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# Effect of ligand donor–acceptor properties on selectivity of catalytic olefin isomerization reaction

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## Abstract

Isomerization reaction of hex-1-ene, 1,5-hexadiene and 1,7-octadiene, catalyzed by  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  and  $\text{HRh}(\text{PPh}_3)_4$  at  $40^\circ\text{C}$  have been studied. Hex-1-ene undergoes total conversion to hex-2-ene at presence of both of catalysts used, whereas isomerization of dienes is catalysed by  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  complex only. To explain observed differences in catalyst activity, theoretical calculations for model structures of  $[\text{HRh}(\text{CO})_3(\text{hexadiene})]$  (I) and  $[\text{HRh}(\text{PH}_3)_3(\text{hexadiene})]$  (II), by Fenske–Hall method have been done. The calculations allowed elucidation of the isomerization reaction course which depends on electron density distribution in rhodium–olefin complex as well as on the way of olefin coordination to the rhodium.

**Keywords:** Carbonyl complexes; Fenske–Hall method; Olefin isomerization; Phosphine complexes; Rhodium; Selectivity

## 1. Introduction

It was frequently observed in our previous studies of rhodium catalyzed hydroformylation of the linear mono- and diolefins that both, the starting olefins, as well as the intermediate, unsaturated monoaldehydes (in case of diolefin hydroformylation) undergo isomerization–double bond migration [1]. Usually, more isomerization reaction products have been observed for rhodium phosphite  $(\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2/\text{P}(\text{OPh})_3)$  than rhodium phosphine  $(\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)/(\text{PPh}_3))$  systems [1,2]. Isomerization of terminal olefins (or diolefins) usually diminish hydroformylation reaction selectivity and therefore is regarded as an undesirable side reaction. However in some cases this reaction can be used for synthesis of specific products like *cis* or *trans* isomers

of certain olefin or unsaturated aldehydes.

The main object of this paper involves studies on the isomerization reaction of hex-1-ene, 1,5-hexadiene and 1,7-octadiene catalyzed with  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  and  $\text{HRh}(\text{PPh}_3)_4$  and then, correlation of experimental data with those obtained from theoretical calculations with Fenske–Hall method [3]. Calculations have been done for model structures  $[\text{HRh}(\text{CO})_3(\text{hexadiene})]$  (I) and  $[\text{HRh}(\text{PH}_3)_3(\text{hexadiene})]$  (II). Those models were selected to get maximum difference of electron density located on rhodium center. It was expected that higher  $\pi$ -acceptor properties of CO compared with that of  $\text{PH}_3$  will result lower electron density on rhodium in the model structure (I) compared with that of structure (II). To reduce the function basis, ligand  $\text{PPh}_3$  was replaced by  $\text{PH}_3$ . The geometries of both

model catalysts under studies were based on X-ray data of  $\text{Rh}(\text{CO})(\text{PPh}_3)_3$  and  $\text{HRh}(\text{PPh}_3)_4$  complexes [4–6].

## 2. Results and discussion

### 2.1. Olefin isomerization catalyzed by $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ and $\text{HRh}(\text{PPh}_3)_4$

Both catalysts,  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  and  $\text{HRh}(\text{PPh}_3)_4$  demonstrate similar activity in hex-1-ene isomerization reaction. In both cases, 100% conversion was achieved in ca. 100 min. The reaction products are *cis* and *trans*-hex-2-ene in comparable yields. In case of  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ , additionally, slow *cis* → *trans* isomerization was observed (Figs. 1 and 2).

Isomerization of 1,5-hexadiene is much more complicated. After 7 h of reaction catalyzed with

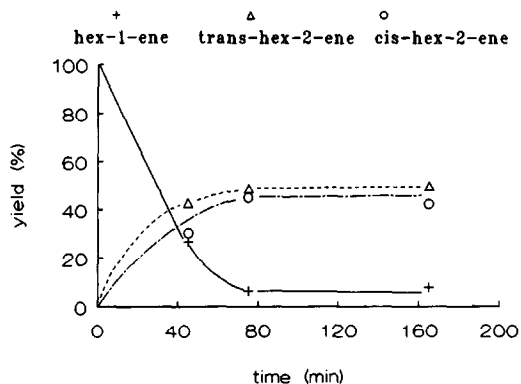


Fig. 1. Isomerization of hex-1-ene with  $\text{HRh}(\text{PPh}_3)_4$  at 40°C. [hex-1-ene]: [Rh] = 160.

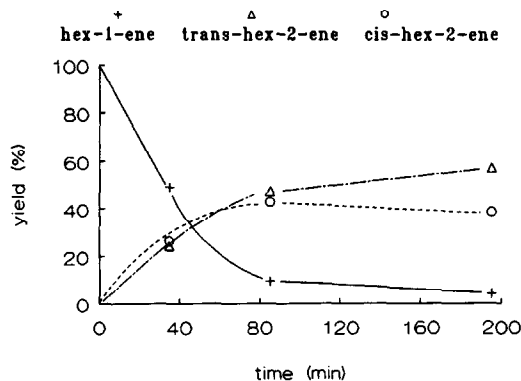


Fig. 2. Isomerization of hex-1-ene with  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  at 40°C. [hex-1-ene]: [Rh] = 160.

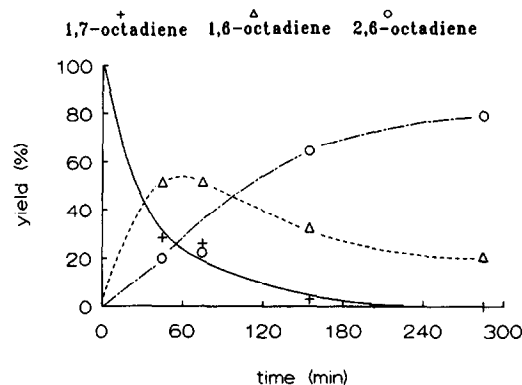


Fig. 3. Isomerization of 1,7-octadiene with  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  at 40°C. [1,7-octadiene]: [Rh] = 120.

$\text{HRh}(\text{PPh}_3)_4$  any isomerization products have been found whereas  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  after 1.5 h produces scarcely 30% of only one product, 2,4-hexadiene (almost equal amounts of *cis* and *trans* isomers). The foregoing reaction was continued for another 2 h but no significant changes in products were found. Lack of catalytic activity of  $\text{HRh}(\text{PPh}_3)_4$  may be explained by difficulties in substrate (1,5-hexadiene) coordination caused by possible steric hindrance. However, catalytic activity of both catalysts is significantly enhanced when dihydrogen (1 atm  $\text{H}_2$ ) is introduced to the reaction medium. In such conditions, in the reaction catalyzed with  $\text{HRh}(\text{PPh}_3)_4$ , after 5 h and ca. 40% conversion the mixture of hex-1-ene and 2,4-hexadienes (*cis* and *trans*) was obtained and then reaction was arrested. The reaction catalyzed with  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  produces after 5 h all possible products, i.e. hex-1-ene, hex-2-ene, 2,4-hexadiene and hexane, and only hexane (100% yield) when reaction is continued up to 6.5 h. The results obtained clearly suggest that both complexes are more active in hydrogenation than in isomerization although both reactions require similar substrate activation, i.e. olefin coordination to rhodium. Therefore, very low concentration of isomerization reaction products cannot be explained by ineffective coordination of 1,5-hexadiene to rhodium centre.

1,7-Octadiene is not isomerized with  $\text{HRh}(\text{PPh}_3)_4$  but isomerization is completed in ca. 3 h with of  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ . The initial main

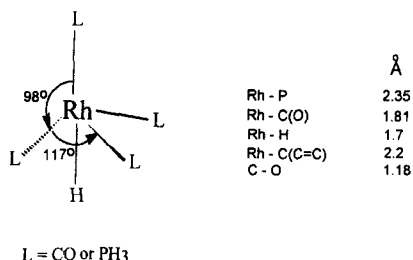


Fig. 4. Model structure of  $\text{HRhL}_4$  complexes with parameters used in calculations.

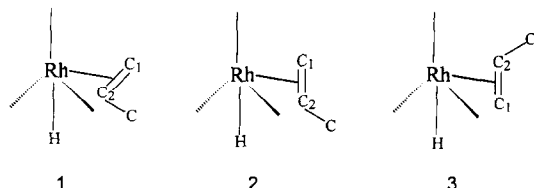


Fig. 5. Model structures of olefin complexes  $\text{HRhL}_3(\text{hexadiene})$  used in calculations.

Table 1  
Calculated parameters for the electronic structure of  $[\text{HRh}(\text{CO})_3(\text{hexadiene})]$  (I)

Isomer	I.1	I.2	I.3
<i>One center densities</i>			
Rh	6.516	6.673	6.777
H	1.355	1.378	1.147
C1	3.177	2.309	3.964
C2	3.508	4.218	2.654
<i>Two center overlap populations</i>			
Rh-H	0.0974	0.1074	0.0893
Rh-C1	0.0369	0.0073	0.0051
Rh-C2	0.0424	0.0068	0.0105
Energy of HOMO (eV):	-6.58	-3.26	-4.02
Energy of LUMO (eV):	-0.72	-0.50	-0.87
$\Delta E_{\text{HOMO}} - \Delta E_{\text{LUMO}}$ (eV):	5.86	2.76	3.15
Character of HOMO:	16.6% Rh	6.0%	9.5%
	22.1%	Rh	Rh
	C1,C2	C2	C1
	24% CO	7.6% H	11.2% H
Character of LUMO:	65.7% CO	68.8%	61.2%
		CO	CO
		10.5% H	

reaction product 1,6-octadiene undergoes further isomerization to 2,6-octadiene (Fig. 3).

From the results obtained it may be concluded that reaction course and yield of products depend both on structure of catalyst as well as that of olefin.

## 2.2. Electronic structure of rhodium-olefin complexes

To understand the isomerization of olefins, especially that of 1,5-hexadiene, the theoretical calculations with Fenske-Hall method have been made for model monoolefinic complexes:  $[\text{HRh}(\text{CO})_3(\text{hexadiene})]$  (I), and  $[\text{HRh}(\text{PH}_3)_3(\text{hexadiene})]$  (II). On the basis of crystallographic data for  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  and  $\text{HRh}(\text{PPh}_3)_4$  [4–6] it was assumed that rhodium surroundings in both model structures (I) and (II) are symmetry intermediates between tetrahedral and trigonal bipyramidal. Three CO (or  $\text{PH}_3$ ) ligands are located in the plane with the rhodium atom placed 0.35 Å above that plane. Hydride ligand lies on a trifold axis passing phosphorous and rhodium (or carbon and rhodium) respectively (Fig. 4). It was assumed that an olefin coordinates to rhodium after dissociation of one ligand in equatorial position. This is in accord with findings by Koga [7] who established that in such a type of complexes coordination of hydride in the axial and olefin in the equatorial positions are preferred. The rotation of olefin around the rhodium-olefin bonding axis is possible and leads to the conformers of different energy [9]. Our calculations have been made for three possible conformers with different orientation of olefin (Fig. 5).  $\text{C}_1=\text{C}_2$  double bond of olefin in isomer (1) lies in a nearly perpendicular plane to the z-axis in such a way that the Rh-C<sub>1</sub> and Rh-C<sub>2</sub> distances are equal 2.2 Å (Fig. 5). The conformers (2) and (3) are formed as a consequence of olefin rotation on +90° and -90° respectively (Fig. 5).

All isomers of complex (I), as expected, have lower electron density on rhodium (6.516–6.777) than that of complex (II) (7.046–7.418) (Table 1 and 2). It seems to be interesting that distribution of one center electron densities in Rh-H fragment is dependent on donor-acceptor properties of remaining ligands. The acceptor character of CO in complexes (I) (structures I.1, I.2 and I.3) causes electron density shift from rhodium to hydrogen which become more hydride in character (one center electron density on hydrogen

Table 2  
Calculated parameters for the electronic structure of  
[HRh(PH<sub>3</sub>)<sub>3</sub>(hexadiene)] (II)

Isomer	II.1	II.2	II.3
<i>One center densities</i>			
Rh	7.046	7.273	7.418
H	0.985	0.942	0.810
C1	2.963	2.869	3.626
C2	3.282	3.857	2.628
<i>Two center overlap populations</i>			
Rh–H	0.1198	0.1255	0.1080
Rh–C1	0.0378	0.0059	0.0041
Rh–C2	0.0439	0.0113	0.0068
Energy of HOMO (eV):	–6.66	–3.05	–4.06
Energy of LUMO (eV):	–1.59	–1.01	–1.91
$\Delta E_{\text{HOMO}} - \Delta E_{\text{LUMO}}$ (eV):	5.07	2.04	2.15
Character of HOMO:	22.2% Rh 20.3% C1,C2	8.9% Rh 41.3% C2 1.3% H	23.8%Rh 28.2% C1 3.4% H
Character of LUMO:	25.3% PH <sub>3</sub>	63.2% PH <sub>3</sub>	45.8% PH <sub>3</sub>

exceeds 1.0). In contrast, PH<sub>3</sub> as a stronger donor ligand shifts electron density towards rhodium (one center electron density on hydrogen is lower than 1.0) (Table 1, 2). Electron density distribution on olefinic carbon atoms (C<sub>1</sub>, C<sub>2</sub>) depends mainly on the conformation of olefin complex. Electron densities on both olefinic carbons (C<sub>1</sub> and C<sub>2</sub>) were found to be almost equal in both isomers I.1 and II.1, respectively. Pronounced asymmetry in the electron density distribution within an olefinic fragment was found for all remaining patterns. That difference is better demonstrated in isomers I.2 and I.3 of [HRh(CO)<sub>3</sub>(hexadiene)] than in II.2 and II.3 of [HRh(PH<sub>3</sub>)<sub>3</sub>(hexadiene)]. Higher electron density is always observed on carbon atoms placed closer to the hydride ligand i.e. on C<sub>2</sub> in I.2 and II.2 isomers and on C<sub>1</sub> in isomers I.3 and II.3, respectively.

That the orbital energy difference ( $\Delta E_{\text{HOMO}} - \Delta E_{\text{LUMO}}$ ) for I.1 and II.1 is twice that of the remaining isomers, demonstrates the higher stability of type 1 isomers (I.1 and II.1) (Table 1 and 2). This is also proved by the higher values

of the total overlap population of Rh–C bond for I.1 and II.1 isomers.

HOMO orbitals of the complexes under study are metal–ligand delocalized orbitals. Their partial hydride character was found in I.2 and I.3 isomers and only traces of hydride character in isomers II.2 and II.3, respectively. The isomers I.2 and II.2 in which the strongest Rh–H bonds were found are of lowest stability according to the ( $\Delta E_{\text{HOMO}} - \Delta E_{\text{LUMO}}$ ) values. In many cases, the existence of strong M–H bonds facilitates insertion of olefin [8].

### 2.3. Mechanism of the isomerization reaction

The insertion of olefin into Rh–H bonding which leads to the rhodium–alkyl intermediate is the key step in the isomerization reaction. It was shown that olefin insertion proceeds more readily when the energy difference between the M–C and M–H bonds is relatively small [8]. Our calculations show clearly that the differences in bond overlap populations of Rh–H and Rh–C bonds are smaller for isomers of complex (I) than those for isomers of complex (II) (Table 1 and 2). Therefore it may be concluded that the presence of a stronger acceptor ligand CO facilitates olefin insertion and isomerization. The above conclusion is confirmed by the results of experiments – catalytic activity of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> (lower electron density on rhodium) in 1,5-hexadiene isomerization was found to be higher than that observed for HRh(PPh<sub>3</sub>)<sub>4</sub> (higher electron density on rhodium).

The insertion of olefin into Rh–H bond may result in the formation of two different alkyl complexes with straight or branched chains. The formation of each of the conformers may be predicted from the electron density distribution in the H–Rh–(C<sub>1</sub>=C<sub>2</sub>) fragment. Least reactive seems to be that complex in which olefin is perpendicularly coordinated to Rh–H bonding (I.1 and II.1). Such a complex is the most stable and additionally has an almost symmetrical electron density distribution on the olefinic core, making both carbon atoms equivalent for the eventual insertion reac-

tion. The insertion is also not favoured by the fact that the energy of the hydride orbital is located below HOMO. In remaining cases the reaction course may depend on the electron density on the hydride ligand as well as on the olefinic carbon atoms. The way of insertion should be in accordance with the rule that the more negative H ligand attacks the carbon atom having the higher electron density. According to this criterion the formation of branched alkyl complexes in the case of isomers I.2 and II.3 can be predicted. In order to realize the isomerization reaction with the complex of lower electron density on rhodium atom (i.e. with the stronger acceptor ligands) the isomer (2), or isomer (3) in case of stronger donor ligands, should arise. Possible formation of those isomers depends on the size of the olefin rotation barrier, which was found to be lower when the  $\pi$ -acceptor ligand is coordinated in the axial position [8]. In our case, easier olefin rotation in complex  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  is demonstrated by its higher reactivity in the isomerization reaction of dienes.

The effect of olefin structure is noticeable when the courses of the isomerization reactions of hex-1-ene and 1,5-hexadiene are compared. The difference in the terminal part of the olefin chains effects drastic changes in reactivity. Hex-1-ene undergoes 100% isomerization to hex-2-ene with  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  and  $\text{HRh}(\text{PPh}_3)_4$  whereas 1,5-hexadiene isomerizes only with  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  to 2,4-hexadiene in ca. 30%. The results obtained may also help to explain the rather low activity of the  $\text{HRh}(\text{PPh}_3)_4$  complex which, owing to steric reasons, scarcely forms isomer (3) in reaction with hexadiene and octadiene.

### 3. Conclusions

The results of the calculations, as well as the experimental studies, allow us to formulate some general findings regarding the formation of active rhodium catalysts of olefin isomerization reaction:

- Electron density on rhodium and coordinated hydride ligand depend on donor–acceptor properties of the remaining coordinated ligands.
- Distribution of electron density on the olefinic carbon atoms of the coordinated olefin depends on the way it is coordinated to the rhodium atom.
- The branched alkyl rhodium complexes are formed only for some of modes of rhodium olefin species (I.2 and II.3) and are determined by the electron density distribution.
- Steric factors, i.e. size of coordinated ligands and shape of the carbon chain are decisive for which isomer of the olefinic complex will be formed.

### 4. Experimental

$\text{HRh}(\text{PPh}_3)_4$  and  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  complexes were prepared according to the literature methods [10].

1,5-Hexadiene, 1,7-octadiene, hex-1-ene and benzene were distilled before use.

Isomerization reactions were studied in a thermostated glass reactor at 40°C in  $\text{N}_2$  atmosphere with constant stirring. For the reactions studied the following amounts of reactants, dissolved in 0.6 cm<sup>3</sup> of benzene, were used: (a) [1,5-hexadiene]:  $3.4 \times 10^{-3}$  mol, [Rh]:  $2.6 \times 10^{-5}$  mol; (b) [1,7-octadiene]:  $2.7 \times 10^{-3}$  mol, [Rh]:  $2.2 \times 10^{-5}$  mol; (c) [hex-1-ene]:  $3.2 \times 10^{-3}$  mol, [Rh]:  $2.0 \times 10^{-5}$  mol.

The reaction products were identified with <sup>1</sup>H NMR (100 MHz, Tesla) and GC–MS, Hewlett-Packard instrument.

### References

- [1] A.M. Trzeciak and J.J. Ziółkowski, *J. Organomet. Chem.*, 464 (1994) 107.
- [2] A.M. Trzeciak and J.J. Ziółkowski, *J. Mol. Catal.*, 43 (1988) 335; A.M. Trzeciak and J.J. Ziółkowski, *J. Organomet. Chem.*, 390 (1990) 105.
- [3] H.B. Hall and R.F. Fenske, *Inorg. Chem.*, 11 (1972) 768.

- [4] R.W. Baker and P. Pauling, *Chem. Commun.*, (1969) 1495.
- [5] S.J. LaPlaca and J.A. Ibers, *J. Am. Chem. Soc.*, 85 (1963) 3501.
- [6] M.R. McLean, R.C. Stevens, R. Bau and T.F. Koetzle, *Inorg. Chim. Acta*, 166 (1989) 173.
- [7] N. Koga, S.-Q. Jin and K. Morokuma, *J. Am. Chem. Soc.*, 110 (1988) 3417.
- [8] E.M. Siegbahn, *J. Am. Chem. Soc.*, 115 (1993) 5803.
- [9] E.G. Lundquist, K. Folting, W.E. Streib, J.C. Huffman, O. Eisenstein and K.G. Caulton, *J. Am. Chem. Soc.*, 112 (1990) 855.
- [10] N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, in G.W. Parshall (Ed.), *Inorganic Synthesis*, Vol. XV, 1974, p. 58.