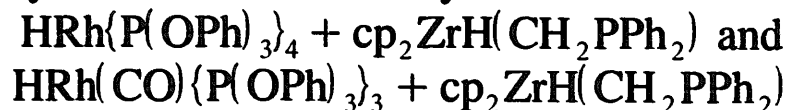


## Hydroformylation of olefins catalysed with bimetallic systems:



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### Abstract

The catalytic activity of bimetallic systems containing the rhodium complex  $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$  or  $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$  and the Zr(IV) complex  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$  was tested in the hydroformylation reaction of 1-hexene and E-Z-2-hexene. An increase in n/iso ratio (from 2.2 to 3.5 in the case of  $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$  and from 0.4 to 3.7 in the case of  $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ ) was observed in 1-hexene hydroformylation in the presence of  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$ .

**Keywords:** Hydroformylation; Bimetallic system; Rhodium; Zirconium; Olefins

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### 1. Introduction

The increasing interest in bimetallic Rh(I)–Zr(IV) catalytic systems observed in recent years has arisen due to the expected high selectivity of such systems in the homogeneous hydroformylation of olefins. Until now, quite satisfactory results for hydroformylation have been obtained with systems in which not only the Zr(IV) species (considered as a special phosphine ligand) but also other phosphorus ligands were applied [1–5].

Particularly high selectivity (n/iso > 5) was obtained in 1-hexene hydroformylation catalysed by the  $\text{HRh}\{\text{P}(\text{OPh})_3\}_4 + \text{cp}_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2$  system [3].

The activity of bimetallic systems with only Zr(IV) ‘phosphine’ was also studied [6–9].

The complex  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$  itself catalyses the isomerization of 1,5-cyclooctadiene to 1,3-cyclooctadiene and 1-hexene to E-Z-2-hexene, whereas in the presence of dihydrogen it catalyses the hydrogenation of mono- and diolefins to the corresponding saturated species [10,11]. This complex was recently applied by us, together with  $\text{Rh}(\text{acac})(\text{CO})_2$ , as a cata-

lyst precursor for the hydroformylation of 1-hexene, 1,5-hexadiene and 1,7-octadiene [9].

$\text{Cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$  reacts with rhodium phosphite complexes  $\{\text{Rh}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}\{\text{P}(\text{OPh})_3\}_3$ ,  $\text{Rh}\{\text{P}(\text{OPh})_3\}_4\text{X}$  (X =  $\text{ClO}_4^-$ ,  $\text{BPh}_4^-$ ) and the structure of the products obtained depends strongly on the structure of the initial rhodium complex used [12].

In reaction with the orthometallated  $\text{Rh}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}\{\text{P}(\text{OPh})_3\}_3$  complex,  $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$  was first obtained, which next resulted in the formation of the substitution reaction product  $\text{HRh}\{\text{P}(\text{OPh})_3\}_3\{\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)\}$  on reaction with a second molecule of  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$ . Mechanistic studies of that reaction show that the  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$  is both a  $\text{H}^+$  and a  $\text{H}^-$  donor [12]. With respect to rhodium complexes of formula  $\text{Rh}\{\text{P}(\text{OPh})_3\}_4\text{X}$  (X =  $\text{ClO}_4^-$ ,  $\text{BPh}_4^-$ ), the Zr(IV) complex may be considered as a  $\text{H}^-$  donor, and  $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$  was formed as a reaction product [12].

In this paper the results of 1-hexene hydroformylation with  $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$  and  $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$  modified with a Zr(IV) complex of formula  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$  are presented. The main task is to elucidate the catalytic activity of the bimetallic systems in comparison with those found for the  $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$  and  $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$  species.

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## 2. Identification of bimetallic complexes

Identification of the bimetallic complexes formed as intermediates in the hydroformylation reaction mixture was successfully carried out using  $^1\text{H}$  and  $^{31}\text{P}$  NMR methods. In the mixture containing  $\text{HRh}(\text{P}(\text{O}Ph)_3)_4$  and  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$ ,  $\text{HRh}(\text{P}(\text{O}Ph)_3)_3\{\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)\}$  was found as the first reaction product. The rate of formation of that complex increased with increasing concentration of  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$ . The above bimetallic complex was obtained earlier from reaction of other rhodium–phosphite complexes, e.g.  $\text{Rh}(\text{P}(\text{O}Ph)_3)_4\text{X}$ , with Zr(IV) species [12].

After over 4 h of reaction of  $\text{HRh}(\text{P}(\text{O}Ph)_3)_4$  with  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$ , additional NMR bands characteristic of the second complex,  $\text{HRh}(\text{P}(\text{O}Ph)_3)_2\{\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)\}_2$ , were observed. The spectroscopic data for both complexes, pointing out their different symmetry, are collected in Table 1.

In the case of complex  $\text{HRh}(\text{P}(\text{O}Ph)_3)_3\{\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)\}$ , three  $\text{P}(\text{O}Ph)_3$  ligands are coordinated in the basal plane of the trigonal bipyramid, whereas  $\text{H}^-$  and  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$  ligands occupy the remaining sites in *trans* position to each other. This kind of coordination is proved by the high value of  $J_{\text{P}_{\text{trans}}-\text{H}} = 72\text{ Hz}$ . The spectroscopic parameters of this complex are very close to those obtained for its analog  $\text{HRh}(\text{P}(\text{O}Ph)_3)_3\{\text{cp}_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2\}$  [3], suggesting a similar structure for both compounds. However, from the  $^1\text{H}$  NMR spectrum of  $\text{HRh}(\text{P}(\text{O}Ph)_3)_3\{\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)\}_2$ , two  $J_{\text{P}-\text{H}}$  values (42 and 6 Hz) were obtained. The larger value is similar to that found for the complex of formula  $\text{HRh}(\text{P}(\text{O}Ph)_3)_4$  ( $J_{\text{P}-\text{H}} = 44\text{ Hz}$ ) [13], which may suggest a similar tetrahedral arrangement of ligands around the rhodium center.

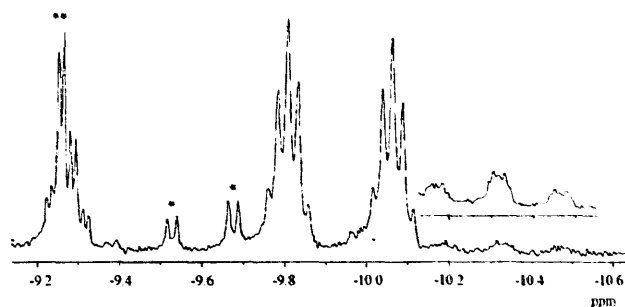


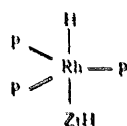
Fig. 1. Hydride region of  $^1\text{H}$  NMR spectrum measured during the reaction of  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3 + \text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$  in  $\text{C}_6\text{D}_6$ .  $[\text{Zr}]:[\text{Rh}] = 2$ .  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3$ ,  $\text{HRh}(\text{P}(\text{O}Ph)_3)_4$ .

The reaction of  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3$  with  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$  is more complicated, and leads to a mixture of  $\text{HRh}(\text{P}(\text{O}Ph)_3)_3\{\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)\}$  and  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_2\{\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)\}_2$  complexes, identified by  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectra (Fig. 1). The formation of bimetallic complexes depends on the CO concentration, whereas the effect of  $\text{H}_2$  atmosphere on the reaction course was not found (Scheme 1).

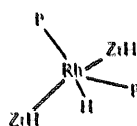
Spectroscopic data for  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_2\{\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)\}_2$  are comparable with those obtained for the bimetallic complex  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_2\{\text{cp}_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2\}$  [3]. Both complexes have a trigonal bipyramidal structure with P-ligands in one plane and  $\text{CO}/\text{H}^-$  in *trans* position. This is proved by the relatively small  $J_{\text{P}-\text{H}}$  and  $J_{\text{Rh}-\text{H}}$  values (Table 1), close to those observed for  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3$  [14]. The complex  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3\{\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)\}$  is stable under hydroformylation reaction conditions and, according to spectroscopic studies of the post-reaction mixture, can be postulated as the main catalytically active form

Table 1  
 $^1\text{H}$  and  $^{31}\text{P}$  NMR data of bimetallic rhodium–zirconium complexes in  $\text{C}_6\text{D}_6$

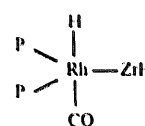
	$\text{HRh}(\text{P}(\text{O}Ph)_3)_3\{\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)\}$	$\text{HRh}(\text{P}(\text{O}Ph)_3)_2\{\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)\}_2$	$\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_2\{\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)\}_2$
$^{31}\text{P}$ NMR			
$\delta_1, \delta_2$ (ppm)	133.3	19.5	131.2
$J_{\text{Rh}-\text{P}}$ (Hz)	247	112.2	266
$J_{\text{P}-\text{P}}$ (Hz)	17	58	125
$J_{\text{P}_{\text{trans}}-\text{H}}$ (Hz)	72	—	249
$J_{\text{P}_{\text{cis}}-\text{H}}$ (Hz)	8	42.6	128
$J_{\text{Rh}-\text{H}}$ (Hz)	8	6	135
$^1\text{H}$ NMR			
$\delta$ (ppm)	doublet of pseudo-quintets	triplet of multiplets	pseudo-quartet of doublets
	-9.9	-10.32	-9.27
$J_{\text{P}_{\text{trans}}-\text{H}}$ (Hz)	72	—	—
$J_{\text{P}_{\text{cis}}-\text{H}}$ (Hz)	8	42.6	5
$J_{\text{Rh}-\text{H}}$ (Hz)	8	6	4

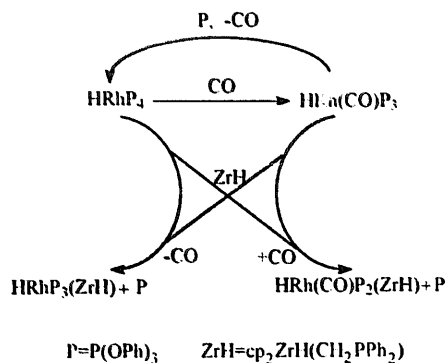


P =  $\text{P}(\text{O}Ph)_3$



ZrH =  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$





Scheme 1.

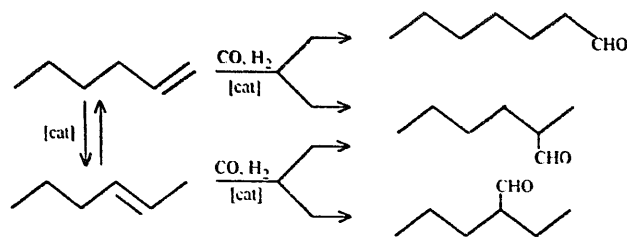
of the bimetallic complex, detected even at small excesses of  $cp_2ZrH(CH_2PPh_2)$ .

### 3. Hydroformylation of 1-hexene and E-,Z-2-hexene

The modifying effect of Zr(IV) 'phosphine' on the rhodium catalyst precursor is considered in relation to the results of hydroformylation of 1-hexene and E-,Z-2-hexene catalysed by only the rhodium catalysts  $HRh\{P(OPh)_3\}_4$  or  $HRh(CO)\{P(OPh)_3\}_3$ , respectively. The common behavior of both catalysts is high activity in the isomerization of 1-hexene to E-,Z-2-hexene under the reaction conditions optimal for hydroformylation (i.e. 80°C, 10 atm  $H_2/CO$ ). After 30 min of hydroformylation of 1-hexene with only  $HRh(CO)\{P(OPh)_3\}_3$ , the reaction mixture contained only aldehydes and E-,Z-2-hexene, which is the next substrate of further hydroformylation (Tables 2 and 3).

Separate studies of the hydroformylation of E-,Z-2-hexene showed that the main reaction products are branched aldehydes: 2-ethylpentanal and 2-methylhexanal with 16% n-heptanal (Scheme 2) and constant n/iso ratio 0.2.

In the hydroformylation of 1-hexene with  $HRh(CO)\{P(OPh)_3\}_3$ , the n/iso ratio was first 0.9 (after



Scheme 2.

30 min) and then decreased to 0.2 (after 160 min).

Both olefins (1-hexene and E-,Z-2-hexene) undergo 100% conversion after 3 h with almost identical selectivity. One may conclude that during 1-hexene hydroformylation the parallel isomerization reaction is much faster, and as a consequence diminishes the selectivity of 1-hexene hydroformylation. A slightly higher selectivity of 1-hexene hydroformylation (n/iso ca. 2) is obtained with the  $HRh\{P(OPh)_3\}_4$  catalyst, which is much less active in the isomerization of 1-hexene to E-,Z-2-hexene, finally allowing a relatively high yield of n-heptanal to be obtained.

The application of Zr(IV) 'phosphine' as a modifying ligand for  $HRh(CO)\{P(OPh)_3\}_3$  and  $HRh\{P(OPh)_3\}_4$  catalysts causes an increase of selectivity in both cases (for the reaction catalysed with  $HRh\{P(OPh)_3\}_4$  at  $[Zr]:[Rh] = 1$ , n/iso = 3.4 was obtained, whereas for the reaction catalysed with  $HRh(CO)\{P(OPh)_3\}_3$  higher selectivity was achieved at  $[Zr]:[Rh] = 1.0$ ).

The presence of Zr(IV) 'phosphine' in both systems led to a decrease of 2-ethylpentanal yield up to total decay. The absence of 2-ethylpentanal manifests the lack of E-,Z-2-hexene hydroformylation [15], as a consequence of small or neglected isomerization of 1-hexene to E-,Z-2-hexene or a very slow rate of hydroformylation of E-,Z-2-hexene. The isomerization is significantly slowed down in the presence of Zr(IV) 'phosphine'. The conversion of 1-hexene after 30 min of hydroformylation with  $HRh(CO)\{P(OPh)_3\}_3$  was total, whereas after the application of a modifying Zr(IV)

Table 2  
Hydroformylation of 1-hexene catalysed by the system  $HRh\{P(OPh)_3\}_4 + cp_2ZrH(CH_2PPh_2)$

[Zr] ( $\times 10^{-5}$ mol)	[Zr]:[Rh]	Products (mol%)			E-,Z-2-hexene	1-Hexene	Time (min)	n/iso
		Aldehydes						
		2-Ethyl pentanal	2-Methyl hexanal	Heptanal				
0	0	6	16	34	36	—	110	1.6
0	0	8	19	58	26	—	160	2.2
1.3	1.0	1	8	32	45	—	95	3.4
2.5	2.0	—	16	55	35	—	345	3.5
5.4	4.0	—	12	33	35	—	280	2.9
6.3	5.0	—	12	34	44	2	290	2.9
10.0	8.0	—	6	12	—	53	515	2.1

Reaction conditions: 80°C, 10 atm,  $H_2/CO = 1$ ,  $[1\text{-hexene}]:[Rh] = 520$ ,  $[Rh] = 1.25 \times 10^{-5}$  mol.

**Table 3**  
Hydroformylation of 1-hexene catalysed by the system  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3 + \text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$

[Zr] ( $\times 10^{-5}$ mol)	[Zr]:[Rh]	Products (mol%)				E-,Z-2-hexene	1-Hexene	Time (min)	n/iso
		Aldehydes							
		2-Ethyl pentanal	2-Methyl hexanal	Heptanal					
0	0	13	29	22	30	—	60	0.5	
0	0	24	46	25	4	—	135	0.4	
1.5	1.0	2	14	59	28	—	200	3.7	
2.5	1.7	—	14	45	17	3	100	3.3	
3.2	2.6	3	14	51	32	—	145	3.1	
3.8	3.0	—	14	44	44	—	235	3.2	
5.8	4.6	—	13	36	50	—	220	2.9	
11.4	9.2	—	5	10	43	34	505	2.0	

Reaction conditions: 80°C, 10 atm,  $\text{H}_2/\text{CO} = 1$ , [1-hexene]:[Rh] = 520, [Rh] =  $1.25 \times 10^{-5}$  mol.

complex 13% of 1-hexene in the reaction mixture was still found after 60 min.

With an increase of Zr(IV) 'phosphine' concentration, a decrease of reaction rate as well as n/iso ratio was observed. The average content of E-,Z-2-hexene in the reaction products was equal to 30%. The highest selectivity was obtained at a small excess of Zr(IV) 'phosphine' ([Zr]:[Rh] = 1 to 3).

Some experiments on E-,Z-2-hexene hydroformylation catalysed with the system containing  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3$  and  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$  have been carried out, and almost solely iso-aldehydes were obtained ( $n/\text{iso} \leq 0.1$ , nearly two times smaller than with  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3$  alone used as a catalyst) (Table 4). The reaction product content suggests that the modification of Rh catalysts with Zr(IV) 'phosphine' restrains almost totally the isomerization of E-,Z-2-hexene to 1-hexene, leading to a decrease of n-heptanal yield.

The presence of  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$  inhibits quite effectively the hydroformylation of E-,Z-2-hexene, and the inhibiting effect is stronger at higher concentrations

(Table 4). The total conversion of E-,Z-2-hexene in the presence of  $\text{HRh}(\text{P}(\text{O}Ph)_3)_3$  or  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3$  was achieved after 4 h, whereas with Zr(IV) 'phosphine' ([Zr]:[Rh] = 2.7) after 8 h 48% of unreacted E-,Z-2-hexene was still found in the reaction mixture.

#### 4. Conclusions

(1) The selectivity of the hydroformylation reaction catalysed with bimetallic Rh–Zr catalysts is higher than that in the reaction catalysed with rhodium only precursors  $\text{HRh}(\text{P}(\text{O}Ph)_3)_3$  or  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3$ .

(2) The selectivity increase is caused by the inhibiting effect of the bimetallic Rh–Zr catalyst on 1-hexene to E-,Z-2-hexene isomerization and E-,Z-2-hexene hydroformylation, whereas the Rh complexes alone are rather effective catalysts in both the isomerization and hydroformylation of E-,Z-2-hexene.

(3) It is worthwhile noting that under the applied reaction conditions the bimetallic system is much less

**Table 4**  
Hydroformylation of E-,Z-2-hexene catalysed by  $\text{HRh}(\text{P}(\text{O}Ph)_3)_3$ ,  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3$ , and  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3 + \text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$

[Zr] ( $\times 10^{-5}$ mol)	[Zr]:[Rh]	Products (mol%)				Time (min)	n/iso
		Aldehydes					
		2-Ethyl pentanal	2-Methyl hexanal	Heptanal	E-,Z-2-hexene		
<i>HRh(P(O)Ph)<sub>3</sub>)<sub>3</sub></i>							
0	0	27	33	11	11	105	0.2
0	0	34	48	13	—	260	0.2
<i>HRh(CO)(P(O)Ph)<sub>3</sub>)<sub>3</sub></i>							
0	0	16	26	10	26	120	0.2
0	0	32	53	16	3	220	0.2
<i>HRh(CO)(P(O)Ph)<sub>3</sub>)<sub>3</sub> + cp<sub>2</sub>ZrH(CH<sub>2</sub>PPh<sub>2</sub>)</i>							
1.5	1.2	43	51	10	3	180	0.1
3.5	2.7	17	17	3	48	480	0.1

Reaction conditions: 80°C, 10 atm,  $\text{H}_2/\text{CO} = 1$ , [E-,Z-2-hexene]:[Rh] = 520, [Rh] =  $1.25 \times 10^{-5}$  mol.

active in isomerization than the Zr(IV) complex alone [10,11]

## 5. Experimental

Rhodium and zirconium complexes were prepared according to the literature methods:  $\text{HRh}(\text{P}(\text{O}Ph)_3)_4$  [13],  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3$  [14],  $\text{cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$  [16]. Solvents (toluene, benzene) and olefins were distilled before use. The hydroformylation reaction was carried out in a thermostated steel autoclave ( $40\text{ cm}^3$ ) with magnetic stirrer. Samples of  $\text{HRh}(\text{P}(\text{O}Ph)_3)_4$  ( $0.017\text{ g}$ ,  $1.25 \times 10^{-5}\text{ mol}$ ) or  $\text{HRh}(\text{CO})(\text{P}(\text{O}Ph)_3)_3$  ( $0.013\text{ g}$ ,  $1.25 \times 10^{-5}\text{ mol}$ ) and the zirconium complex ( $0.005$  to  $0.05\text{ g}$ ,  $1.3 \times 10^{-5}$  to  $1.3 \times 10^{-4}\text{ mol}$ ) were introduced into the autoclave in nitrogen atmosphere. Next, toluene ( $1.5\text{ cm}^3$ ) and 1-hexene ( $0.8\text{ cm}^3$ ) were added. Finally, the autoclave was filled up with a  $\text{H}_2/\text{CO} = 1$  mixture at 10 atm. Reaction products were identified after vacuum distillation by GC-MS (Hewlett-Packard) using xylene as internal standard. In all analyses the separate signals of Z- and E-hexene-2 have been found in GC. A HP column  $5\text{ m} \times 25\text{ m} \times 0.2\text{ mm} \times 0.33\text{ }\mu\text{m}$  (film thickness) was used for product analysis. IR spectra were recorded on a Nicolet Impact 400 and NMR spectra on a Bruker 300 MHz (121.5 MHz for  $^{31}\text{P}$  NMR).

MS data of reaction products:

(a) *n*-Heptanal. 114 ( $\text{M}^+$ , 1); 96 (7); 95 (1); 86 (10); 81 (15); 71 (21); 70 (61); 68 (13); 57 (48); 55 (50); 45 (20); 44 (100); 43 (74); 42 (57); 41 (74); 39 (28).

(b) 2-Methylhexanal. 114 ( $\text{M}^+$ , 1); 96 (1); 91 (1); 85 (2); 81 (1); 72 (7); 71 (4); 58 (100); 57 (20); 53 (2); 43 (70); 41 (25).

(c) 2-Ethylpentanal. 114 ( $\text{M}^+$ , 1); 85 (4); 72 (45); 57 (49); 43 (100); 41 (32); 39 (13).

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