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CATALYSIS BY PALLADIUM SALTS

VI. AN INVESTIGATION OF STRAIGHT-CHAIN OLEFIN ISOMERIZATION IN APROTIC SOLVENTS*

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Summary

The stoichiometric isomerization of 1-pentene coordinated to palladium(II) chloride has been investigated in aprotic solvents. The action of basic cocatalysts has been discovered. The observed selective formation of *cis*-2-pentene in the stoichiometric process may explain some aspects of the stereoselectivity observed in the first stages of catalytic isomerization.

Introduction

Olefin catalysis by palladium(II) salts has been thoroughly investigated in the last ten years after its succesful industrial application to the oxidation of ethylene to acetaldehyde [1]. A few review articles have been published on homogeneous palladium(II) catalysis [2,3].

Special emphasis has been laid on the reactions involving simple substrates such as ethylene, propylene and butadiene, particularly in the field of oxidative carbonylation [4], dimerisation and co-dimerisation [5,6] and, finally, the synthesis of vinyl derivatives [7,8]. However, much work has also been devoted to higher α-olefins [9,10]. In the latter case, double bond migration takes place as a secondary reaction, which decreases the selectivity with which the required reaction products are obtained. The degree of isomerization depends on the nature of the solvent and olefin and on the reaction conditions.

Many investigations have been carried out by different authors such as

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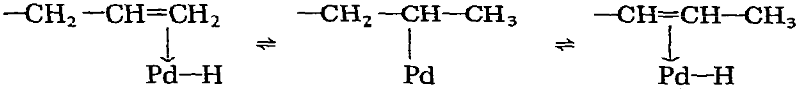
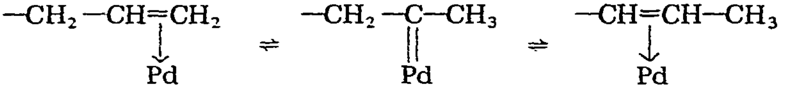
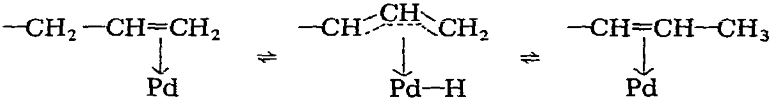
Sparke [11], Harrold and Chalk [12], Davies [13], Cramer [14], Bond [15] and others [16] on the molecular mechanism of olefin isomerization by palladium salts. Four different mechanisms [1 - 4] have been proposed to explain the hydrogen migration in non protic solvents [13].



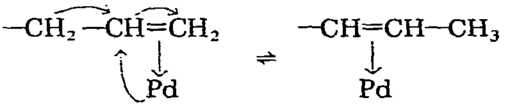
$$\underset{\downarrow\atop \text{Pd—H}}{\text{—CH}_2\text{—CH=CH}_2} \rightleftharpoons \underset{|\atop \text{Pd}}{\text{—CH}_2\text{—CH—CH}_3} \rightleftharpoons \underset{\downarrow\atop \text{Pd—H}}{\text{—CH=CH—CH}_3} \qquad (1)$$



$$\underset{\downarrow\atop \text{Pd}}{\text{—CH}_2\text{—CH=CH}_2} \rightleftharpoons \underset{\|\atop \text{Pd}}{\text{—CH}_2\text{—C—CH}_3} \rightleftharpoons \underset{\downarrow\atop \text{Pd}}{\text{—CH=CH—CH}_3} \qquad (2)$$



$$\underset{\downarrow\atop \text{Pd}}{\text{—CH}_2\text{—CH=CH}_2} \rightleftharpoons \underset{\downarrow\atop \text{Pd—H}}{\text{—CH}\overset{\text{CH}}{\cdots}\text{CH}_2} \rightleftharpoons \underset{\downarrow\atop \text{Pd}}{\text{—CH=CH—CH}_3} \qquad (3)$$



$$\underset{\downarrow\atop \text{Pd}}{\text{—CH}_2\text{—CH=CH}_2} \rightleftharpoons \underset{\downarrow\atop \text{Pd}}{\text{—CH=CH—CH}_3} \qquad (4)$$

However, no convincing evidence concerning the actual nature of the transition state has been reported so far.

The olefin isomerization in aqueous solution was carefully investigated by Moiseev and coworkers [17] who proposed a Pd^{II}—Pd^{0} redox process. All the above reported studies were carried out under catalytic conditions corresponding to the presence of excess olefin compared to the palladium(II) salts or complexes used as catalysts.

The syntheses and characterisation of complexes of palladium chloride with 1-pentene, *cis*- and *trans*-2-pentene have been recently reported by some of us [18]. Now, we can determine directly the isomerization rates of the olefin coordinated to the palladium atom. This approach allows us to avoid the complexity of the system due the exchange equilibria between free and coordinated olefins.

Results

*Stoichiometric isomerization studies**

A chloroform solution of the dimeric palladium(II) complex of 1-pentene, in the absence of excess olefin, was chosen for the investigation of the stoichiometric isomerization of α-olefins. When this compound is dissolved in pure dry chloroform or benzene at 25° the coordinated olefin isomerizes very slowly (nearly 10% after one hour); by raising the temperature or by addition of small amounts of cocatalytic substances such as ethanol, the isomerization takes place smoothly and can be followed by IR and NMR spectroscopy. Figure 1 shows the region of carbon—carbon double bond stretching in pure chloroform (41°)

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* We call "stoichiometric" the isomerization of an olefin bound to a palladium complex.

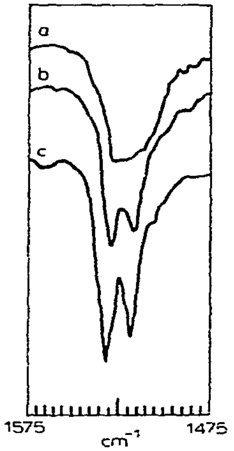


Fig. 1. IR spectra in the 1575 - 1475 cm^{-1} region of [PdCl$_2$(1-C$_5$H$_{10}$)]$_2$ (isomer III) [18] run in pure CHCl$_3$ at 41° at different times (minutes in parenthesis); a (0), b (60), c (90).

at different times. The initial spectrum (a) shows a broad band at 1525 cm^{-1} which can be attributed to a mixture of two isomeric complexes of 1-pentene [18]. After 60 min (spectrum b) two absorption bands at 1532 and 1518 cm^{-1} appear, which have been assigned to well-defined isomers of *trans*- and *cis*-2-pentene complexes respectively. The isomerization of coordinated 1-pentene has occurred to a considerable extent by 90 min (spectrum c) and the final ratio *trans*- to *cis*-olefin is about 1.2. Figure 2 shows that the isomerization at 32° of a 0.5 molar solution of the 1-pentene—palladium complex in deuterochloroform stabilised with alcohol, can be considered complete after 45 min with a final ratio *trans*- to *cis*-2-pentene of 1.2.

We have followed the stoichiometric isomerization of coordinated 1-pen-

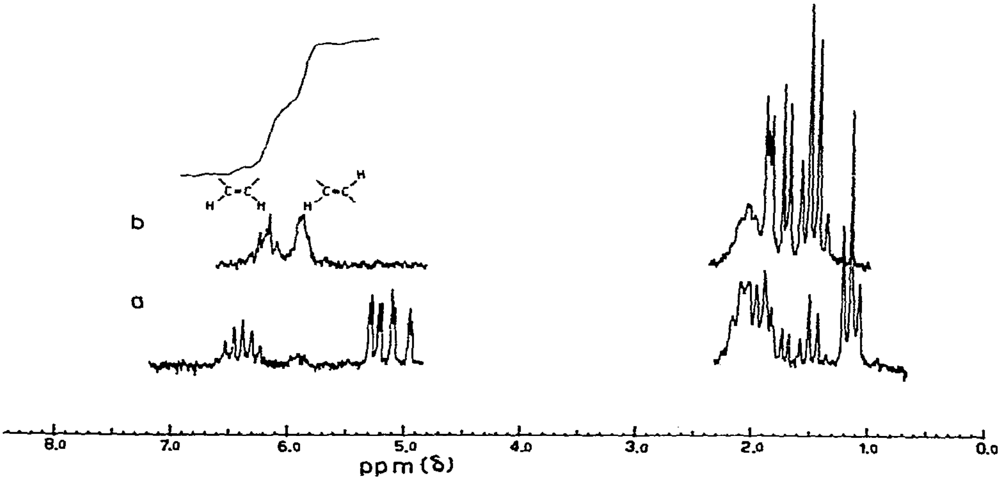


Fig. 2. NMR spectra in CDCl$_3$ of [PdCl$_2$(1-C$_5$H$_{10}$)]$_2$ (isomer III) at 32°; on dissolution (a) and after 45 min (b).

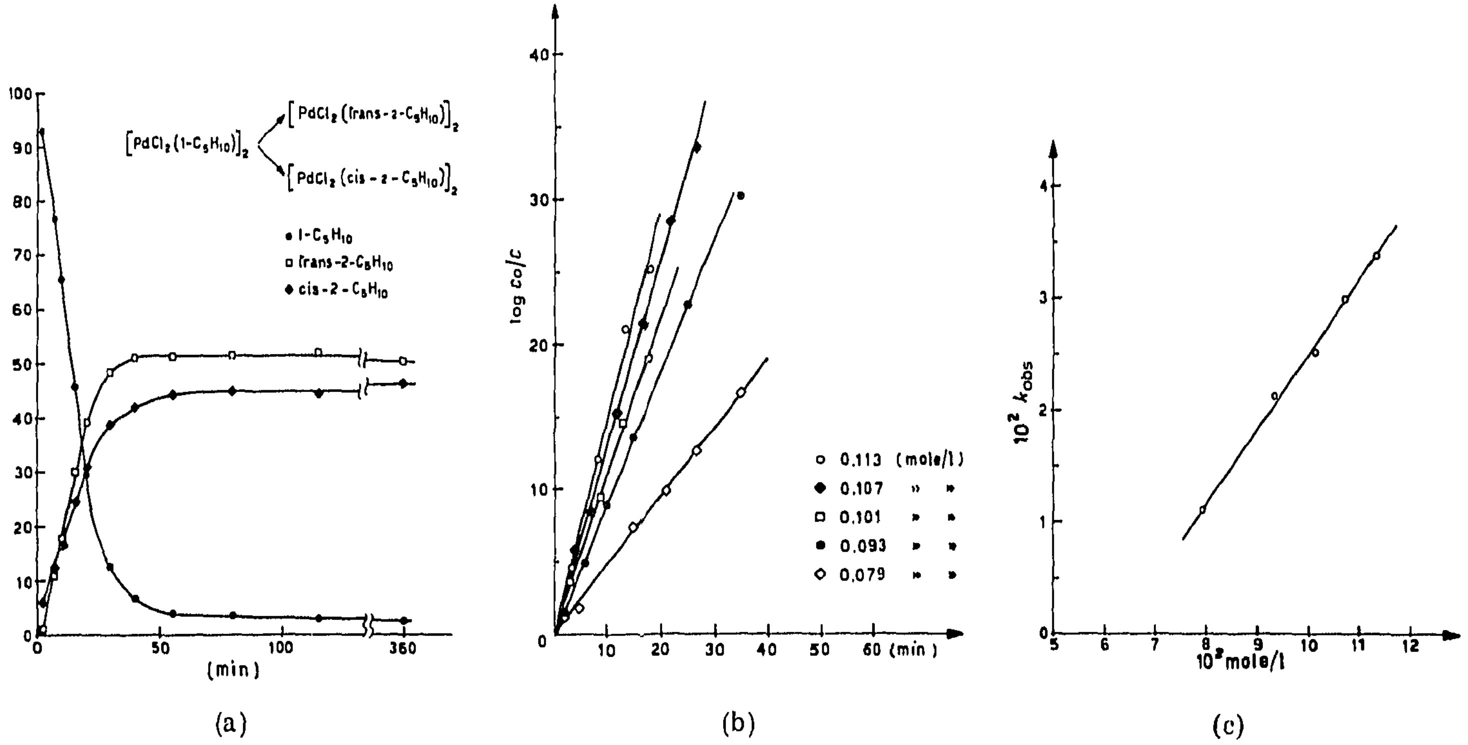


Fig. 3. An example of the stoichiometric isomerization of $[PdCl_2(1\text{-}C_5H_{10})]_2$ (isomer III) [18] (0.055 *M*) at 25° in reagent grade chloroform (a); first order plots of $[PdCl_2(1\text{-}C_5H_{10})]_2$ (0.04 *M*) isomerization at 25° at different ethanol concentrations (b); observed rate constant at 25° against ethanol concentrations (c).

tene by GLC analysis of the olefin mixture obtained by displacement from the palladium coordination sphere with 1,5-cyclooctadiene. This displacement reaction is complete and takes place without alteration of the isomeric composition of the coordinated olefin [18]. The isomerization of the coordinated 1-pentene in "reagent grade" chloroform at 25° is illustrated in Fig. 3a. The reaction can be considered complete after one hour and gives *trans-* and *cis-*2-pentene complexes in the same ratio as shown from the above reported spectroscopic investigations.

Having established that the same results could be obtained with different analytical techniques, we investigated the effect of the cocatalyst, which as far as we know has not been clearly reported until now. Ethanol was chosen as cocatalyst and a kinetic investigation was carried out using a range of ethanol-palladium chloride ratios between 1/1 and 1/1.4. In this range the kinetics are first order both in the complex (Fig. 3b) and in the alcohol concentration (Fig. 3c) until the isomerization is nearly 40% complete. Although linearity seems to be quite satisfactory in this concentration range, first order kinetic constants do not satisfy the Arrenhius law in the temperature range 0—35°. Therefore, the isomerization mechanism is complex and the observed rate constants do not correspond to true kinetic constants of the rate-determining step.

The complexity of the mechanism is confirmed by the lower order in the alcohol when the molar ratio of ethanol to palladium chloride is below one, so that simple kinetic equations in this range of alcohol concentration cannot be proposed. On the other hand, by increasing the ethanol concentration above the ratio 1.4, a considerable increase in the isomerization rate is observed but palladium reduction takes place simultaneously, with separation of metal. To a first approximation, in the range 1—1.4 ethanol to palladium molar ratio, the overall rate of olefin isomerization could be written as follows:

$$r = k_1 \cdot [\mathrm{C}] + k_2 \cdot [\mathrm{C}] \cdot [\mathrm{B}] = k_{\mathrm{obs}} \cdot [\mathrm{C}]$$

where [C] represents the $[PdCl_2(1\text{-}C_5H_{10})]_2$ concentration, [B] the ethanol concentration and $k_{\mathrm{obs}} = k_1 + k_2 \cdot [\mathrm{B}]$. The first term k_1 corresponds to a slow double bond migration in the absence of a "cocatalyst". Under these conditions, the relatively negligible isomerization may be due to the cocatalytic action of

TABLE 1

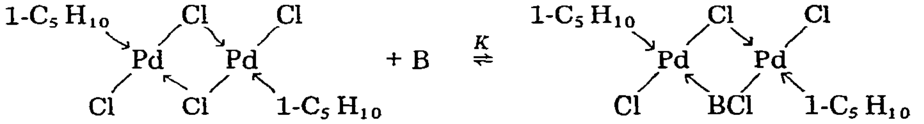
STOICHIOMETRIC ISOMERIZATION OF $[PdCl_2(1\text{-}C_5H_{10})]_2$ (ISOMER III) [18] IN THE PRESENCE OF DIFFERENT COCATALYSTS [a]

Cocatalyst	$\frac{\text{Moles isomerized}}{\text{Mole cocatalyst}}$
None	≈ 0
C_6H_5OH	≈ 0
$(CH_3)_3COH$	Traces
2-Hexene	0.07
$C_6H_5CH_2OH$	0.12
$(CH_3)_2CHOH$	0.13
CH_3CH_2OH	0.25
C_5H_5N	0.51

[a] $[PdCl_2(1\text{-}C_5H_{10})]_2$ concentration, 0.035 *M*; cocatalyst concentration, 0.05 *M*; reaction time, 30 min.; temperature, 25 ± 0.1°.

some free olefin formed by dissociation of the palladium complex. This hypothesis is supported by the cocatalytic role played by the addition of free olefin, as will be shown later.

The second term $k_2 \cdot [B]$ (the only one which we have tried to interpret) could be explained by the breaking of a chloride bridge and the formation of a species that is active in the isomerization. Therefore the role of the alcohol could be interpreted just as that of a base that splits the halogen bridges; indeed a similar cocatalytic action was obtained with different bases (see Table 1) and the catalytic activity increases with the basicity of the donor atom (eqn. 5).



(5)

However, the displacement of a terminal chloride ligand cannot be excluded although it is known that terminal chlorides are less reactive than bridging chlorides [19].

In conclusion, the kinetic results can be interpreted on the basis of a fast pre-equilibrium to form activated palladium species, followed by the disappearance of these species by two isomerization paths to *cis*- and *trans*-2-olefin complexes. Owing to its lability [19], the monobridge complex could also be the precursor of monomeric species, which may be the true reaction intermediates.

An alternative interpretation of the mechanism can be based on a simple displacement of the coordinated olefin by the base, followed by the cocatalytic effect of the free olefin just formed (see Table 1). In any case, in a narrow range of ethanol to palladium molar ratio (1—1.4) the rate of olefin isomerization can be written to first approximation as follows:

$$r = (k_{trans} + k_{cis}) \cdot \{[Pd_2Cl_4(B)(1\text{-}C_5H_{10})]\}$$

$$= K \cdot (k_{trans} + k_{cis}) \cdot [B] \cdot \{[PdCl_2(1\text{-}C_5H_{10})]_2\}$$

As would be expected from the kinetic law for two parallel first-order reactions a straight line has been obtained by plotting the $[PdCl_2(trans\text{-}2\text{-}C_5H_{10})]_2$ concentration against $[PdCl_2(cis\text{-}2\text{-}C_5H_{10})]_2$ concentration (see Fig. 4). From the slope of this line the ratio $k_{trans}/k_{cis} = 1.60 \pm 0.10$ has been obtained.

This kinetic investigation cannot support a well-defined molecular mechanism of the isomerization process of an olefin bound to a palladium ion, but sheds some new light on this controversial topic. Homogeneous isomerization of olefins by transition metal complexes seems to proceed in a large number of cases via a transition metal hydride followed by an olefin insertion into the metal—hydrogen bond to form an intermediate σ metal—alkyl [16]. However, we could not obtain evidence for such a hydridic mechanism under the conditions investigated in this work. To establish a possible hydridic mechanism in which the alcohol was the source of the hydride, we have used tetradeuteromethanol as the cocatalyst in a concentration range in which the methanol to palladium chloride molar ratio was about 1. No deuterium was found in the olefin displaced from the palladium complexes after isomerization. Moreover, hydrogen chloride did not act as a cocatalyst, although in other cases it acts as

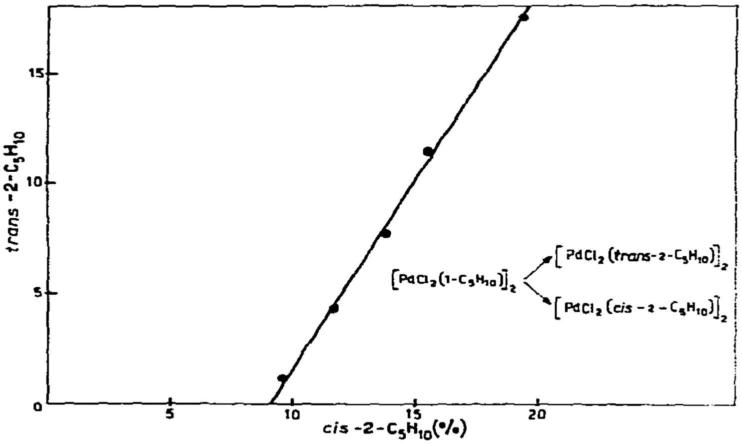


Fig. 4. Plot (arbitrary units) of $[PdCl_2(trans\text{-}2\text{-}C_5H_{10})]_2$ against $[PdCl_2(cis\text{-}2\text{-}C_5H_{10})]_2$ during the stoichiometric isomerization of $[PdCl_2(1\text{-}C_5H_{10})]_2$ (isomer III) in reagent grade chloroform at 25°.

a well known source of metal hydrides by oxidative addition to a metal ion and consequently as a cocatalyst [14].

The large increase in the isomerization rate when the ratio ethanol to palladium is more than 1.4 (corresponding to a third term in the overall rate) also cannot be explained by a hydridic mechanism. The precipitation of palladium could indicate the presence of intermediate Pd—H bonds formed during the reduction by alcohols. We therefore used tetradeuteromethanol as cocatalyst, but no deuterium was found in the isomerized olefin, so that the hydridic route cannot be invoked in these conditions either. The increase in the isomerization rate is probably due to an increase in the free olefin concentration due to the decomposition of the palladium complex. These are not unexpected results: for instance in a recent investigation [20] into the *cis*- to *trans*-isomerization of $C_2H_2D_2$, $PdCl_2$(benzonitrile)$_2$ was the only catalyst that did not give results in agreement with the formation of an intermediate σ-alkylpalladium derivative.

Finally it is interesting to point out that, in contrast to the rather fast isomerization of the coordinated 1-pentene, the rate of isomerization at 25° of $[PdCl_2(cis\text{-}2\text{-}C_5H_{10})]_2$ and $[PdCl_2(trans\text{-}2\text{-}C_5H_{10})]_2$ is very slow (nearly two and 10% in one hour respectively). Also, in this system an induction period of ten minutes has been observed.

Catalytic 1-pentene isomerization

Many authors [3,16] have already reported that, in the early stage of the catalytic isomerization of α-olefins by palladium(II) complexes, the thermodynamically less stable *cis*-isomer of internal olefins is formed preferentially. This kind of stereoselectivity was explained by assuming different energies for some conformational geometries in the transition states. The high stability of the complexes of *cis* olefins (e.g. with silver) has been invoked [15] to explain the selective formation of *cis* isomer. However, as has already been pointed out, the real nature of the transition state and its geometry are not known in detail. Using previous data on the isomerization of coordinated olefins in the absence of

TABLE 2

PSEUDO-FIRST ORDER, k_{obs} AND SPECIFIC RATE CONSTANT, k at 25° IN $CHCl_3$ [a]

$[PdCl_2(1\text{-}C_5H_{10})]_2$ (M)	$10^2 \times k_{obs}$ (min)	k (M^{-1} min^{-1})
0.04	1.25	3.1
0.06	1.74	2.9
0.07	2.21	3.1

[a] 1-Pentene concentration, 3.5 M.

free olefin, we can contribute to the understanding of the catalytic isomerization. We have therefore studied the isomerization of 1-pentene in pure chloroform in the presence of $[PdCl_2(1\text{-}C_5H_{10})]_2$ (isomer III) [18] as catalyst.

The isomerization rate is first order in the palladium dimeric complex in the concentration range 0.04—0.07 mole/l (Table 2). The reaction also appears to be first order in the olefin concentration after a large induction period (Fig. 5). An activation energy of 19.7 ± 0.7 Kcal/mole has been calculated between 25 and 50° (Table 3). These results agree fully with those previously reported by Davies et al. [21] for the isomerization of 4-phenyl-1-butene catalysed by $(PhCN)_2PdCl_2$.

The induction period is of some interest. Bond and Hellier [15] reported that the isomerization of *cis*-2-pentene to *trans*-2-pentene in benzene in the pre-

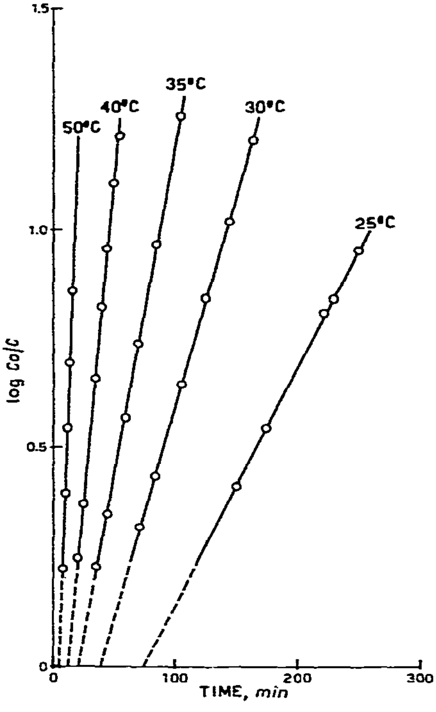


Fig. 5. First order plot of 1-pentene isomerization at different temperatures catalyzed by $[PdCl_2(1\text{-}C_5H_{10})]_2$ (isomer III); 1-pentene concentration, 3.5 M; $[PdCl_2(1\text{-}C_5H_{10})]_2$ concentration, 0.04 M. Dotted lines, induction time.

TABLE 3

RATE CONSTANTS, k_{obs} AT VARIOUS TEMPERATURES [a]

T (K)	$10^2 \times k_{obs}$ (min)
298	1.25
303	2.17
308	4.08
313	6.80
323	16.2

[a] $[PdCl_2(1\text{-}C_5H_{10})]_2$ concentration, 0.04 *M*; 1-pentene concentration, 3.5 *M*.

sence of $(PhCN)_2PdCl_2$ took place after an induction period, which varied inversely with catalyst concentration. This induction period was eliminated if catalytic amounts of 1-pentene were present, while no induction period was observed in the isomerization of 1-pentene at 70°. However an induction period was found by Davies et al. [21] (at lower temperatures) in the isomerization of 4-phenyl-1-butene. We have now observed that the induction period depends on the reaction temperature, as shown in Fig. 5. Isomerization takes place after an induction period of 75 min at 25° but only of 4 min at 50°. This would explain why the induction period was undetectable at the temperature of Bond's experiments [15].

Stereoselectivity in the 1-pentene isomerization

In the course of the isomerization reaction we analysed the composition of both free olefin and olefin coordinated to palladium. The composition of the coordinated olefins during the catalytic isomerization of 1-pentene is reported in Fig. 6a. It is possible to define three different steps:

(i) less than 30 min: a very slow isomerization takes place with evident formation of only the *cis*-2-pentene complex;

(ii) between 30—50 min: a fast isomerization takes place with predominant formation of the *cis*-2-pentene complex;

(iii) after 50 min: the isomerization of 1-pentene is pratically complete and the ratio *cis*- to *trans*-2-pentene is that corresponding to the equilibrium [18]:

$$[PdCl_2(trans\text{-}2\text{-}C_5H_{10})]_2 + 2\,cis\text{-}2\text{-}C_5H_{10} \overset{K_1}{\rightleftharpoons} [PdCl_2(cis\text{-}2\text{-}C_5H_{10})]_2 + 2\text{-}trans\text{-}2\text{-}C_5H_{10}$$

The composition of the free olefin is shown in Fig. 6b. Also in this case three different steps may be defined:

(i) less than 30 min: an induction period exists during which *cis*- and *trans*-2-pentene are formed in a ratio which is nearly twice the thermodynamic one;

(ii) between 30—80 min: a fast isomerization takes place which obeys first order kinetics in both the olefin and the palladium complex;

(iii) after 80 min: the 1-pentene conversion is more than 90% and the *trans* to *cis* ratio approaches the thermodynamic value*.

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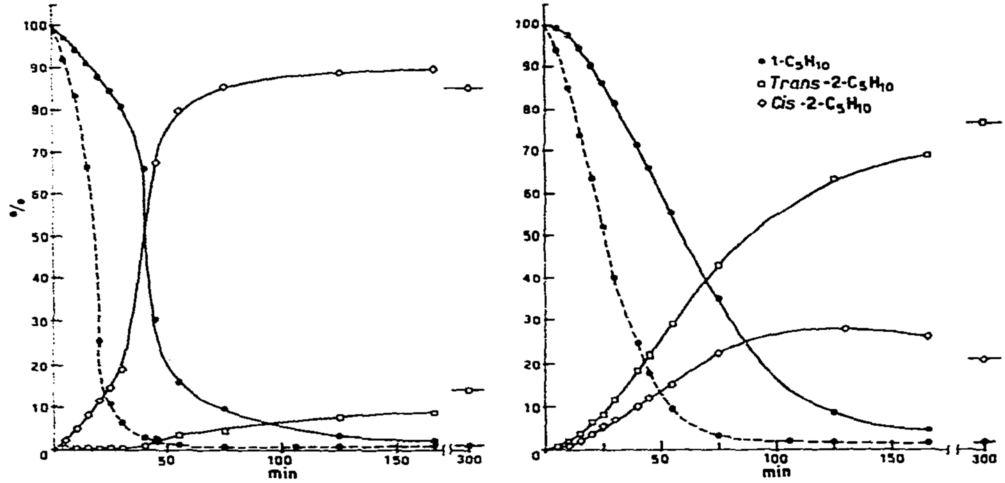
* The real thermodynamic value may be attained only when a large excess of free olefin (compared to the palladium complex) is used.



(a) (b)

Fig. 6. Catalytic isomerization of 1-pentene in the presence of $[PdCl_2(1\text{-}C_5H_{10})]_2$ (isomer III) at 25°; 1-pentene concentration, 3.5 *M*, $[PdCl_2(1\text{-}C_5H_{10})_2]_2$, 0.15 *M*. Dependence of the free olefin composition (a) and of the coordinated olefin composition (b) on time. Dotted lines indicate isomerization in the presence of ethanol (0.1 *M*).

The induction period can be reduced and the kinetic constant increased nearly twofold when ethanol is used as a cocatalyst in a ratio ethanol/palladium = 1/1 (dashed line). An interesting point can be deduced from the above data: The three olefin palladium complexes are present, after 300 min, at concentrations corresponding to the exchange equilibrium constants already reported [18]. In fact the equilibrium constants, which can be calculated using the catalytic isomerization data (Fig. 6a and 6b), are in a good agreement with those obtained from exchange studies between free and coordinated olefins [18]. It follows

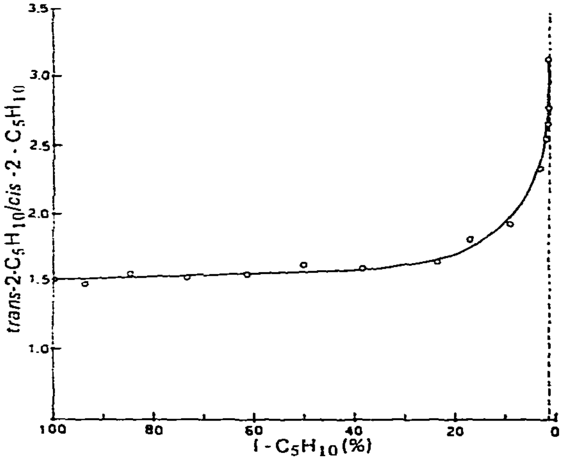


Fig. 7. Dependence of *trans*- to *cis*-2-pentene concentration on 1-pentene conversion during the palladium catalyzed isomerization (for conditions see legend to Fig. 6).

that the catalytic isomerization can be explained by assuming an isomerization of the 1-olefin coordinated to the metal followed by a rapid exchange of the isomerized olefins with the excess 1-pentene.

If the direct *trans*- to *cis*-2-pentene isomerization is considered to be a slow process (and, as previously mentioned, it is so in comparison with the 1-olefin isomerization), in the first stage of the reaction, the *trans*- to *cis*-ratio must be related to the kinetic ratio (k_{trans}/k_{cis} = 1.6) obtained from stoichiometric studies. In order to prove this hypothesis we have calculated the total amount of *trans*- and *cis*-2-pentene in the catalytic isomerization (considering the sum of both coordinated and free olefins). The ratio *trans*- to *cis*-2-C_5H_{10} is reported as a function of the 1-pentene per cent composition (Fig. 7). The above ratio is 1.5—1.6 until 1-pentene conversion has reached about 60%, then the ratio increases only in the last stage of the reaction to 3.1, which corresponds to the thermodynamic value at 25°.

We can therefore conclude that internal olefins are kinetically produced in a ratio of *trans*- to *cis*- of 1.5—1.6 also under catalytic conditions; this value is very little affected by the nature of the cocatalyst. Only later, when the 1-pentene concentration in the free olefin is too low to have a substantial concentration of the palladium 1-pentene complex, does the direct isomerization of *cis*- to *trans*-2-pentene take place and the free olefin composition approach the thermodynamic equilibrium.

Conclusion

We may now draw the following conclusions about the complex mechanism of the catalytic isomerization reaction in aprotic solvents.

(1). The palladium catalysis requires the presence of a basic cocatalyst, which may be the olefin itself.

(2). This base does not act directly as a source of a palladium hydride, but principally as an electron pair donor. Therefore its action may be related to the formation of monomeric or bridge-split species. The base (with probably the exception of the olefin itself) may not directly participate in the internal olefin isomerization process.

(3). Thus the true catalytic complex could be either a monobridge dimeric π complex or the monomer $PdCl_2$(olefin)(base) or $PdCl_2$(olefin)$_2$. A monomeric complex of the first type in which the base is *N,N'*-dimethylformamide has been characterised with certainty [22], and the existence of the bis(olefin) monomeric complex in the presence of excess free olefin has already been suggested by some infrared evidence [18]. The presence of two olefins bound to the same palladium atom has been invoked by Ketley and co-workers [5] to explain the palladium-catalysed dimerisation of ethylene. However the order of 1 with respect to the dimeric palladium complex is not in agreement with the formation of such monomeric species. In fact, we could not observe in our range of palladium concentrations a kinetic term corresponding to an order of ½ in the palladium dimer (which becomes important at low palladium concentrations) as observed by Henry in the palladium-catalysed isomerization of vinylic halides [23,24]. We cannot exclude a priori the appearance in our rate equation of a term which is half order in the palladium dimer concentration at low total palla-

dium concentrations. Unfortunately this range of concentrations cannot be explored using our experimental approach.

(4). In agreement with the now accepted hypothesis that catalytic olefin isomerization takes place in the palladium coordination sphere followed by fast displacement by the excess of free olefin, the k_{trans} to k_{cis} ratio (≈ 1.6) observed under both stoichiometric and catalytic conditions can explain the stereoselective course of the reaction in the early stages of the reaction. It is noteworthy that the stereoselective formation of the *cis*-isomer (compared to the thermodynamic amount) follows the highest known stability of metal complexes with *cis* olefins when compared to those with *trans*. This could imply a certain resemblance of the transition state geometry with that of the final olefin complex. The previously reported isomerization of 4-methyl-1-pentene [11] and 4-phenyl-1-butene [21] (which apparently does not proceed step by step) may be also explained by means of the already observed high stability of complexes of *cis* internal olefins [18], which are not therefore totally displaced from the palladium coordination sphere even by an excess of 1-olefin. The double bond shift in the palladium coordinated *cis*-internal olefins may occur before displacement [21] avoiding in this way the observation of a step by step formation of all the isomeric internal olefins in the free olefin mixture.

(5). The formation of π-complexes without the direct intervention of any other external reagent to cause olefin isomerization is therefore well established. Very recent investigations by Henry [23,24] have reached the same conclusions even in a protic solvent such as acetic acid. The exact mechanism or mechanisms whereby the isomerization occurs is uncertain; π-allylic or palladium(II) hydride mechanisms [3] were recently eliminated by non-kinetic experiments [23,24] in the case of enol propionates [23] and vinylic halides [24]. We have no evidence to exclude a π-allyl mechanism. However, the observed deuterium scrambling between 1-octene and tritium labelled octene [25] together with the observation of Davies et al. [13] of a deuterium shift from C-3 to C-2 would support a rather complex mobility of the hydrogen atoms that we cannot at the moment rationalise with a unique mechanism.

Experimental

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, and infrared spectra with a Perkin—Elmer 225 spectrophotometer. $PdCl_2$ was a C. Erba product; 1-pentene (purity 95%) and *cis*-2-pentene (purity 95%) were produced by Shuchardt and *trans*-2-pentene (purity 99%) by Fluka. All olefins were distilled under nitrogen and purified from peroxides by percolation through an alumina column prior to use. Pure chloroform and deuterochloroform were purified from ethanol before use. CD_3OD was a Merck product. $[PdCl_2(olefin)]_2$ (olefin: 1-, *trans*-2- and *cis*-2-pentene) was prepared according to the procedures already described [18].

Stoichiometric isomerization of $[PdCl_2(1\text{-}C_5H_{10})]_2$

(a) Infrared analyses. $[PdCl_2(1\text{-}C_5H_{10})]_2$ (III) isomer (68 mg) [18] was

dissolved in pure chloroform (1 ml) and a series of spectra were recorded, at 41°, in the ν(C=C) stretching region. The molar ratios $[PdCl_2($*cis*-2-$C_5H_{10})]_2$ to $[PdCl_2($*trans*-2-$C_5H_{10})]_2$ were calculated from the absorption coefficients of the bands at 1532 and 1518 cm^{-1} [18].

(b) Kinetic experiments. The kinetic experiments were carried out in a 50 ml thermostatted cylindrical reactor equipped with a magnetic stirrer and a short sidearm closed with a serum cap. The solution was obtained by rapid mixing together, under nitrogen atmosphere, of 5 ml of a 0.04 molar pure chloroform solution of $[PdCl_2(1\text{-}C_5H_{10})]_2$ (III isomer) [18] with 5 ml of chloroform containing the cocatalyst (ethanol or other basic compounds). Small samples (0.5 ml) were extracted through the serum cap using a hypodermic syringe at suitable intervals, treated with 0.1 g of 1,5-cyclooctadiene in a 5 ml test tube and immediately cooled to —78°; the liquid samples were analyzed by gas chromatography.

Catalytic isomerization of 1-pentene

The kinetic experiments were carried out using the same apparatus as that used for stoichiometric isomerizations. 1-Pentene (5 ml) was rapidly added to a clear solution obtained by dissolving $[PdCl_2(1\text{-}C_5H_{10})]_2$ (III isomer) [18] (0.3—1 g) in pure chloroform (7.5 ml). Small samples (0.2 ml) were extracted through the serum cap at suitable intervals using a hypodermic syringe, treated with 1,5-cyclooctadiene (0.1 g) in a 5 ml test tube and immediately cooled to —78°. The liquid samples, free from the palladium complexes, were directly analysed by gas chromatography. Since in all the kinetic experiments the molar ratio 1-pentene to palladium was more than 22, the olefin displaced by 1,5-cyclooctadiene could be neglected in comparison with free olefin. When the composition of both free and coordinated olefins was to be determined, two series of samples were extracted at suitable intervals. The first was treated with 1,5-cyclooctadiene and the total olefin displaced was analysed by GLC. The second was cooled to —78° and treated with n-pentane (ten volumes of n-pentane per volume of solution). The solid that separated at that temperature was washed with n-pentane, dried under vacuum, and the coordinated olefin was recovered by exchange reaction with 1,5-cyclooctadiene.

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