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Hydroformylation of olefins catalysed by alkoxycarbonylcyclopentadienyl complexes of rhodium(I)

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Abstract

The hydroformylation of hex-1-ene and styrene with syngas (30 bar of 1:1 CO/H_2) in the presence of the alkoxycarbonylcyclopentadienyl rhodium(I) complexes [Rh{$C_5H_4CO_2X$}(L,L)] [X = $–CH_2CH{=}CH_2$, $–(CHR)_2OH$ (R = H, Me); L,L = 2CO, NBD] has been studied and compared with the unsubstituted system [Rh(C_5H_5)NBD]. The influence of various reaction parameters on the catalytic activity and selectivity is presented and discussed.

Keywords: Alkoxycarbonylcyclopentadienyl; Rhodium(I) complexes; Hydroformylation; Hex-1-ene; Styrene

1. Introduction

The hydroformylation of unsaturated bonds is a long-standing synthesis for industrial chemistry. Although several catalysts are known to promote the hydroformylation reaction with good yields and regioselectivity, this is still an area of great interest due to the wide utilisation of aldehydes in the synthesis of bulk and fine chemicals.

Rhodium is one of the most important homogeneous catalyst for this reaction [1]. In spite of the enormous amount of research on the synthesis and use of phosphorus-containing rhodium catalysts, the interest on phosphine-free complexes has been poor. Among these last compounds cyclopentadienyl rhodium complexes have shown to be efficient catalysts for hydroformylation [2–6] and many other reactions [7,8].

Recently, in the course of our studies concerning the development of new ester-functionalised Cp ligands, we have presented the high yields, one-step synthesis of a variety of alkoxycarbonylcyclopentadienides Na[$C_5H_4CO_2X$] [X = Ph [9], $–CH_2CH{=}CH_2$ [10b], $–(CHR)_2OH$ (R = H [10], Me [11])]. The easy availability of such new ligands provided a valuable and straightforward route to rhodium complexes of the type [Rh{$C_5H_4CO_2X$}(L,L)] [L,L = 2CO, NBD] and in preliminary tests, lately presented, we briefly reported that complexes in which X = $–(CHR)_2OH$ (R = H, Me) resulted catalytically active in the hydroformylation of hex-1-ene [11].

This preliminary investigation prompted a more extensive study and we herein report the results of the catalytic activity of some alkoxycarbonylcyclopentadienyl rhodium(I) complexes (Scheme 1) in the hydroformylation of hex-1-ene and styrene. The influence

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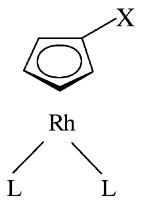

Scheme 1. L,L = NBD, X = $–CO_2CH_2CH_2OH$ (**1**); L,L = 2CO, X = $–CO_2CH_2CH_2OH$ (**2**); L,L = 2CO, X = $–CO_2CH_2CH{=}CH_2$ (**3**); L,L = NBD, X = (*dl*)$–CO_2CH(Me)CH(Me)OH$ (**4**); L,L = NBD, X = (*S*,*S*)$–CO_2CH(Me)CH(Me)OH$ (**5**); L,L = NBD, X = H (**6**).

of various reaction parameters on the catalytic activity and selectivity is presented and discussed.

2. Experimental

2.1. Instruments

A GC Shimadzu GC-14A, equipped with a flame ionization detector (FID), and integrator Shimadzu C-R4A was used to evaluate the hydroformylation products, while a GC Perkin-Elmer mod. 8320, equipped with a FID detector, was employed to analyse the composition of the residual hexenes. A GC-MS Shimadzu QP 5050 instrument was used to verify the identity of the products obtained. A 150 ml Parr autoclave was employed for the catalytic tests. IR spectra were recorded with a FT-IR Perkin-Elmer 1760-X instrument, using a PC and the PE-SPECTRA V2000 program.

2.2. Materials

All manipulations were routinely performed under nitrogen atmosphere, using Schlenk tube techniques. THF (RPE C. Erba) was dried by refluxing over Na/K under nitrogen atmosphere, distilled (bp 65 °C) and stored under nitrogen. Hex-1-ene (Aldrich), eluted through an Al_2O_3 column and distilled, had bp 64 °C. Styrene (Aldrich), distilled prior to use, had bp 145 °C. The complexes **1**–**6** were prepared as previously described [10,11].

2.3. Catalytic hydroformylation experiments

The reactions were carried out in a 150 ml stainless steel Parr autoclave stirred with a self-sealing packing gland and electrically thermostatted (±1 °C). A solution of 0.02 mmol of complexes **1**–**6** and 2 mmol of hex-1-ene or styrene in 25 ml of THF was prepared in a Schlenk tube and transferred into the autoclave by suction. The autoclave was pressurised at room temperature with CO/H_2 mixture (1/1) at 30 bar. The reaction mixture was stirred and heated at the prefixed temperature for the established time. After cooling the autoclave to r.t. the gases were vented and the solution collected. The reaction products were analysed by GC. GC-MS spectra were collected to confirm the nature of the products obtained.

A PPG column ('Polypropylene Glycol' supported on Chromosorb W LB-550 X) was used to analyse the hex-1-ene hydroformylation products. The oven was kept at 35 °C for 5 min, then heated at a rate of 5 °C/min up to 50 °C and kept at this temperature for 2 min, then heated up to 100 °C, with a rate of 1 °C/min and kept at this temperature for 60 min. A Chrompack capillary column Al_2O_3/Na_2SO_4 PLOT (length: 50 m, diameter: 0.45 mm) was used to analyse the residual hexenes: the column was kept at 130 °C for 32 min, heated with a rate of 30 °C/min up to 200 °C and kept at this temperature for 16 min.

A 2 m FFAP packed column ('Free Fatty Acids Phase' supported on Chromosorb G AW-DMCS 5%) was used to analyse the styrene hydroformylation products; the column was kept at 40 °C for 15 min, then heated with a rate of 5 °C/min up to 140 °C and kept at this temperature for 40 min.

2.4. Reactivity of *1* with CO

A THF solution (10 ml) of **1** (10 mg, 0.029 mmol) was introduced in a Parr autoclave and 15 bar of CO was added. The vessel was heated at 60 °C for 4 h. Every hour a sample of the solution was collected and immediately analysed by IR spectroscopy in the range between 2500 and 1500 cm^{-1}. The IR spectra were unchanged with respect to the initial one.

2.5. Reactivity of *1* with CO and H_2

A THF solution (10 ml) of **1** (10 mg, 0.029 mmol) was introduced in a Parr autoclave, 15 bar of CO and 15 bar of hydrogen were added. The vessel was heated at 60 °C for 4 h. Every hour a sample of the solution was collected and immediately analysed by IR in the

range between 2500 and 1500 cm^{-1}. The IR spectra were unchanged with respect to the initial one.

3. Results and discussions

The complexes **1**–**6** employed to investigate their catalytic activity in the hydroformylation are shown in Scheme 1. The conditions adopted were: a temperature range among 40 and 100 °C, a THF solution, an olefin/catalyst ratio of 100 and a syngas pressure of 30 bar (CO/H_2: 1/1). The reaction products were readily analysed and identified by GC-MS spectra and quantified by GC analysis. The data obtained are reported in Tables 1–3.

3.1. Catalytic activity in the hydroformylation of hex-1-ene

The catalytic activity of the complexes **1**–**3** is strongly affected by the reaction temperature (Tables 1 and 2).

In the presence of **1**, rising the temperature from 40 to 60 °C, the olefin conversion increases from 7.8% (entry 1) to 98.8% (entry 2). As a consequence the aldehyde yield increases from 3.3 to 70.2%. An analogous behaviour is shown by **3** (entries 8 and 9). In the same way the complex **2**, containing two CO groups instead of a norbornadiene (NBD) ligand, does not show any activity at 40 °C (entry 3), however at 60 °C the conversion of hex-1-ene is 68.0% (entry 4) with an aldehydes yield of 41.7%.

Different substituents on the cyclopentadienyl moiety affect the catalytic activity as shown by the data summarised in Fig. 1.

The presence of a lateral chain on the cyclopentadienyl ligand extensively improves the catalytic activity. Working at 60 °C the olefin conversion increases from 21.5%, using **6** (entry 14), to 98.8% in the presence of **1** (entry 2), and this behaviour is reflected by a strong increase of hydroformylation products (70.2% compared to 2.7%).

Surprisingly, the complex **1** containing the NBD ligand gives a higher conversion and a higher amount of aldehydes (entry 2) than the corresponding dicarbonyl complex **2** (entry 4). The higher catalytic activity of **1** implies that the NBD ligand is not easily displaced by CO. A test was performed under hydroformylation conditions to confirm this hypothesis. The NBD ligand, present in **1**, is not displaced by CO if this complex is heated at 60 °C for 4 h under a CO atmosphere of 15 bar. Furthermore, even if H_2 (15 bar) was subsequently added to the system and the solution heated again at 60 °C for 4 h, the complex **1** remained unchanged.

The catalytic activity of **2**, containing a $–CH_2–CH_2–OH$ group on the lateral chain of the cyclopentadienyl ligand (entry 4), is almost the same of that

Table 1
Hydroformylation of hex-1-ene

Entry no.	Catalyst	*T* (°C)	*p*(CO) (bar)	*p*(H_2) (bar)	Conversion (%)	Aldehydes (%)	Regioselectivity (heptanal/aldehydes) (%)	Isomerised olefins (%)	Hydrocarbons (%)
1	**1**	40	15	15	7.8	3.3	63.2	4.0	0.5
2	**1**	60	15	15	98.8	70.2	68.1	28.1	0.5
3	**2**	40	15	15	0	0	ND	0	0
4	**2**	60	15	15	68.0	41.7	69.5	25.3	1.0
5	**2**	60	30	15	74.0	44.0	66.4	29.6	0.4
6	**2**	60	15	30	69.8	47.7	68.0	21.6	0.5
7	**2**	80	15	15	97.4	51.2	43.6	45.5	0.7
8	**3**	40	15	15	3.7	1.9	59.7	1.5	0.2
9	**3**	60	15	15	71.4	43.0	70.6	27.9	0.5
10	**4**	60	15	15	43.2	22.6	67.7	20.8	0
11	**4**	80	15	15	94.6	28.3	71.0	66.0	0.4
12	**4**	100	15	15	96.9	72.5	42.7	23.0	1.4
13	**5**	60	15	15	20.5	4.6	69.6	15.0	0.9
14	**6**	60	15	15	21.5	2.7	74.8	13.2	5.6

Reaction conditions: catalyst, 20 μmol; hex-1-ene, 2 mmol; THF, 25 ml; reaction time, 4 h.

Table 2
Hydroformylation of hex-1-ene—reaction products composition

Entry no.	Catalyst	T (°C)	p(CO) (bar)	p(H_2) (bar)	Hexane (%)	Hex-1-ene (%)	*cis*-Hex-2-ene (%)	*trans*-Hex-2-ene (%)	*cis*-Hex-3-ene (%)	*trans*-Hex-3-ene (%)	Heptanal (%)	2-Methyl-hexanal (%)	2-Ethyl-pentanal (%)
15	**1**	40	15	15	0.5	92.2	2.0	1.1	0.3	0.6	2.1	1.2	0
16	**1**	60	15	15	0.5	1.2	9.7	14.5	0.7	3.1	47.9	22.4	0
17	**2**	40	15	15	0	100	0	0	0	0	0	0	0
18	**2**	60	15	15	1.0	32.0	7.6	15.1	0.1	2.5	29.0	12.7	0
19	**2**	60	30	15	0.4	26.0	7.5	17.1	0.4	4.6	29.2	14.8	0
20	**2**	60	15	30	0.5	30.2	7.0	13.3	0.6	0.7	32.4	15.3	0
21	**2**	80	15	15	0.7	2.6	9.7	25.1	1.0	9.7	22.3	22.5	6.4
22	**3**	40	15	15	0.2	96.3	0.7	0.3	0.2	0.4	1.1	0.8	0
23	**3**	60	15	15	0.5	28.6	8.1	18.5	0.3	0.9	30.4	12.7	0
24	**4**	60	15	15	0	56.8	7.9	12.7	0	0	15.3	7.3	0
25	**4**	80	15	15	0.4	5.4	14.2	38.0	2.8	10.9	20.1	8.2	0
26	**4**	100	15	15	1.4	3.1	4.1	11.8	3.0	4.2	30.9	31.4	10.1
27	**5**	60	15	15	0.9	79.5	5.5	5.5	1.8	2.2	3.2	1.4	0
28	**6**	60	15	15	5.6	78.5	5.3	6.0	1.1	0.8	2.0	0.7	0

Reaction conditions: catalyst, 20 μmol; hex-1-ene, 2 mmol; THF, 25 ml; reaction time, 4 h.

Table 3
Hydroformylation of styrene

Entry no.	Catalyst	Conversion (%)	2-Phenylpropanal (%)	3-Phenylpropanal (%)	Regioselectivity (2-phenylpropanal/aldehydes) (%)
29	**1**	53.1	30.0	23.1	56.4
30	**2**	78.6	42.6	36.0	54.2
31	**3**	53.5	28.8	24.7	54.0
32	**4**	51.5	26.4	25.1	51.1
33	**5**	30.0	23.5	6.5	78.4
34	**6**	27.0	15.6	11.4	57.9

Reaction conditions: catalyst, 20 μmol; styrene, 2 mmol; THF, 25 ml; p(CO), 15 atm; $p(H_2)$, 15 atm; T, 80 °C; reaction time 4 h.

reported for **3**, containing a $–CH_2–CH=CH_2$ group (entry 9). These two catalysts give the same olefin conversion and amount of hydroformylation products.

On the other hand, an increment of the steric hindrance on the lateral chain of the cyclopentadienyl ligand, introducing two methyl substituents, reduces the catalytic activity of **4** (conversion 43.2%, entry 10) if compared to that reported for **1** (conversion 98.8%, entry 2) containing the $–CH_2–CH_2–OH$ group. Surprisingly the catalytic activity of **4** is higher than that shown by the catalyst containing an unsubstituted cyclopentadienyl ring **6** (conversion 21.5%, entry 14). As a consequence of the reduced activity, also the amount of aldehyde formed is different using the complexes **4**, **1** and **6** (22.6, 70.2 and 2.7%, respectively).

The racemic complex **4** shows a higher olefin conversion and yield of aldehydes than its diastereoisomer, the *S,S* complex **5** that, as reported earlier [11], significantly differs in the conformation and configuration of the –CH(Me)CH(Me)OH side chain containing two chiral centres.

A comparison of the catalytic activity of **2** at different hydrogen pressures (15 or 30 bar, entries 5 and 6) shows that an increase of hydrogen pressure slightly reduces the olefin conversion, somewhat increases the formation of aldehydes. The beneficial effect of a higher pressure of H_2 is in agreement with the hypothesis that the rate determining step is connected with the hydrogenolysis of a [Rh(acyl)] complex as reported by van Leeuwen for phosphine substituted rhodium complexes [12–14] and by Garland for unmodified rhodium catalysts [14]. Furthermore, as reported by Garland and co-workers [14] the hydrogenolysis of acyl rhodium complexes follows a first-order kinetic rate with respect to hydrogen, in agreement with a beneficial influence of the hydrogen pressure observed using cylopentadienyl rhodium catalysts (entry 6).

3.2. Selectivity in the hydroformylation of hex-1-ene

Heptanal and 2-methylhexanal are the aldehydes usually formed in the hydroformylation of hex-1-ene (Table 2). Catalysts **1**–**5** give the linear aldehyde with almost the same regioselectivity at 60 °C (heptanal/total aldehydes = 67.7–70.6%), while **6** gives a slightly higher regioselectivity (74.8%, entry 14). The regioselectivities obtained using these catalysts are almost the same of those obtained by Lazzaroni et al. [15] in the hydroformylation of the same olefin at 100 °C in the presence of $Rh_4(CO)_{12}$.

The different catalytic activity but the same regioselectivity showed by complexes **1** and **2** in the hydroformylation of hex-1-ene supports the hypothesis that a common catalytically active intermediate is formed starting from the two precursors containing the same cyclopentadienyl ligand.

The regioselectivity is apparently affected by the reaction temperature: it is 67.7% or higher at 60 °C, but lower than 50% at 80 °C (entry 7). This decrease is more rapid in the presence of **4**: the regioselectivity is 71.0% at 80 °C (entry 11), but goes down to 42.7% at 100 °C (entry 12). The decrease of the regioselectivity when the reaction temperature increases is not usual for $Rh_4(CO)_{12}$ catalyst as reported by Lazzaroni et al. [15]. This behaviour may be easily explained if we consider that already at 80 °C the residual olefin is largely isomerised (entry 25) and consequently at 100 °C with an almost complete conversion of the starting olefin, the hydroformylation of internal olefins, formed in the course of the reaction, gives mainly branched aldehydes. As a consequence

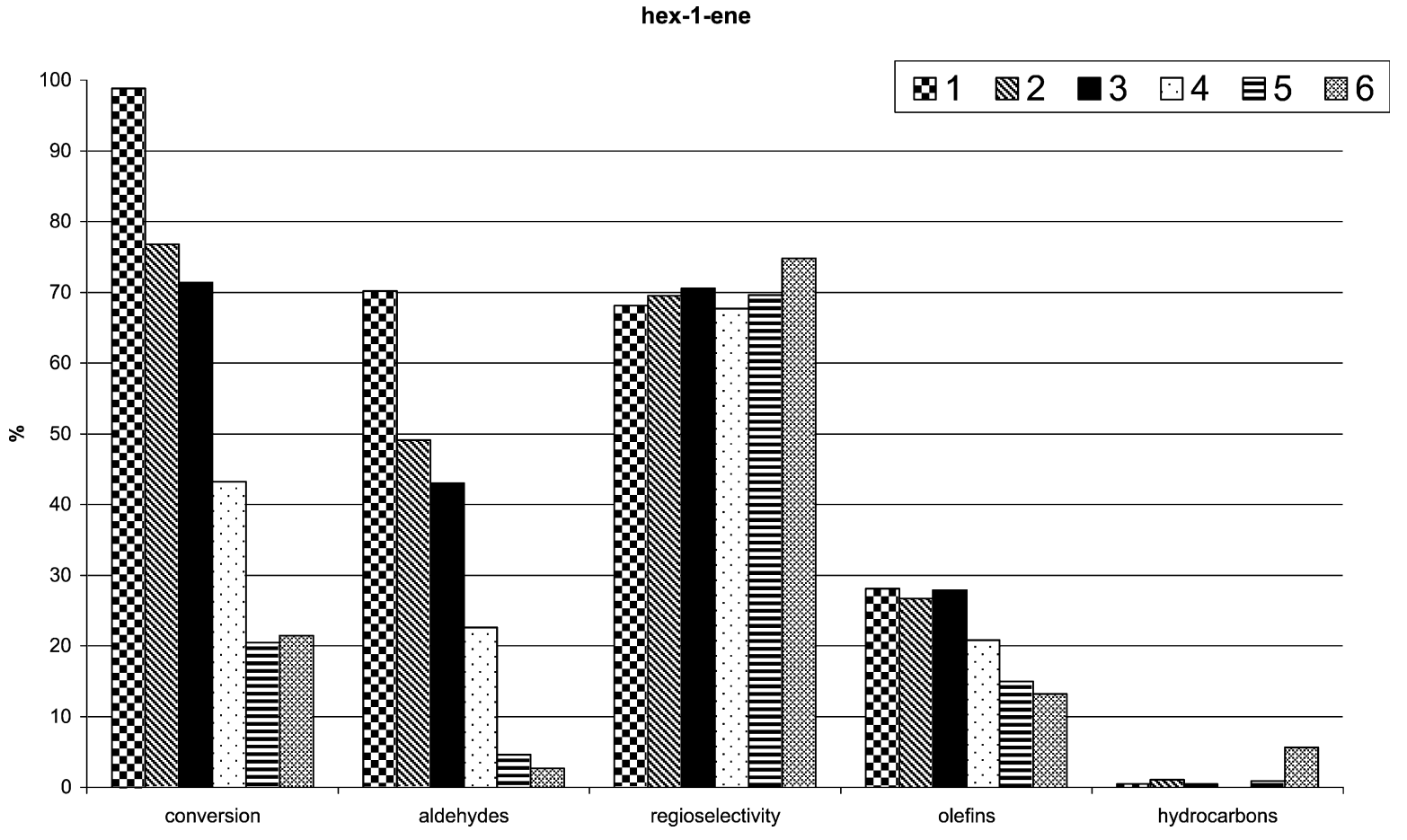

Fig. 1. Catalytic reactions of hex-1-ene: substrate, 2.0 mmol; complex, 0.02 mmol; THF, 25 ml; $p(H_2)$, 15 bar; $p(CO)$, 15 bar; reaction time, 4 h; temperature, 60 °C. Catalysts (1)–(6), see Scheme 1.

the regioselectivity goes down. The formation of low amounts of 2-ethylpentanal, in the presence of **4** at 100 °C or **2** at 80 °C (10.1 and 6.4%, respectively, entries 26 and 21) is in agreement with this suggestion. The presence of this branched aldehyde confirms that these catalysts are able to hydroformylate internal olefins, even if with different rate with respect to terminal ones.

The composition of the reaction products is affected in a low extent by different CO or H_2 pressures. As shown in Tables 1 and 2 when the reaction was carried out in the presence of **2** with a CO pressure of 30 bar the data collected are comparable to those obtained with 15 bar.

In the conditions required for hydroformylation, all the catalysts are also active in the isomerisation of the starting olefin.

The presence of a lateral chain on the cyclopentadienyl ligand affects the isomerisation activity as displayed by the results obtained at 60 °C using the catalyst **1**, **4** and **6**: the amount of isomerised olefins decreases, in the order, from 28.1 to 20.8 to 13.2% (entries 2, 10, 14, respectively).

The concentration of the internal olefins increases, when a high reaction temperature is employed (Table 2).

On the contrary, a very low hydrogenation activity is displayed by catalysts **1**–**6** during hydroformylation. Usually the hydrogenation does not exceed 1.5%, with the sole exception of **6**, at 60 °C.

3.3. Catalytic activity in the hydroformylation of styrene

The catalytic activity of **1**–**6** in the hydroformylation of styrene is by far lower than that found in the hex-1-ene case. Infact reaction temperature of 60 °C is required but, in these conditions, conversions are in the range among 1.5 and 4.0%.

At higher temperature (80 °C, Table 3) conversions increase considerably with all the catalysts tested: for instance, the complex **3** increases its catalytic activity from 1.8 to 53.5% (entry 31), the yield of 2-phenylpropanal rises from 1.5 to 28.8%, and that of 3-phenylpropanal from 0.3 to 24.7%.

In these conditions, the catalysts tested are not able to hydrogenate styrene or the aldehydes formed.

The influence of the ancillary ligand on the catalytic activity is opposite to that shown with hex-1-ene. The substitution of NBD with CO ligands increases the catalytic activity. Complex **2**, if compared to **1**, gives a higher conversion that is reflected in a higher yield of 2-phenylpropanal and 3-phenylpropanal.

The presence of methyl groups on the lateral chain of the cyclopentadienyl ligand in **4** reduces, although in a slight extent, the catalytic activity. The conversion decreases from 53.1% using **1** (entry 29), to 51.5% in the presence of **4** (entry 32). Moreover, as reported for the hydroformylation of hex-1-ene, the catalytic activity of the racemic complex **4** (entry 32) is higher than that one found for the *S*,*S* complex **5** (entry 33): The olefin conversions are 51.5 and 30.0%, respectively.

However, as reported for the hydroformylation of hex-1-ene, the presence of a lateral chain on the cyclopentadienyl ligand improves the catalytic activity of the complexes **1** and **4** if correlated to **6**, containing an unsubstituted cyclopentadienyl group (Fig. 2). The conversion, in the presence of **1**, is 53.1% (entry 29) while, using **6**, is 27.0% (entry 34). According to these data, the formation of 2-phenylpropanal and 3-phenylpropanal increases.

Finally, opposite to what observed in the hydroformylation of hex-1-ene, the substitution of the $–CH_2–CH=CH_2$ group on the lateral chain of the cyclopentadienyl ligand in **3** with a $–CH_2–CH_2–OH$ in **2**, significantly affects the catalytic activity. This change helps the olefin conversion (78.6% versus 53.5%), the yield of 2-phenylpropanal (42.6% compared to 28.8%), and 3-phenylpropanal (36.0% versus 24.7%).

3.4. Selectivity in the hydroformylation of styrene

Regioselectivity in the hydroformylation of styrene at 80 °C giving 2-phenylpropanal as the main product is in the range among 51.1 and 78.4%. The highest value was obtained in the presence of **5**. Higher values may be reached at lower temperature (60 °C, working in the reaction conditions reported in Table 3), i.e. **4** gives a total regioselectivity towards 2-phenylpropionaldehyde, but the small yield (4.0%) rules out any practical interest to this result. This regioselectivity, opposite to that found in the hydroformylation of hex-1-ene, is usually observed when an aromatic olefin is hydroformylated and may be connected to the conjugation of the double bond

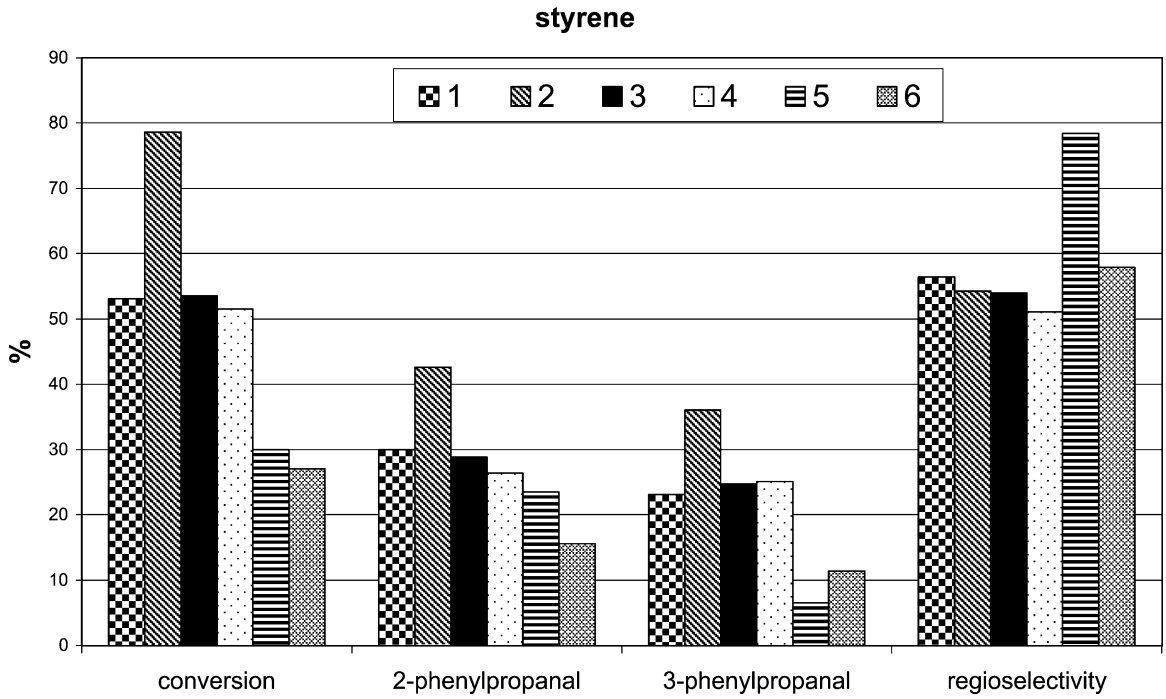

Fig. 2. Catalytic hydroformylation of styrene: substrate, 2.0 mmol; catalyst, 0.02 mmol; THF, 25 ml; $p(H_2)$, 15 bar; $p(CO)$, 15 bar; reaction time, 4 h; temperature, 80 °C. Catalysts (1)–(6), see Scheme 1.

with the aromatic ring and to the formation of an internal alkylrhodium complex instead of a terminal one [13,16]. Furthermore, the regioselectivities obtained are lower than those reported using unmodified rhodium catalysts [15] indicating an influence of the cyclopentadienyl group on the catalytic activity of these rhodium complexes.

The presence of a $–CO_2CH_2CH_2OH$ group in **1** does not affect the regioselectivity of the catalyst (56.4%, entry 29) if correlated to that of **6** (57.9%, entry 34), however the presence of methyl groups on the lateral chain of the cyclopentadienyl ligand in **4** reduces the regioselectivity to 51.1% (entry 32), while the regioselectivity increases up to 78.4%, when the chiral complex **5** was employed.

4. Conclusions

We may draw the following conclusions from the current study.

- The catalytic activity of compounds **1**–**6** in the hydroformylation of hex-1-ene is higher than that of other Rh cyclopentadienyl complexes previously reported [3–6]. The main product is the linear aldehyde followed by 2-methylhexanal, while the formation of 2-ethylpentanal takes place working in more severe conditions. Compound **1** shows the best catalytic activity towards olefin conversion and hydroformylation with a good regioselectivity. An analogous regioselectivity has been obtained using the Wilkinson catalyst without an excess of free phosphine, in the same conditions [16].
- Under a CO/H_2 atmosphere, compounds **1**–**6** are also catalytically active in the isomerisation of hex-1-ene. The linear isomers are formed in the following order: *trans*-hex-2-ene > *cis*-hex-2-ene > *trans*-hex-3-ene > *cis*-hex-3-ene (Table 2). These catalysts hydrogenate the substrate in a low extent.
- In the hydroformylation of styrene the higher conversion is obtained in the presence of **2**, with a regioselectivity towards 2-phenylpropanal of 54.2%.

A total regioselectivity is reached in the presence of **4** at 60 °C but in these conditions the olefin conversion is very low (4.0%).

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