

**RHODIUM(I) CATALYZED *E/Z* ISOMERIZATION OF DIMETHYL BUTENEDIOATE**

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Hydride complexes of Rh(I) represent highly effective homogeneous catalysts of the isomerization of (*Z*)-dimethyl butenedioate (*I*) yielding (*E*)-dimethyl butenedioate (*II*) in benzene at 25°C. The reaction catalyzed by  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4$  is first order both in *I* and in the catalyst,  $k = 0.51 \text{ l} \cdot \text{mol}^{-1} \text{ s}^{-1}$ ,  $E_a = 48 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -46 \text{ J mol}^{-1} \text{ K}^{-1}$ . At high substrate-to-catalyst ratios the catalyst is inactivated, which consists mainly in deoxygenation and decarbonylation of the *E*- and *Z*-esters with formation of methyl 2-butenolate, triphenylphosphine oxide, and carbonyl complexes of Rh(I). Statistical redistribution of deuterium during the isomerization of equimolar mixture of *I* and [2,3-<sup>2</sup>H<sub>2</sub>]-*I* and other experimental evidence are consistent with the addition-elimination hydride mechanism of the isomerization involving  $\sigma$ -alkyl rhodium complexes as the intermediates and  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_2$  as the catalytically active species.

Homogeneous catalysis with transition metal compounds<sup>1,2</sup> finds applications in olefin chemistry for hydrogenation, hydroformylation, oligomerization, oxidation, metathesis, and other processes. These reactions are often accompanied by prototropic and *E/Z* isomerizations. Selectivity of the catalysts for the individual reactions can be increased by proper choice of the catalyst and reaction conditions. This paper deals with catalysis of isomerization of dimethyl (*Z*)-butenedioate (*I*) forming dimethyl (*E*)-butenedioate (*II*) by compounds of transition metals in benzene solution at 25°C. The isomerization was investigated by many authors at various conditions from the point of view of kinetics<sup>3-6</sup>, equilibria<sup>3-7</sup>, and preparative aspects<sup>4,8</sup>. The reaction can be facilitated photochemically<sup>9</sup> or by catalysis with primary and secondary amines<sup>4,6,7</sup>, halogens<sup>10,11</sup>, and paramagnetic compounds<sup>12</sup>, the reaction order and thermodynamic parameters being in accordance with simple mechanisms. It was found qualitatively that a number of other substances catalyze this isomerization: imidazole<sup>13</sup>, tertiary phosphines and phosphites<sup>14,15</sup>, carbenes<sup>16</sup>, triazene radicals<sup>17</sup>, polymeric conjugated olefins<sup>18</sup>, some complexes of cobalt<sup>19</sup> and of ruthenium<sup>20</sup>.

Our qualitative experiments carried out in benzene solutions at room temperature showed that a surprisingly small number of the 150 transition metal compounds tested are catalytically active at these conditions. Many common catalysts, as *e.g.*

compounds of Ni(II), Ni(0), and Ir(I), form non-reactive adducts with the substrate; efficient are some complexes of Pd(II), Ru(II), and especially of Rh(I).

Further experiments were focused on the rhodium complexes. The efficiency of the compounds tested (Table I) can be described qualitatively by the following series:  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4 \approx \text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_3 > \text{RhH}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_3 \gg \text{RhCl}$ .

$\cdot(\text{P}(\text{C}_6\text{H}_5)_3)_3 + \text{SnCl}_2\cdot\text{aq}$ . The complexes  $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$ ,  $\text{RhH}((\text{C}_6\text{H}_5)_2\text{PCH}_2\cdot\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_2$ ,  $(\text{RhCl}(\text{C}_2\text{H}_4)_2)_2$ , and  $(\text{Rh}(\text{CO})\text{CH}_3\text{COCHCOCH}_3)_2$  do not catalyze the isomerization at the conditions mentioned, the complex  $\text{Rh}^{\text{III}}\text{H}_2\text{Cl}\cdot(\text{P}(\text{C}_6\text{H}_5)_3)_3$  hydrogenates the substrate being transformed into inactive  $\text{RhCl}\cdot(\text{P}(\text{C}_6\text{H}_5)_3)_3$ .

For detailed studies we chose the stable and easily obtainable complex  $\text{RhH}\cdot(\text{P}(\text{C}_6\text{H}_5)_3)_4$ . Its high efficiency enables easy following of the reaction course with the half-life in minutes at the substrate/catalyst molar ratios from 50 to 100. However, the reproducibility of the kinetic measurements is critically dependent on complete elimination of some compounds which affect the catalyst activity.

According to ref.<sup>4</sup> the equilibrium constant  $K(E/Z)$  is about  $10^3$ , and reliable determination of the respective concentrations of *I* in the equilibrium solutions is experimentally difficult. It was found that – for this purpose – it is possible to make use of selective substitution of ethene by the ester *I* in the trigonal bipyramidal complex of divalent platinum,  $\text{PtCl}_2(\text{C}_2\text{H}_4)\text{L}$ , where  $\text{L} = (\text{CH}_3)_3\text{CN}(\text{H})\text{CH}_2\cdot\text{CH}_2\text{N}(\text{H})\text{C}(\text{CH}_3)_3$ , coordinated in the equatorial plane together with the olefin, hinders sterically similar substitution with the ester *II* (ref.<sup>21</sup>). The UV absorption of the complex *I* enables determination of 0.01–0.5% *I* in *II* with the accuracy of  $\pm 3$  rel.%. The method cannot be applied to following the isomerization kinetics

TABLE I

Rate constants of the second order reaction in benzene at 25°C for various catalytic systems: 0.470 mol l<sup>-1</sup> (*Z*)-dimethyl butenedioate, 0.003 mol l<sup>-1</sup> Rh

Catalyst	$k, \text{l mol}^{-1} \text{s}^{-1}$
$\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4$	0.51(4)
$\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_3$	0.52(6)
$\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4 + 1 \text{ P}(\text{C}_6\text{H}_5)_3$	0.49(3)
$\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4 + 10 \text{ P}(\text{C}_6\text{H}_5)_3$	0.54(5)
$\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4 + 90 \text{ P}(\text{C}_6\text{H}_5)_3$	0.37(3)
$\text{RhH}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_3$	0.12(3)
$\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3 + 4 \text{ SnCl}_2\cdot\text{aq}$	$7(4) \cdot 10^{-6}$
$\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$	$< 5 \cdot 10^{-7}$

from the side of *II*, because the platinum complex also slightly catalyzes this reaction. Table II summarizes results of determination of the equilibrium constant with various catalysts. Its average value  $K(E/Z) = 1.23(6) \cdot 10^3$  agrees well with the values calculated from the thermodynamic parameters given by Davies and Evans<sup>4</sup>.

The reaction kinetics was followed from the side of *I* in the concentration regions of  $0.15 - 0.85 \text{ mol l}^{-1}$  *I* and  $0.0002 - 0.015 \text{ mol l}^{-1}$  catalyst. At high concentrations

TABLE II  
Equilibrium constant  $K(E/Z) = II/I$  in benzene at 25°C

Initial concentration of <i>I</i> , mol l <sup>-1</sup>	Catalyst	Catalyst concentration, mmol l <sup>-1</sup>	$K \cdot 10^{-3}$
0.328	RhH(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>4</sub>	2.16	1.15
0.328	RhH(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>4</sub>	5.71	1.30
0.515	RhH(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>4</sub>	6.39	1.24
0.159	RhH(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>4</sub>	1.58	1.28
0.328	RhH(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>3</sub>	2.16	1.19
0.328	RhH(CO)(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>3</sub>	2.16	1.21

TABLE III  
Rate constant  $k = (t \cdot [\text{Rh}])^{-1} \ln(100/a)$  in benzene at 25°C for the catalyst RhH(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>4</sub>

Initial concentration of <i>I</i> , mol l <sup>-1</sup>	Rh, mmol l <sup>-1</sup>	Extent of reaction %	$k$ l mol <sup>-1</sup> s <sup>-1</sup>
0.842	15.30	40 <sup>a</sup>	0.56
0.615	9.41	72 <sup>a</sup>	0.49
0.470	11.18	100	0.52
0.470	6.32	100	0.50
0.470	0.21	37 <sup>b</sup>	0.57
0.270	5.58	100	0.44
0.270	0.79	71 <sup>b</sup>	0.49
0.270	0.14	26 <sup>b</sup>	0.49
0.204	3.86	100	0.53
0.153	0.25	13 <sup>b</sup>	0.55

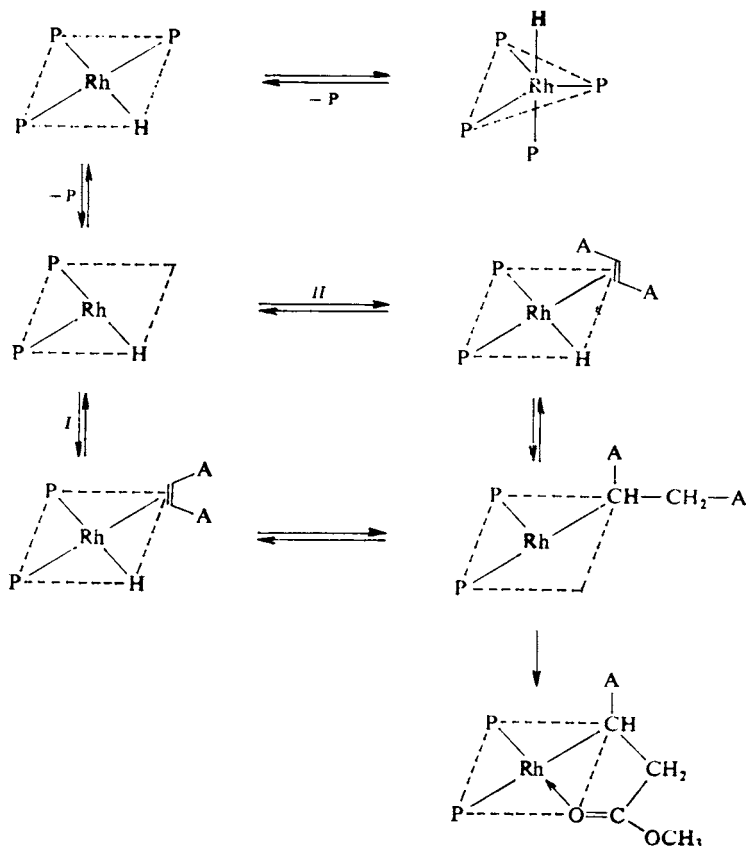
<sup>a</sup> Precipitation of *II*; <sup>b</sup> deactivation of the catalyst.

of the substrate the reaction course could only be followed until crystallization of *II* commenced (solubility of *II* in benzene at 25°C is about 0.5 mol l<sup>-1</sup>). The reaction is first order in *I* and first order in the catalyst; the rate constants calculated from the equation  $k[\text{Rh}] = t^{-1} \ln(100/a)$  (where *a* is the percentage of the unreacted *I*) for the catalytic second order reaction are given in Table III. The calculation was carried out by the least squares fit of 8–15 points measured in the given range of the reaction course. The rate constant  $k = 0.51(4) \text{ l mol}^{-1} \text{ s}^{-1}$  (turnover number ~300) qualifies the complex  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4$  as (so far) the most efficient catalyst of the *E/Z* isomerization of *I*. Temperature dependence of the rate constant (in the interval of 5–35°C) obeys the Arrhenius equation with the parameter  $E_a = 48(3) \text{ kJ mol}^{-1}$ ,  $A = 2 \cdot 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ ; the calculated value  $\Delta S^\ddagger$  is  $-46(7) \text{ J mol}^{-1} \text{ K}^{-1}$ . In accordance with the mechanism given below the activation energy is markedly decreased and the frequency factor is increased as compared with those of the non-catalyzed process<sup>4</sup>; the activation entropy remains unchanged.

The isomerization rate is not affected by addition of hydroquinone, azobis(isobutyronitrile), and small amounts of triphenylphosphine. Only at the ratio  $\text{P}(\text{C}_6\text{H}_5)_3 : \text{Rh} > 80$ , the reaction rate decreases. The reaction is distinctly retarded by traces of thiophene in benzene, traces of peroxides in *I*, and it is immediately inhibited by gaseous oxygen. Check tests involving addition of further catalyst showed that – in all the cases – the inhibition consisted in a reaction of the inhibitors with the catalyst.

After some time of the isomerization course, side reactions between the catalyst and *I* or *II* begin to take place which leads to deactivation of the catalyst; in general, the isomerization does not proceed to completion at the  $[\text{ester}] \times [\text{catalyst}]$  concentration product lower than  $2.5 \cdot 10^{-4}$ . The side reactions are inhibited by triphenylphosphine which thus can serve as a cocatalyst of the isomerization. Investigation of deactivation of the catalyst by means of spectral methods showed that several processes are involved, but the mechanism of deactivation cannot be explained from these data. The following reactions and products were established: *a*) decarbonylation of *I* and *II* with formation of catalytically inactive Rh(I) complexes containing terminal carbon monoxide as a ligand<sup>22</sup>; *b*) deoxygenation of *I* and *II* with formation of triphenylphosphine oxide<sup>23</sup>; the processes (*a*) and (*b*) degrade the substrate asymmetrically to give methyl 2-butenate. *c*) Formation of dimethyl butanedioate by transfer-hydrogenation involving hydride and olefinic hydrogens with simultaneous formation of  $\sigma$ -vinyl complexes of Rh(I) of the type  $\text{Rh}-\text{C}(\text{COOCH}_3)=\text{CH} \cdot (\text{COOCH}_3)$  and  $\text{Rh}-\text{C}(\text{COOCH}_3)=\text{C}(\text{COOCH}_3)-\text{Rh}$ . All the reactions given have precedents<sup>22,24–31</sup>, but only above 60°C. Their inhibition with triphenylphosphine indicates that the first step consists in coordination of the substrate to rhodium through the carbonyl oxygen atom.

These observations make it possible to propose the mechanism of the catalytic *E/Z* isomerization given in Scheme 1.



SCHEME 1

$A = \text{COOCH}_3$

The addition-elimination mechanism involving  $\sigma$ -alkyl complexes as intermediates is further supported by the following facts: 1) The rhodium complexes not containing hydride ligands are catalytically inactive. An exception is  $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$  in the presence of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , but in this case hydrides originating from water molecules are presumably also present<sup>32</sup>. Analogous system with anhydrous  $\text{SnCl}_2$  is inactive. 2) Dissociation of one molecule of triphenylphosphine from  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4$  is indicated by extreme crowding of this complex in the solid state<sup>33</sup>; the structure and dynamics in solution are a matter of discussion<sup>34-36</sup>. Obviously, the discrepancies can be explained by strong dependence of the equilibrium constant  $K = [\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4] / ([\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_3][\text{P}(\text{C}_6\text{H}_5)_3])$  on temperature and solvent<sup>35</sup>. In this work it was found that saturated solution of  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4$  in benzene contains  $1.1 \pm 0.2$  mol

free triphenylphosphine per 1 mol rhodium at 25°C. The free triphenylphosphine can be proved by TLC, and the amount given can be precipitated from the solution as the adduct<sup>36</sup>  $\text{P}(\text{C}_6\text{H}_5)_3 \cdot \text{BCl}_3$ . Ultraviolet spectra of  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4$  and  $\text{RhH} \cdot (\text{P}(\text{C}_6\text{H}_5)_3)_3$  are identical in the region of the charge-transfer bands. The  $\text{RhH} \cdot (\text{P}(\text{C}_6\text{H}_5)_3)_3$  complex exhibits the same catalytic activity as  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4$  for the *E/Z* isomerization, and the inhibition by triphenylphosphine is not significant until the ratio of  $\text{P}(\text{C}_6\text{H}_5)_3 : \text{Rh}$  becomes higher than 80. On the contrary, the non-dissociated chelate  $\text{RhH}((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_2$  is catalytically inactive. These facts strongly suggest that the trigonal bipyramidal  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4$  is completely dissociated giving square planar  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_3$  and  $\text{P}(\text{C}_6\text{H}_5)_3$  in benzene solution at 25°C; the *K* value is greater than 1 (at the 0.001 mol l<sup>-1</sup> catalyst and 0.08 mol . l<sup>-1</sup> triphenylphosphine concentrations the solution contains less than 5%  $\text{RhH} \cdot (\text{P}(\text{C}_6\text{H}_5)_3)_4$  which is the amount which could already be detectable by the kinetic measurements at the given precision). In accordance with the fact that the equilibrium between  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4$  and  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_3$  is established rapidly<sup>36</sup>, no induction period was observed in the kinetic measurements. It is known that the virtual catalytically active species in the system containing  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_3$  is the coordinatively unsaturated complex  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_2$  which is present in very low concentration because of its reactivity<sup>34-36</sup>. Therefore, this species as well as any further intermediate of the catalytic cycle could not be detected by direct spectral methods or even isolated in the solid state, as it is usual in the case of kinetically labile Rh(I) complexes<sup>31,32</sup>. Addition of *I* to solution of  $\text{RhH}(\text{P}(\text{C}_6\text{H}_5)_3)_4$  immediately causes slight change in the UV spectrum, further changes being observed during the reaction, but no reliable interpretation is possible, as the changes are inappreciable and the process is complicated by side reactions. Such difficulties in interpretation of UV spectra of rhodium complexes are notorious<sup>32</sup>. 3) Neither the radical initiator – azobis(isobutyronitrile) – nor the inhibitor – hydroquinone – affected the reaction rate. 4) The isomerization of a mixture of 50% *I* and 50% dimethyl (*Z*)-[2,3-<sup>2</sup>H<sub>2</sub>]butenedioate results in a redistribution of deuterium which approaches statistical proportions: 30.1% <sup>2</sup>H<sub>0</sub>, 36.1% <sup>2</sup>H<sub>1</sub>, 32.2% <sup>2</sup>H<sub>2</sub>, and traces of <sup>2</sup>H<sub>3</sub> and <sup>2</sup>H<sub>4</sub>. A blank experiment with the mixture of 50% *II* and 50% dimethyl (*E*)-[2,3-<sup>2</sup>H<sub>2</sub>]butenedioate (at the same conditions) showed much slower deuterium exchange: 46.1% <sup>2</sup>H<sub>0</sub>, 9.7% <sup>2</sup>H<sub>1</sub>, 42.8% <sup>2</sup>H<sub>2</sub>.

## EXPERIMENTAL

### Reagents

After final fractional distillation, dimethyl (*Z*)-butenedioate<sup>37</sup> was kept in ampoules sealed under argon (one ampoule for each experiment) and stored at -18°C in darkness. No detectable amount of peroxides and of the *E*-isomer were present even after a half year storage. The sample of *II* prepared by isomerization of *I* in the presence of 1% diethylamine<sup>38,39</sup> was recrystallized from a ben-

zene-light petroleum mixture until constant m.p. 101.5°C. Dimethyl (*Z*)-[2,3-<sup>2</sup>H<sub>2</sub>]butenedioate was prepared by reaction of dimethyl butyenedioate with <sup>2</sup>H<sub>2</sub>O in tetrahydrofuran in the presence of triphenylphosphine<sup>40</sup> and was purified *via* (*E*)-[2,3-<sup>2</sup>H<sub>2</sub>]butenedioic acid<sup>41</sup> and [<sup>2</sup>H<sub>2</sub>]maleic anhydride<sup>42</sup>. The final product contained 77.5% <sup>2</sup>H<sub>2</sub>, 16.7% <sup>2</sup>H<sub>1</sub>, and 1.3% <sup>2</sup>H<sub>0</sub>, besides traces <sup>2</sup>H<sub>3</sub> and <sup>2</sup>H<sub>4</sub>; the *E*-isomer could not be detected. Dimethyl (*E*)-[2,3-<sup>2</sup>H<sub>2</sub>]butenedioate was prepared by the isomerization of the above compound in the presence of 1% diethylamine and subsequent sublimation at 100°C/2 kPa; the distribution of the isotopes remained practically unchanged. The rhodium complexes were prepared from RhCl<sub>3</sub>·3 H<sub>2</sub>O (Safina, Vestec) by established methods: RhCl(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub> (ref.<sup>43</sup>), RhH(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>4</sub> (ref.<sup>44</sup>), RhH(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub> (ref.<sup>34</sup>), RhH(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub> (ref.<sup>44</sup>), RhH((C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>)<sub>2</sub> (ref.<sup>45</sup>), (RhCl(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>)<sub>2</sub> (ref.<sup>46</sup>), (Rh(CO)CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>2</sub> (ref.<sup>47</sup>). The following reagents were also prepared according to literature data: (CH<sub>3</sub>)<sub>3</sub>CN(H)CH<sub>2</sub>CH<sub>2</sub>N(H)C(CH<sub>3</sub>)<sub>3</sub> (ref.<sup>48</sup>), PtCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)·[(CH<sub>3</sub>)<sub>3</sub>CN(H)CH<sub>2</sub>CH<sub>2</sub>N(H)C(CH<sub>3</sub>)<sub>3</sub>] (ref.<sup>21</sup>), Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>·(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O (ref.<sup>49</sup>), and (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>·PCH<sub>2</sub>CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (ref.<sup>50</sup>). Triphenylphosphine was recrystallized from ethanol. Benzene was first freed from thiophene and further purified by standard procedures. Immediately before use, it was refluxed with addition of benzophenone and sodium metal for several hours (until purple colour persisted), and then it was distilled under argon (which was deoxygenated by a chromium. (II) solution and then dried with silica gel and by freezing out at -78°C). The solutions for spectral measurements were handled by means of a syringe technique in inert atmosphere.

#### Analytical Methods

The reaction course was followed qualitatively by TLC (Silufol, Kavalier, Votice), ethyl acetate-hexane 2 : 7, detection with KMnO<sub>4</sub> solution; *R<sub>F</sub>*: the Rh-containing components below 0.05, *I* 0.36, *II* 0.54, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PO 0.70, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P 0.88). Quantitative determination of the isomers was carried out by means of gas chromatography (Chrom 4 apparatus, nitrogen as the carrier gas, solid phase OV 275, flame-ionisation detector). Precision of the determination was ±3 rel.% (calibration), that of determination of the isomers ratio was ±0.8 rel.% within the limits of 4 to 96% of one of the isomers. The UV spectra were measured with a Pye Unicam SP 8800 apparatus, the IR spectra were taken on a Perkin-Elmer 684, the <sup>1</sup>H NMR spectra were obtained with a Tesla 487 (80 MHz) apparatus ( $\delta$  scale, *J* in Hz, tetramethylsilane), the <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} spectra were measured with a Varian XL 200 apparatus (50.300 and 80.983 MHz, respectively; tetramethylsilane and 85% H<sub>3</sub>PO<sub>4</sub> as the internal and external standards, respectively). The mass spectra were measured with a JEOL DMS D 100 apparatus using the technique of direct inlet from capillaries at the temperature of 80–100°C.

For determination of low concentrations of *I* in the reaction mixtures containing *II* and the catalyst, volatile components were separated first at 25°C/2 Pa by trapping at -196°C. Thereafter, benzene was removed at 25°C/2 kPa, the residue in the trap was dissolved in dichloromethane, and the total content of esters was determined by titration. An aliquot sample was treated with dichloromethane solution of PtCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)[(CH<sub>3</sub>)<sub>3</sub>CN(H)CH<sub>2</sub>CH<sub>2</sub>N(H)C(CH<sub>3</sub>)<sub>3</sub>] (*III*) in a 2–5 fold molar excess with respect to *I*. The absorbance was measured at 305 nm against the reference solution of *III* of the same concentration (molar absorptivities: *III* 550, mixture 7 830; up to 10<sup>4</sup>-fold excess of *II* has no effect).

The kinetic and equilibrium runs were carried out in 15 ml jacketed vessels (thermostating with water) equipped with the argon inlet and outlet, screw for septum, and magnetic stirrer. The catalyst was weighed and charged into the vessels (in a box filled with nitrogen, when the catalyst was air-unstable) which were closed with the septum made of silicone rubber laminated with Teflon, the vessels were arranged in a series connected with Teflon tubing and repeatedly

evacuated and filled with argon. In a stream of tempered argon saturated with benzene vapours, solvent was added into the vessels by means of a syringe, and, after thermostating, the reaction was started by addition of *I* with stirring. With regard to the small volume of *I*, the temperature change due to the addition was negligible. All the components were measured and/or weighed with the precision better than 0.5 rel.%, the temperature was kept within  $\pm 0.1^\circ\text{C}$ . In the faster reactions, the samples were taken out by means of a syringe through the septum, in the slower reactions or for determination of equilibrium, a number of samples were withdrawn in inert atmosphere, sealed, and kept in an air thermostat ( $\pm 0.5^\circ\text{C}$ ) in darkness, wherefrom they were gradually taken and measured. The reaction was quenched by addition of a slight excess of benzoic acid (relative to the catalyst). For measurements of the mass spectra the reaction was quenched with acetic acid, the volatile components were evaporated at  $25^\circ\text{C}/2\text{ kPa}$ , and the product was sublimed at  $25^\circ\text{C}/2\text{ Pa}$  into a trap cooled at  $-196^\circ\text{C}$ .

Deactivation of the catalyst was studied spectroscopically in solutions of the catalyst and *I* and/or *II* in the ratios 2 : 1 to 1 : 4 at  $25^\circ\text{C}$  in inert atmosphere. The spectra of the solutions did not change after 48 h and showed that the overall molar ratio of the components in the deactivation reactions is close to 1 : 1. IR spectrum (both solution in  $\text{C}_6^2\text{H}_6$  and solid product after evaporation of the volatile components): 1 965 vs,  $\nu(\text{Rh}-\text{C}=\text{O})$  (ref.<sup>51</sup>), 1 182 vs, 1 116 s, 858 m,  $\text{P}=\text{O}$  (ref.<sup>23</sup>), 1 584 m,  $\nu(\text{Rh}-\text{C}=\text{C})$  (ref.<sup>24</sup>). UV spectrum ( $\text{C}_6^2\text{H}_6$ ): 380 nm ( $\epsilon_{\text{M}} 4\ 200$ ),  $\text{Rh}-\text{C}=\text{C}$  (ref.<sup>25</sup>).  $^{13}\text{C}\{^1\text{H}\}$  spectrum ( $\text{C}_6^2\text{H}_6$ ): 17.9 s, 51.7 s, 123.0 s, 144.4 s, 166.2 s, (*E*)- $-\text{CH}_3\text{CH}=\text{CHCOOCH}_3$  (ref.<sup>52</sup>); 28.9 s, 33.2 s, 173.0 s,  $\text{CH}_3\text{OCOCH}_2\text{CH}_2\text{COOCH}_3$  (ref.<sup>53</sup>); 179.2 d,  $^1J(\text{Rh}, \text{C}) 68.3$ ,  $\text{Rh}-\text{C}\equiv\text{O}$  (ref.<sup>54</sup>); 134.5 dd,  $^1J(\text{Rh}, \text{C}) 86.2$ ,  $^2J(\text{Rh}, \text{C}) 9.8$ ,  $\text{Rh}-\text{C}=\text{C}-\text{Rh}$ ; 132.3 d,  $^1J(\text{Rh}, \text{C}) 75.5$ , 131.1 d,  $^2J(\text{Rh}, \text{C}) 3.0$ ,  $\text{Rh}-\text{C}=\text{CH}$ .  $^{31}\text{P}\{^1\text{H}\}$  spectrum ( $\text{C}_6^2\text{H}_6$ ): 25–37 m,  $\text{Rh}-\text{P}$ ; 50–56 m,  $\text{P}=\text{O}$ ; the existence of the multiplets arises from the  $\text{Rh}, \text{P}$  and  $\text{P}, ^2\text{H}$  couplings due to partial exchange of hydrogen and deuterium between triphenylphosphine and  $\text{C}_6^2\text{H}_6$ .

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