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# The Isomerization of Olefins by Palladium Complexes

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Certain palladium complexes have been found to be very efficient catalysts for the low-temperature liquid phase isomerization of olefins. The reaction is completely specific for isomerization and only double-bond migration occurs with no detectable skeletal rearrangement; concentrations of palladium complexes of 0.1 mole % give virtually complete thermodynamic equilibration of some olefins at temperatures of 50–60°C.

The olefin-palladium chloride complex appears to be the true catalyst and this may be formed *in situ* by the addition to the olefin to be isomerized of palladous chloride, or more conveniently a palladous chloride complex with a displaceable ligand, e.g. palladium chloride bis(benzonitrile). The relative rates of isomerization of various methylpentenes have been determined and a brief examination made of linear olefins and unsaturated ketones.

Although a close approach to the thermodynamic equilibrium is eventually achieved, during the course of the isomerization certain olefin isomers are preferentially formed. A simple stepwise migration of the double bond does not appear adequately to explain the results.

Olefins are known (*1*) to be isomerized by acidic and by basic catalysts in processes which go via carbonium ions and carbanions, respectively. Some metals, especially those which catalyze hydrogenation, can also bring about isomerization via uncharged species (*2*). Basic and metallic catalysts cause only *cis-trans* isomerization or a double-bond shift, whereas acidic catalysts can in addition promote skeletal rearrangement, cracking, and polymerization. We have recently noted briefly (*3*) the discovery of novel catalysts, i.e. the well-known olefin-palladium(II) chloride complexes $(C_nH_{2n}\cdot PdCl_2)_2$ (*4*), which are specific for double-bond isomerization. A more detailed account of our findings is presented here.

It is surprising that although these complexes have been known for many years their activity in olefin isomerization has not previously been recorded. During the course of this work there appeared two patents (*5*) to Feller in which the double-bond isomerization of *normal 1-olefins* to internal olefins, in the presence of platinum or palladium compounds and either phosphorus oxychloride or trichloroacetic acid, was described. The present catalyst system is simpler, and is not restricted to linear olefins.

In this paper 4-methylpentene-1 is abbreviated to 4MP1, the other methylpentenes are similarly designated, and palladium chloride bis(benzonitrile) is PCBB.

## EXPERIMENTAL

### 1. *Materials*

PCBB was prepared by Kharasch's method (*4*). The corresponding bromide was prepared in the same way, but was not obtained very pure (Found: Pd 21.1%; Calc for $PdBr_2\cdot C_{14}H_{10}N_2$: Pd 22.6%).

Ethylene- and cyclohexene-palladium(II) chlorides were prepared by adding the olefin to a saturated solution of PCBB in benzene at 20°C, filtering the brown precipitate rapidly, washing with benzene, and drying briefly *in vacuo* at room temperature. Ethylene platinum(II) chloride was prepared by Anderson's method (*6*).

Methylpentenes were purified by fractional distillation, and analysed by gas-liquid chromatography on either 6 m of dimethylsulfolane (20% wt) on Embacel at 20°C, or at 0°C on 33 m of stainless-steel coated with squalane.

A sample of isomesityl oxide was prepared by fractionally distilling commercial mesityl oxide through a 100-plate column to give a forerun containing 67% of the iso compound and 33% of mesityl oxide.

### *2. Isomerization*

(a) **With palladium chloride.** 4MP1 (13.6 g) was boiled under reflux with powdered palladium chloride (1.0 g). After 1 hr the olefin was distilled off and analyzed.

(b) **Isomerization of $C_6$ olefins with PCBB.** The olefin and finely powdered PCBB (0.1 mole % based on olefin) were boiled under reflux (55–65°C, liquid temperature). At the end of a run the olefin was distilled off and analyzed.

(c) **Relative rates of isomerization of four methylpentenes.** The course of the isomerization of 4MP1, *trans*-4MP2, 2MP2, and 2MP1 was determined as follows. PCBB (0.0608 g, 0.04 mole % based on olefin) was placed in a two-necked 150-ml flask fitted with a water condenser surmounted by a cold-finger trap at −78°C, and with a capillary tube from which samples could be drawn off. The apparatus was rigorously dried before use. After air had been displaced by dry nitrogen the olefin (34.45 g) was introduced and the flask at once immersed in an oil bath at 50° ± 0.2°C. The mixture was magnetically stirred with a Teflon-covered iron rod. The start of the reaction was taken as the point at which all of the catalyst had dissolved—about 6 min after mixing. Samples taken at fixed intervals were analyzed on the dimethylsulfolane column, with an Embacel guard bed to retain catalyst.

(d) **Isomerization of 4MP1 with complexes other than PCBB.** Ethylene- and cyclohexene-palladium(II) chlorides, palladium bromide bis(benzonitrile), and ethylene-platinum(II) chloride were tested as in (b).

(e) **Isomerization of butene-1.** The olefin (25 ml) and PCBB (varying amounts—see Table 2) were sealed in a Carius tube and heated in a rocking autoclave. The product was analyzed on the dimethylsulfolane column.

(f) **Isomerization of isomesityl oxide.** The 67% concentrate (10 ml) of isomesityl oxide was heated at 100°C with PCBB (0.2 g) for 4 hr. A yellow solid separated when the product was set aside for 48 hr. The liquid product was removed by decantation and analyzed by gas-liquid chromatography on 50 m of squalane-coated steel capillary at 150°C.

## RESULTS

When 4MP1 was boiled with palladium chloride a small amount dissolved to give a brown solution, and after 1 hr the olefin was found to have been isomerized to a mixture of its double-bond isomers in the proportions corresponding to the equilibrium mixture (7) at about 60°C; see Run 1, Table 1. Palladium chloride proved to be erratic in action, and on several occasions the reaction failed.

PCBB (0.1 mole % on olefin) dissolved smoothly in boiling 4MP1 to give an orange solution which turned brown after about 15 min, and sometimes deposited a little palladium after about 30 min. After 1 hr at the boiling point the 4MP1 had isomerized to the equilibrium mixture of double-bond isomers. Hexene-1, *cis*-4MP2, 2MP2, and 2MP1 behaved similarly—see Runs 11, 29, 35, 53, and 69 in Table 1. No products of skeletal isomerization, polymerization, or cracking were ever detected in the isomerized materials—the analytical method would have revealed any such by-products down to a concentration of about 0.05% wt.

The detailed course of 4MP1 isomerization is shown in Fig. 1. A comparison under identical conditions of the isomerization of four methylpentenes at 50°C is represented in Figs. 2–5, from the curves in which the maximum rates of disappearance were calculated as: 2MP1 98, 2MP2 34, 4MP1 25, and *trans*-4MP2 8%/hr. The 2MP2 isomerization (Fig. 4) came almost to a halt after 40 min, by which time the color of the solution had faded markedly, suggesting that the

TABLE 1

Isomerization of $C_6$ Olefins with Palladium Complexes[a]

| Run No. | Olefin Compound | Olefin Purity (wt %) | Catalyst Compound | Catalyst Mole % on olefin | Duration (hr) | Product (wt %) 4MP1 | 4MP2 | 2MP1 | 2MP2 | Rest[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4MP1 | 97.9 | $PdCl_2$ | 3.5 | 1.0 | 0.5 | 14.0 | 13.8 | 69.6 | 1.1 |
| 11 | 4MP1 | 99.9 | $PdCl_2 \cdot 2PhCN$ | 0.1 | 1.0 | 0.5 | 10.0 | 11.6 | 77.9 | 0 |
| 53 | *cis*-4MP2 | 100 | | | 1.65 | 0.4 | 9.8 | 12.0 | 77.8 | 0 |
| 35 | 2MP2 | 97.2 | | | 2.8 | 0.3 | 7.3 | 11.5 | 78.8 | 2.1 |
| 69 | 2MP1 | 100 | | | 1.0 | 0.5 | 11.3 | 12.7 | 75.4 | 0 |
| 51 | 4MP1+<br>4MP2 | 72.7<br>24.3 | $PdCl_2 \cdot 2PhCN$ | 0.01 | 5.8 | 25 | 43 | 6 | 25 | — |
| 63 | 4MP1 | 92.5 | $(cyclo\text{-}C_6H_{10} \cdot PdCl_2)_2$ | 0.1 | 1.0 | 0.6 | 11.9 | 11.6 | 75.0 | 0.9 |
| 67 | 4MP1 | 92.5 | $(C_2H_4 \cdot PdCl_2)_2$ | | 1.4 | 0.6 | 11.4 | 12.0 | 75.0 | 1.0 |
| 49 | 4MP1 +<br>4MP2 | 72.7<br>24.3 | $PdBr_2 \cdot 2PhCN$ | | 3.3 | 71.3 | 25.6 | 0.3 | 0.9 | 0.9 |
| | | | Equilibrium composition at 60°C: | | | 0.35 | 10.6 | 14.1 | 75.0 | — |
| | | | | | | *cis*-H-3 + *trans*-H-2 | H-1 + *trans*-H-3 | *cis*-H-2 | | |
| 29 | Hexene-1 | 98.3 | $PdCl_2 \cdot 2PhCN$ | 0.1 | 1.0 | 60.1 | 23.4 | 14.4 | | |
| | | | Equilibrium composition at 60°C: | | | 56.5 | 26.5 | 17.0 | | |

[a] At reflux temperatures.

[b] Mainly *n*-hexenes.

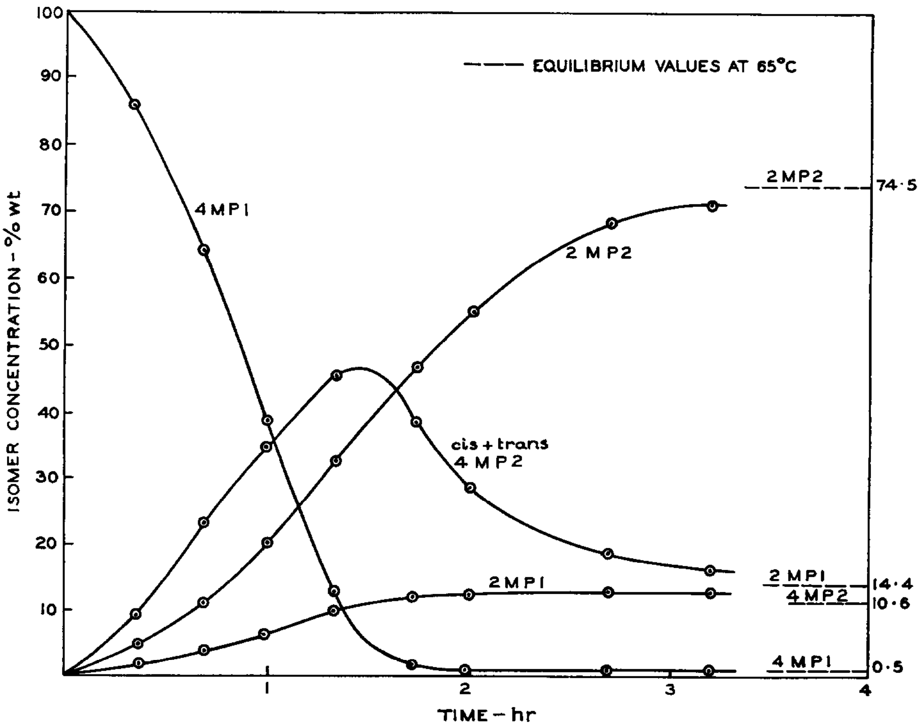


FIG. 1. Isomerization of 4MP1 at reflux.

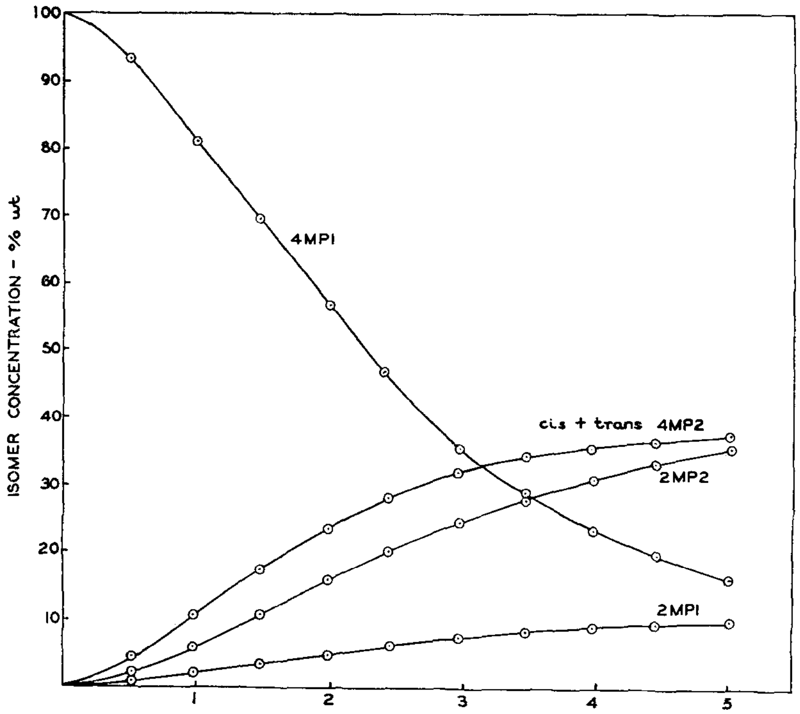


FIG. 2. Isomerization of 4MP1 at 50°C.

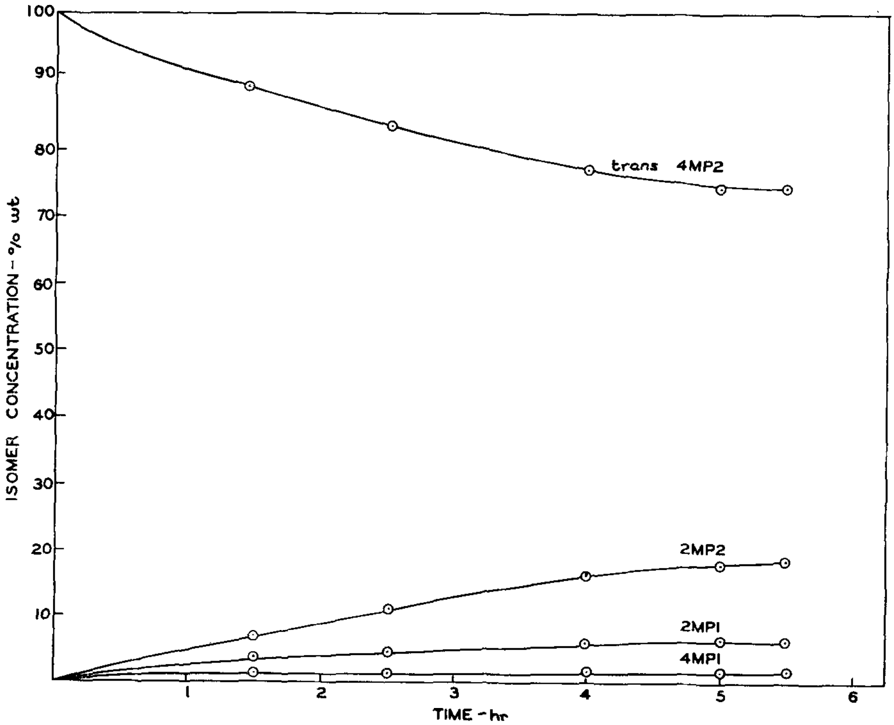


FIG. 3. Isomerization of *trans*-4MP2 at 50°C.

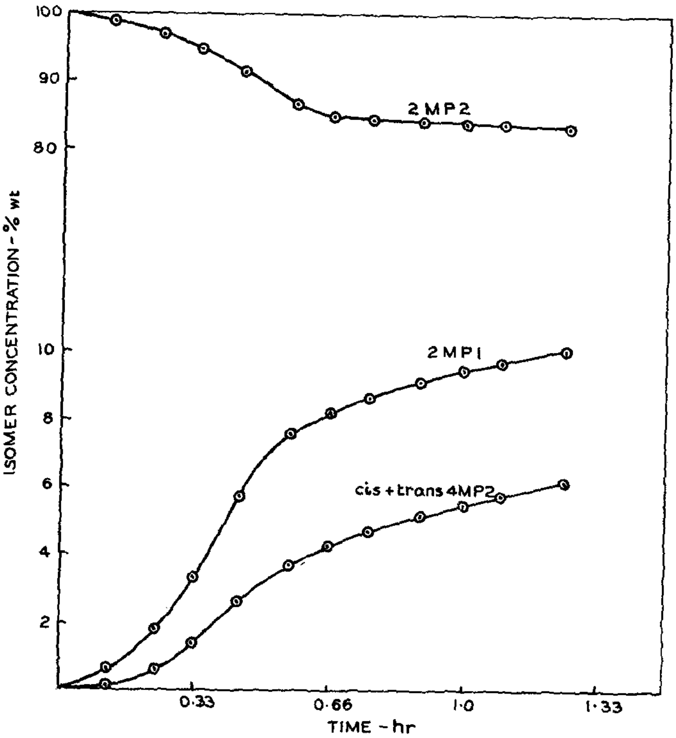


FIG. 4. Isomerization of 2MP2 at 50°C.

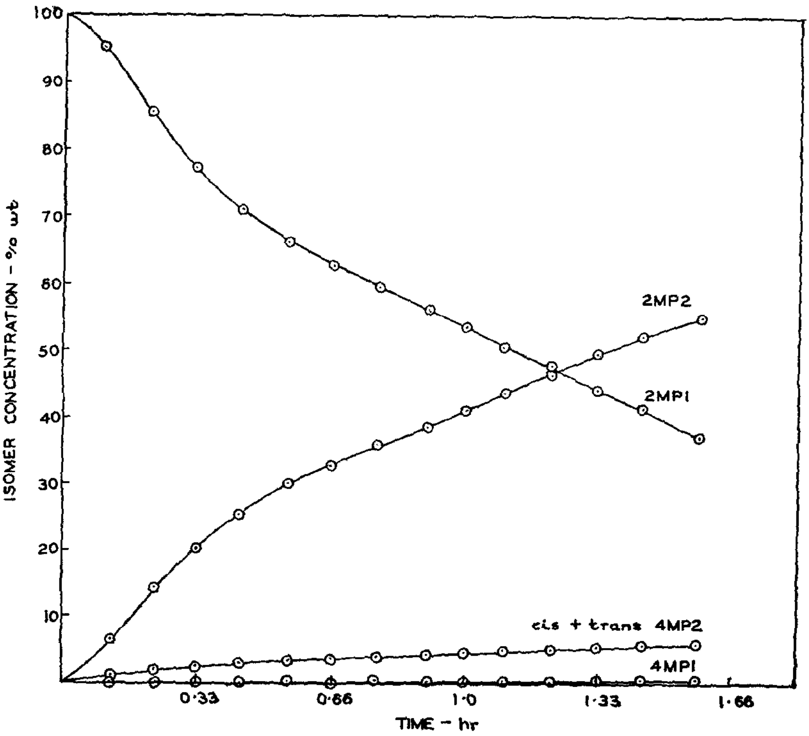


FIG. 5. Isomerization of 2MP1 at 50°C.

catalyst had been destroyed, possibly before the maximum rate of 2MP2 isomerization had been reached. The reason why the catalyst was destroyed so early with this olefin is not known. Color fading was observed in many experiments with low catalyst concentrations if reflux was continued for long enough.

Rigorous drying of the apparatus before use eliminated any precipitation of palladium during these runs.

The variation of the (*cis* and *trans*) 4MP2 concentration and the *cis*/*trans* ratio during the isomerization of 4MP1 is shown in Fig. 6. The *cis*/*trans* 4MP2 ratio was initially above the equilibrium value, but fell below it in the later stages.

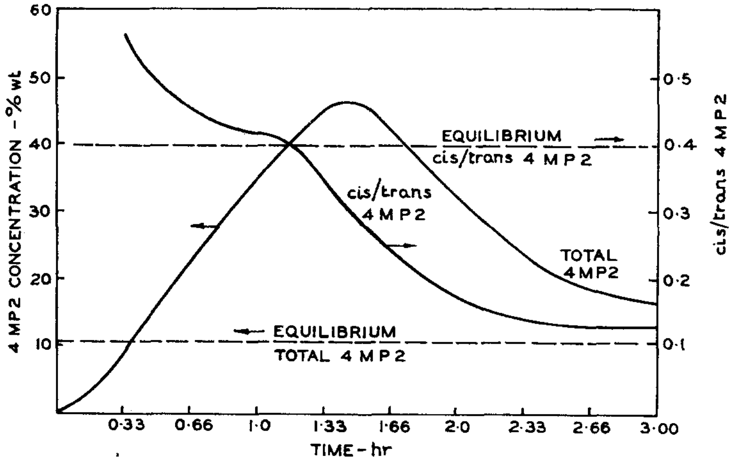


FIG. 6. Ratio of *cis*- to *trans*-4MP2 during isomerization.

The isomerization of butene-1 required more vigorous conditions than did that of the methylpentenes, but after 6 hr at about 80°C in the presence of 1 mole % of PCBB the equilibrium mixture (7) was obtained. Three runs at differing butene-1 conversions, shown in Table 2, indicated that initially the *cis*/*trans* butene-2 ratio was greater than the equilibrium value, but that it approached this as the reaction neared completion.

Isomesityl oxide (initially 67%, plus 33% mesityl oxide) was converted by PCBB at 100°C into a mixture containing 85% mesityl oxide, 14.4% isomesityl oxide, and 0.6% of unidentified material.

On several occasions the isomerization of 4MP1 in the presence of PCBB failed to go to completion. Such olefin samples were found to have become peroxidized on storage, and freshly prepared, peroxide-free material never failed to undergo the reaction. When it was attempted to use only 0.01 mole % of PCBB even fresh samples of 4MP1 were not isomerized completely before the solution turned almost colorless and the reaction ceased—Run 51, Table 1.

Ethylene- and cyclohexene-palladium chlorides promoted the isomerization of

TABLE 2

ISOMERIZATION OF BUTENE-1 WITH PCBB

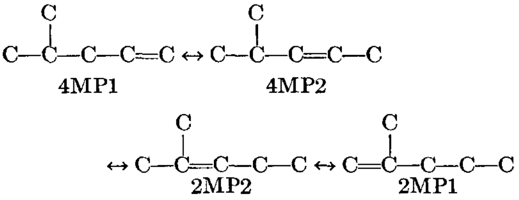
| Run No. | PCBB, mole % on olefin | Temperature (°C) | Duration (hr) | Product (wt %) | | | *cis*/*trans* Butene-2 |
|---|---|---|---|---|---|---|---|
| | | | | B-1 | *cis*-B-2 | *tr*-B-2 | |
| 145 | 0.1 | 50–60 | 1 | 72.6 | 12.9 | 13.9 | 0.93 |
| 117 | 0.1 | 50–75 | 2 | 54.8 | 21.4 | 23.5 | 0.91 |
| 146 | 1.0 | 70–90 | 6 | 4.3 | 29.2 | 66.0 | 0.44 |
| Equilibrium composition at 80°C: | | | | 6 | 26 | 68 | 0.38 |

4MP1 about as effectively as PCBB (Runs 63, 67; Table 1). Palladium bromide bis-(benzonitrile) was only slightly soluble in methylpentenes, and had only slight activity—Run 49, Table 1. Attempts to prepare the benzonitrile complexes of palladium iodide, cyanide, thiocyanate, and nitrate, by the same method as was used to make the complex of the chloride, failed.

## Discussion

Heating an olefin at 60–100°C with a small amount (1 mole % is convenient) of palladium chloride bis(benzonitrile) is a simple and 100% selective way of promoting double-bond isomerization. Palladium chloride alone varies in its effectiveness from sample to sample, possibly because it is a hygroscopic and polymeric material the surface of which varies in physical state and degree of hydration. However, that palladium chloride alone can work is important because it strongly suggests that the true catalyst is the olefin complex $(C_nH_{2n}{\cdot}PdCl_2)_2$, the formation of which is confirmed by the brown color of the olefin solution. Further, since the ethylene, cyclohexene, and benzonitrile complexes of palladium chloride are equally effective as catalysts for 4MP1 isomerization it is reasonable to suppose that they are all converted into a common intermediate in 4MP1 solution, *viz.* the (4MP1 − $PdCl_2$) complex.

The isomerization of the methylpentenes by PCBB has some interesting features. At first glance the process, starting for example with 4MP1 (Fig. 1), appears to be stepwise, proceeding by a discrete series of 1:3 hydrogen shifts, thus moving the double bond along the chain and producing consecutively each of the olefin isomers in turn.



$$\underset{\text{4MP1}}{\mathrm{C{-}\overset{\overset{C}{|}}{C}{-}C{-}C{=}C}} \leftrightarrow \underset{\text{4MP2}}{\mathrm{C{-}\overset{\overset{C}{|}}{C}{-}C{=}C{-}C}} \leftrightarrow \underset{\text{2MP2}}{\mathrm{C{-}\overset{\overset{C}{|}}{C}{=}C{-}C{-}C}} \leftrightarrow \underset{\text{2MP1}}{\mathrm{C{=}\overset{\overset{C}{|}}{C}{-}C{-}C{-}C}}$$

In the early stage of the reaction as 4MP1 disappears 4MP2 is the main product. When the conversion of M4P1 is nearly complete (i.e., its concentration approaches that of equilibrium) the 4MP2 concentration starts to fall and that of 2MP2 rises at its maximum rate. An anomaly is, however, apparent in the formation of 2MP1, which if the process is truly stepwise can be formed only from 2MP2, such that at any moment during the isomerization the 2MP1/2MP2 ratio can be less than (prior to the establishing of equilibrium) or equal to (at equilibrium) the equilibrium value of 0.19 at 60°C (*7*). In fact the concentration of 2MP1 rises to near its equilibrium value (14.1% at 60°C) well before that of 2MP2. Thus after 1½ hr, in Fig. 1, the ratio 2MP1/2MP2 is 0.28, which is 50% above the equilibrium value, and this is well outside the limits of experimental error. The observation was made several times; see for example Fig. 2, in which after 3 hr the 2MP1/2MP2 ratio in the products of 4MP1 isomerization was 0.3. On this evidence, therefore, it is possible that 2MP1 is formed not only from 2MP2 but also from 4MP2, and even 4MP1. The stepwise nature of this novel isomerization is thus by no means certain.

In the isomerization of 4MP1 to *cis-* and *trans-*4MP2 the *cis* isomer is preferentially formed in the early stages of reaction, as is the case in a number of base-catalyzed olefin isomerizations (*8*). This is shown in Fig. 6 in which the data in Fig. 1 are plotted in detail for 4MP2. While there is a net production of 4MP2 corresponding to the rising "total 4MP2" curve, the *cis/trans* ratio is well above the equilibrium value of 0.4, at 60°C (*7*). On the falling part of the "total 4MP2" curve when 4MP2 is being isomerized faster than it is being formed, the *cis/trans* ratio falls well below its equilibrium value. After 3 hr, when equilibrium has been approached—there is at this point about 4% too much 4MP2 and 4% too little 2MP2—the 4MP2 *cis/trans* ratio is at a minimum, i.e. 0.13. This could indicate that not only is *cis*-4MP2 the preferred isomer to disengage from the initially formed 4MP1 complex but that it also forms the 4MP2 complex more easily than *trans* 4MP2.

Preferential formation of the *cis* isomer is also apparent in the isomerization of butene-1 to butene-2, as shown in Table 2. In this case the *cis/trans* ratio is again high at lower conversions, but approaches the equilibrium value as the isomerization nears completion because the simple butene-1: butene-2 system is not perturbed by the existence of a third isomer formed from butene-2.

PCBB was clearly very effective in catalyzing the isomerization of isomesityl oxide to mesityl oxide, but since the equilibrium data for this system do not appear to be known it cannot be said whether equilibrium was reached in the single experiment carried out. The yellow solid which separated on allowing the reaction product to stand was probably the π-allyl complex $(C_6H_9OPdCl)_2$ discovered by Wilkinson (*9*).

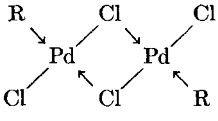
Only limited comment can be made about the mechanism of this interesting isomerization. If the olefin-palladium chloride complex is the true catalyst then all olefin molecules must pass into and out of the complex for isomerization to occur, i.e. there must be exchange between free and complexed olefin molecules. Rearrangement of the olefin could take place within the complex, or the isomerization could occur as the olefin entered the complex:

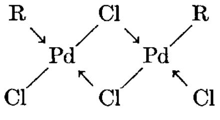
$$\text{4MP1-Pd} + \text{4MP1}^* \leftrightarrow \text{4MP2}^*\text{-Pd} + \text{4MP1}$$

or as it was displaced from the complex:

$$\text{4MP1-Pd} + \text{4MP1}^* \leftrightarrow \text{4MP1}^*\text{-Pd} + \text{4MP2}$$

Such exchange in a homogeneous solution of complex in olefin is inherently likely, and there is some precedent for supposing that it occurs. Thus the similar bridged palladium complexes (I), (II), and (III) ($R = -PPh_3$) exist in solution as a mixture of all three isomers (*10*), which implies that the R and Cl groups at the ends of the complex are labile, and can exchange. It is significant that the platinum analogs do not isomerize in solution, suggesting that the groups are not labile—this could explain the low activity of ethylene-platinum(II) chloride in 4MP1 isomerization.


(I)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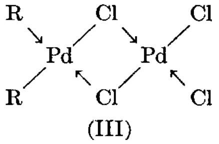
(III)

Different relative rates of complex formation and displacement from the complex would be expected for the various olefin isomers of a given system. This could give rise to the preferential formation of certain isomers during the pre-equilibrium stages. The system could become analogous to those heterogeneous catalyst systems where rearrangement of the chemisorbed species can be more rapid than desorption. Here preferential formation of certain isomers (comparable to the rapid formation of 2MP1 from 4MP1 reported here) is, in fact, also observed.

Davies (*11*) has recently studied the isomerization of olefins in the presence of $Na_2Pd_2Cl_6$ dissolved in dry acetic acid, and reported that octene-1 did, whereas 2MP1 did not, isomerize. The catalyst system is in this respect similar to that described by Feller (*5*) and noted above. We hope to comment on this in a future communication.

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