is 3.3.

Consequently, the order of the stability for the different complexes in the presence of olefin is: *cis*-2-pentene > 1 pentene > *trans*-2-pentene, in agreement with the stabilities reported for silver complexes[20].

CONCLUSION

This investigation shows that palladium–olefin complexes can exist in many different isomeric forms, which have different stabilities in solution. Our results suggest that the less stable isomers can exist in solution in low concentration, and they can, in fact, be isolated in the solid state. These less stable species could be the operative catalytic complexes when special steric and electronic requirements makes them the only effective catalytic entities while the other isomers are inactive. This suggestion, which has already been made by others to explain aspects of catalytic reactions[7], requires additional investigation.

Our results on the composition of free and complexed olefins in the presence of palladium salts have confirmed features which until now could be suggested only by analogy with the corresponding silver complexes, and which are of importance in explaining aspects of selective palladium catalysis, such as stereoselective isomerisation[10,12].

EXPERIMENTAL

All the elementary and the chromatographic analyses were carried out in the Analytical Laboratory of Montecatini–Edison, Research Centre of Bollate (Milan). Nuclear magnetic resonance spectra were recorded with a Varian 100 spectrometer, infrared spectra with a Perkin–Elmer 225 spectrometer and X-ray powder patterns with a Philips diffractometer.

$PdCl_2$ was obtained from C. Erba; 1-pentene (purity 95%) and *cis*-2-pentene (purity 95%) were obtained from Schuchardt, and *trans*-2-pentene (purity 99%) was obtained from Fluka. 1,3-diethylene-2,4-dichloro-μ-dichlorodipalladium(II), (I), was prepared as described by Kharasch[11]. All the olefins were freed from peroxides and distilled under nitrogen before use.

Preparation of π-complexes

1,4-diethylene-2,3-dichloro-μ-dichlorodipalladium(II), (III)-isomer

Two grams of (III) or (I) $[PdCl_2(cis\text{-}2\text{-}C_5H_{10})]_2$ (see below), were dissolved in 20 ml of pure chloroform. A stream of ethylene (15 l/min) was passed through the solution, and after traces of insoluble material had been filtered off, the solvent was evaporated in about 50 min (the temperature dropped from 24° to 15°). The brown-red residue was washed twice with small amounts of n-pentane, and the solid (1.4 g) was rapidly dried under vacuum. Similar results were obtained using benzene as a solvent. (Found: C, 11.0; H, 1.9; Cl, 34.4. $C_2H_4Cl_2Pd$ calcd.: C, 11.7; H, 1.9; Cl, 34.6%.)

1,3-di-cis-2-pentene-2,4-dichloro-μ-dichlorodipalladium(II), (I)-isomer

(*a*). One gram of 1,3-diethylene-2,4-dichloro-μ-dichlorodipalladium(II) was suspended at 25° in 5 ml of *cis*-2-C_5H_{10}, and a rapid evolution of ethylene took place. After 5 min the solid was washed with n-pentane and dried under vacuum (1.1 g). (Found: C, 23.6; H, 4.3. $C_5H_{10}Cl_2Pd$ calcd., C: 24.2; H, 4.05%.)

(*b*). Two grams of 1,4-di-*cis*-2-pentene-2,3-dichloro-μ-dichlorodipalladium(II) were dissolved in 20 ml of pure chloroform; 5 ml of *cis*-2-C_5H_{10} was added, and, after traces of insoluble material had been filtered off the solution was cooled to −78° and treated with 100 ml of n-pentane at −78°. The solid which separated at that temperature was washed with pentane, and dried under vacuum (1.7 g). The compound showed the same analysis, the same infrared spectrum, and the same X-ray powder pattern as the compound obtained in (*a*). Both compounds reacted with 1,5-cyclooctadiene to give *cis*-2-C_5H_{10} (purity 98%).

1,4-*di-cis-2-pentene-2,3-dichloro-μ-dichlorodipalladium (II)*, *(III)-isomer*

(*a*). One gram of anhydrous $PdCl_2$ was stirred with 14 g of *cis*-2-C_5H_{10} at 25°. The reaction was practically complete after 4–5 h. The solid obtained was washed with n-pentane and dried under vacuum (quantitative yields). (Found: C, 23.6; H, 4.0; Cl, 28.8. $C_5H_{10}Cl_2Pd$ calcd.: 24.2; H, 4.05; Cl, 28.7%.)

(*b*). Two grams of $PdCl_2$ were stirred at 25° with 2 g of *cis*-2-C_5H_{10} in 10 ml of pure chloroform. After 4 h, 1.7 g of a yellow-orange compound were recovered by filtration. This compound showed the same infrared spectrum and the same X-ray powder pattern as the compound obtained in (*a*). From the solution, after addition at −78° of 60 ml of n-pentane, 0.8 g of a yellow material were obtained. The X-ray powder spectrum showed that this compound was mainly 1,3-di-*cis*-2-C_5H_{10}-2,4-dichloro-μ-dichlorodipalladium(II) with nearly 5% of 1,4-di-*cis*-2-C_5H_{10}-2,3-dichlorodipalladium(II). Both compounds reacted with 1,5-cyclooctadiene to yield *cis*-2-C_5H_{10} (purity >97%).

1 g of 1,4-di-*cis*-2-pentene-2,3-dichloro-μ-dichlorodipalladium(II) was dissolved in pure chloroform at 30°, and 0.15 g of a light brown compound were obtained by adding 35 ml of isopentane after 15 min. The product did not easily dissolve in benzene or chloroform, but dissolved in the presence of a slight excess of *cis*-2-pentene. (Found: C, 18.2; H, 3.3; Cl, 31.0. $C_{10}H_{20}Cl_6Pd_3$ calcd.: C, 17.8; H, 3.0, Cl, 31.5%.)

1,4-*di-trans-2-pentene-2,3-dichloro-μ-dichlorodipalladium(II)*, *(III)-isomer*

One gram of 1,3-diethylene-2,4-dichloro-μ-dichlorodipalladium(II) was suspended with stirring in 3 ml of *trans*-2-C_5H_{10} and 5 ml of *n*-pentane at 25°. After 3 h the yellow-orange solid was filtered off, washed with n-pentane, and dried under vacuum. The coordinated olefin, was shown to be *trans*-2-C_5H_{10} (purity >98%) by displacement with 1,5-cyclooctadiene. (Found: C, 23.3; H, 3.7; Cl, 28.7. $C_5H_{10}Cl_2Pd$ calcd.: C, 24.2; H, 4.05, Cl, 28.7%.)

1,3-*di-1-pentene-2,4-dichloro-μ-dichlorodipalladium(II)*, *(I)-isomer*

Two grams of 1,3-di-*cis*-2-pentene-2,4-dichloro-μ-dichlorodipalladium(II) were dissolved in 10 ml of pure chloroform containing 40 ml of 1-C_5H_{10}. The solution was immediately cooled to −78°, and a yellow compound was precipitated by addition of 50 ml of n-pentane at −78°. The solid was filtered off at −78°, washed three times with 20 ml of n-pentane, and dried in a stream of nitrogen at 0° (yield 1.7 g). The compound melts at ~14°. The coordinated olefin is 1-C_5H_{10} (purity 96%). (Found: $C_5H_{10}/PdCl_2$, 0.95. $C_5H_{10}/PdCl_2$ calcd.: 1.0.)

1,4-*di-1-pentene-2,3-dichloro-μ-dichlorodipalladium(II)*, *(III)-isomer*

(*a*). A suspension of 3 grams of 1,3-diethylene-2,3-dichloro-μ-dichlorodipalladium(II) in 30 ml of 1-C_5H_{10} and 30 ml of iso-pentane was stirred for 2 h at 25°. The mixture was set aside for 16 h at −78°, and the solid obtained was filtered off, washed with n-pentane, and dried under vacuum. The pale yellow compound (m.p. 54°) was soluble in chloroform and in benzene, but from both solutions only 1,3-di-1-

pentene-2,4-dichloro-μ-dichlorodipalladium(II) was recovered. The olefin displaced by 1,5-cyclooctadiene was 1-C_5H_{10} (>96% purity). (Found: C, 23.6; H, 3.5; Cl, 28.5. $C_5H_{10}Cl_2Pd$ Calcd.: C, 24.2; H, 4.05; Cl, 28.7%.)

(*b*). One gram of 1,4-diethylene-2,3-dichloro-μ-dichlorodipalladium(II) was suspended with stirring at 0° in 3 ml of 1-C_5H_{10}. After 45 min the evolution of ethylene ceased, and the solid product was isolated as in (*a*).

Equilibrium studies

(*i*). *Method* 1: *Determination of* K_1 *and* K_2. Two mmoles of (III) $[PdCl_2(cis\text{-}2\text{-}C_5H_{10})]_2$ were dissolved in 2.5 ml of chloroform at 25° in an inert atmosphere. After addition of 1 ml of *trans*-2-C_5H_{10}, the solution was maintained in a thermostat at the desired temperature (±0.1°) for five min. Addition of 20 ml of n-pentane at the same temperature gave an orange precipitate. After 2 h the precipitate (95% for the starting complex) was collected by centrifugation, washed twice with 10 ml of n-pentane, and dried under vacuum. The coordinated olefins in the mixture were displaced by 1,5-cyclooctadiene, and analysed by GLC. The equilibrium composition of the free *trans*- and *cis*-2-C_5H_{10} was obtained from the molar balance. An analogous procedure was used for the determination of K_2. The values of K_1 and K_2 are reported in Table 4 and Table 5, respectively.

(*ii*). *Method* 2: *Determination of* K_1. The IR spectrum was recorded in tetrachloroethane using a low-temperature cell equipped with KRS-5 windows. The absorption coefficients of the bands at 1532 cm^{-1} corresponding to ν(C=C) of $[PdCl_2(trans\text{-}2\text{-}C_5H_{10})]_2$, and at 1518 cm^{-1}, corresponding to ν(C=C) of $[PdCl_2(cis\text{-}2\text{-}C_5H_{10})]_2$, were determined by use of the Beer–Lambert law, which is assumed to be satisfied in the range of temperature studied (from −53° to +41°). The IR spectrum of a tetrachloroethane solution (1.0 ml) containing 0.066 g of (I) $[PdCl_2(cis\text{-}2\text{-}C_5H_{10})]_2$ and 0.25 ml of *trans*-2-C_5H_{10} was recorded in the 1500–1450 cm^{-1} region, and the molar ratios $[PdCl_2(cis\text{-}2\text{-}C_5H_{10})]_2/[PdCl_2(trans\text{-}2\text{-}C_5H_{10})]_2$ were calculated at different temperatures. The proportions of free *cis*- and *trans*-2-C_5H_{10} at each temperature were obtained from the molar balance. 1-C_5H_{10} formed by isomerisation was not detected in the experiment. The values of K_1, reported in Table 6, obtained by the two methods can be compared. The values of K_1 satisfy the Van t'Hoff equation, with a value of $\Delta H = -2.7$ kcal/mole.

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