

One-pot syntheses of alcohols from olefins through Co/Ru tandem catalysis

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Abstract

The one-pot synthesis of cyclohexylmethanol from cyclohexene has been realized using a tandem catalytic system formed by the $\text{Co}_2(\text{CO})_8$ complex for hydroformylation and different $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ (X: Cl, Br, I) complexes for hydrogenation. The sole ruthenium(II) complexes $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ (X: Cl, Br, I) are also able to synthesize cyclohexylmethanol from cyclohexene but a large part of the olefin is hydrogenated to alkane. Furthermore the sole ruthenium complexes are able to hydrogenate aldehydes to the corresponding alcohols even in the presence of carbon monoxide. The tandem catalytic system (Co-Ru) allows for the syntheses of several primary alcohols from the corresponding olefins with a total conversion and a very high selectivity (up to 97%).

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1. Introduction

Primary alcohols are an important class of products that finds application as intermediates in organic synthesis for agrochemicals, detergents, pharmaceuticals or directly used as solvent or oxygen containing compounds in fuel blending.

Alcohols may be synthesised from olefins through a two steps process [1]. In the first one the olefin is transformed into the corresponding aldehyde (hydroformylation process) and in the second step aldehyde is hydrogenated to alcohol. However the possibility to realize the one-pot syntheses of primary alcohols is actually very attracting [2]. Several papers are reported concerning the direct synthesis of alcohols from olefins both in homogeneous or heterogeneous phase using Co, Ru, Rh, Pd catalysts [3–7]. The main problem concerning the one step reaction is the parallel hydrogenation of alkene and sometimes the severe reaction conditions required.

In this paper we report on the one-pot syntheses of alcohols from olefins using the tandem catalytic system $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2/\text{Co}_2(\text{CO})_8$ (X: Cl, Br, I). The sole $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ (X: Cl, Br, I) complexes also catalyze the one-pot

formation of alcohol but the yields are not so high due to the hydrogenation of alkene in a large extent.

2. Experimental

2.1. Instruments and materials

A Shimadzu GC14 chromatograph was equipped with two FID detectors, and a 2 m packed columns filled with PPG monostearate supported on chromosorb as stationary phase. The response factors of reagents and products were evaluated for quantitative analyses. The identity of the products was confirmed by GC-MS using a Shimadzu apparatus (GCMS-QP5050A) equipped with a capillary column SPTM-1 (length 30 m, diameter 0.25 mm, film thickness 0.1 μm).

Elemental analyses were performed with a Perkin-Elmer Analyzer model 2400 Series II CHNS/O.

IR spectra were recorded with a Perkin-Elmer mod. 1760 FTIR spectrometer.

¹H, ¹³C and ³¹P NMR spectra were recorded using a Varian VXR300 spectrometer operating at 299.987 MHz for ¹H NMR, at 75.429 MHz for ¹³C NMR and at 121.421 MHz for ³¹P NMR, using solutions of appropriate solvents. Residual hydrogens of solvents were used as internal standard for ¹H NMR, the carbon atoms of the solvent for ¹³C NMR, and H₃PO₄ (85%) as external

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Table 1
Spectroscopic data of mononuclear (1)–(3) and binuclear (5)–(7) ruthenium complexes

Complex	IR		NMR (ppm)			
	Solvent	ν CO (cm ⁻¹)	Solvent	³¹ P	¹ H	¹³ C
[Ru(CO) ₂ (PPh ₃)Cl ₂] ₂	CH ₂ Cl ₂	2059 (s), 1996 (s)	CDCl ₃	17.04	8.2–7.8, 7.7–7.5	CO: 207.20 (s); Ph: 134.50–128.00
[Ru(CO) ₂ (PPh ₃)Br ₂] ₂	CH ₂ Cl ₂	2058 (s), 1996 (s)	CDCl ₃	13.12	7.7–7.2	CO: 208.50 (s); Ph: 134.44 (d, C _i , J _{CP} 10.4 Hz); 133.35 (s, C _p); 132.64 (d, C _m , J _{CP} 10.7 Hz); 129.15 (d, C _o , J _{CP} 12.4 Hz)
[Ru(CO) ₂ (PPh ₃)I ₂] ₂	CH ₂ Cl ₂	2056 (s), 1996 (s)	CDCl ₃	7.68	7.8–7.2	CO: 207.10 (s); Ph: 134.62 (d, C _i , J _{CP} 8.9 Hz); 132.65 (s, C _p); 131.96 (d, C _m , J _{CP} 10.0 Hz); 128.78 (d, C _o , J _{CP} 12.1 Hz)
Ru(CO) ₃ (PPh ₃)Cl ₂	C ₆ D ₆	2129 (s), 2072 (vs), 2034 (s)	C ₆ D ₆	16.28	8.25–8.10; 7.05–6.8	CO: 192.50 (s), 185.80 (s); Ph: 135.00–128.00
Ru(CO) ₃ (PPh ₃)Br ₂	C ₆ D ₆	2128 (s), 2071 (s), 2036 (vs)	C ₆ D ₆	11.68	7.60–7.35; 7.03–6.88	CO: 196.40 (s), 187.20 (s); Ph: 134.15 (d, C _i , J _{CP} 9.4 Hz); 133.50 (s, C _p); 132.64 (d, C _o , J _{CP} 8.3 Hz); 129.60 (d, C _m , J _{CP} 21.4 Hz)
Ru(CO) ₃ (PPh ₃)I ₂	C ₆ D ₆	2113 (s), 2062 (vs), 2035 (s)	C ₆ D ₆	4.29	7.50–7.30; 6.96–6.80	CO: 196.50 (s), 186.80 (s); Ph: 134.34 (d, C _i , J _{CP} 9.1 Hz); 133.03 (s, C _p); 132.14 (d, C _o , J _{CP} 10.6 Hz); 129.01 (d, C _m , J _{CP} 13.7 Hz)

standard for ³¹P NMR (signals reported as positive downfield to the standard). ¹³C and ³¹P NMR spectra were acquired using a broad band decoupler.

All manipulations were routinely carried out under a nitrogen atmosphere using standard Schlenk techniques.

Hydroformylations were performed in a stainless steel high pressure autoclave (125 ml) equipped with a stopper and a manometer, heated in an oil bath kept at the required temperature (±1 °C). In the course of the reaction the total pressure of the reaction was kept constant supplying the appropriate amount of CO/H₂ mixture from a high pressure cylinder.

Benzene and toluene were deoxygenated and dried by refluxing under nitrogen atmosphere and distilling over sodium/potassium amalgam.

Cyclohexene, pent-1-ene, oct-1-ene, 4-methylpent-1-ene were commercial products, purified by elution on an Al₂O₃ column, then dried by refluxing and distilling on Na.

2.2. Synthesis of complexes

The following complexes were prepared according to the literature: [Ru(CO)₂(PPh₃)Cl₂]₂ (**1**) [8], [Ru(CO)₂(PPh₃)Br₂]₂ (**2**) [8], [Ru(CO)₂(PPh₃)I₂]₂ (**3**) [8], Co₂(CO)₈ (**4**) [9]. Their spectroscopic characteristics are reported in Table 1.

The following complexes were also synthesised as reference compounds.

2.2.1. Synthesis of Ru(CO)₃(PPh₃)Cl₂ (**5**)

A solution of [Ru(CO)₂(PPh₃)Cl₂]₂ (0.5 g, 0.51 mmol) in toluene (20 ml) was introduced in the autoclave, the vessel pressurized to 115 bar with CO and the reactor kept in a thermostated oil bath, rocked and heated at 100 °C for 5 h. The autoclave was cooled, the gas vented and a white solution collected. Pentane was added and 0.52 g (1.00 mmol) of Ru(CO)₃(PPh₃)Cl₂ (**5**) was precipitated as yellow-lemon crystals with 98% yield. A cyclohexane solution of the product show IR bands, in the 2100–1800 cm⁻¹ region, at 2033 (m), 2075 (s), 2133 (m), while the IR, the ¹H, ¹³C and ³¹P NMR signals, in C₆D₆, are reported

in Table 1. Elemental analysis for C₂₁H₁₅Cl₂O₃PRu was: % C 48.57 (48.67), % H 2.87 (2.92), % Cl 13.77 (13.68). The IR bands are in agreement with those reported by Johnson et al. [10] for the same product obtained through another procedure.

2.2.2. Synthesis of Ru(CO)₃(PPh₃)Br₂ (**6**)

A solution of [Ru(CO)₂(PPh₃)Br₂]₂ (0.5 g, 0.43 mmol) in toluene (20 ml) was introduced in the autoclave, the vessel pressurized to 115 bar with CO and the reactor kept in a thermostated oil bath, rocked and heated at 100 °C for 5 h. The autoclave was cooled, the gas vented and a light yellow solution collected. Pentane was added and 0.515 g (0.85 mmol) of Ru(CO)₃(PPh₃)Br₂ (**6**) was precipitated as light yellow crystals with 98% yield. A cyclohexane solution of the product show IR bands, in the 2100–1800 cm⁻¹ region, at 2036 (m), 2073 (s), 2128 (m), while the IR, the ¹H, ¹³C and ³¹P NMR signals, in C₆D₆, are reported in Table 1. Elemental analysis for C₂₁H₁₅Br₂O₃PRu was: % C 41.30 (41.54), % H 2.48 (2.49), % Br 26.29 (26.32). The IR bands are in agreement with those reported by Johnson et al. [10] for the same product obtained through another procedure.

2.2.3. Synthesis of Ru(CO)₃(PPh₃)I₂ (**7**)

A solution of [Ru(CO)₂(PPh₃)I₂]₂ (0.5 g, 0.37 mmol) in toluene (20 ml) was introduced in the autoclave, the vessel was pressurized to 115 bar with CO and the reactor kept in a thermostated oil bath, rocked and heated at 100 °C for 5 h. The autoclave was cooled, the gas vented and a yellow lemon solution collected. Pentane was added and 0.512 g (0.73 mmol) of Ru(CO)₃(PPh₃)I₂ (**7**) was precipitated as yellow-lemon crystals with 98% yield. A cyclohexane solution of the product show IR bands, in the 2100–1800 cm⁻¹ region, at 2037 (m), 2060 (s), 2116 (m), while the IR, the ¹H, ¹³C and ³¹P NMR signals, in C₆D₆, are reported in Table 1. Elemental analysis for C₂₁H₁₅I₂O₃PRu was: % C 35.90 (35.97), % H 2.15 (2.16), % I 35.50 (35.20). The IR bands are in agreement with those reported by Johnson et al. [10] for the same product obtained through another procedure.

Table 2
Hydroformylation of cyclohexene in the presence of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (1)–(3) as catalyst

Run no.	X	$p(\text{H}_2)$ (bar)	$p(\text{CO})$ (bar)	Induction time (min)	Reaction time (min)	Conversion (%)	Reaction products composition (%)				Selectivity ^a (%)
							Alkane	Alcohol	Aldehyde	Others ^b	
1	Cl	101	9	52	360	52.8	67.6	29.2	2.0	1.2	33.2
2	Br	101	9	–	360	90.3	59.5	38.8	<1.0	0.7	40.9
3	I	101	9	52	360	26.3	63.6	32.5	2.8	1.1	36.4
4	Cl	110	20	45	655	87.5	39.0	59.0	0.4	1.6	61.0
5	Br	110	20	55	655	96.5	44.8	51.7	0.4	3.1	55.2
6	I	110	20	60	655	59.0	32.5	60.0	2.5	5.0	67.5

Cyclohexene 98.7 mmol; toluene 30 ml; catalyst 17.3 mmol; T 150 °C.

^a Selectivity: mol hydroformylation products/mol total products.

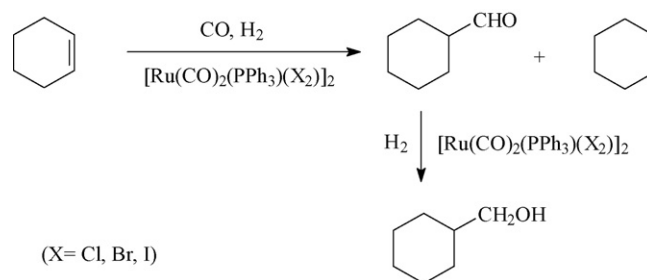
^b Others: $\text{C}_6\text{H}_{11}\text{CH}(\text{OCH}_2\text{C}_6\text{H}_{11})_2$.

Table 3
Hydrogenation of cyclohexylformaldehyde in the presence of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (1)–(3) as catalyst

Run no.	X	Induction time (min)	Conversion (%)	Selectivity ^a (molar ratio)
7	Cl	28	79.3	96.5
8	Br	48	27.6	86.0
9	I	47	27.0	87.0

Cyclohexylformaldehyde 50.0 mmol; toluene 30 ml; catalyst 11.5 mmol; T 120 °C; $p(\text{H}_2)$ 102 bar; $p(\text{CO})$ 19 bar, reaction time 20 min.

^a Selectivity: mol alcohol/mol products.



Scheme 1.

2.3. Hydroformylation

A typical experiment is described: the same procedure was employed for all catalysis. The data collected are reported in Tables 2–6.

The catalyst was introduced into the autoclave, the vessel closed, air evacuated and a solution containing the solvent and the substrate introduced by suction. The autoclave was pressurized with CO and H_2 at the desired pressure and the reactor placed in a thermostated oil bath. When the pressure was reduced of 4 bar, the same amount of gas mixture was reintroduced in the reactor from a high pressure cylinder containing the same gas mixture.

When the absorption of the gas was ceased or after a prefixed time, the autoclave was cooled to room temperature, and the gas vented. The solution was collected, analyzed by GC and the products identified through GC-MS technique.

3. Results and discussion

3.1. Hydroformylation of cyclohexene in the presence of (1)–(3) as catalysts

The catalytic activity of the ruthenium complexes (1)–(3) was tested at 150 °C using a hydrogen pressure among 100–110 bar and a CO pressure of 9 or 20 bar. Cyclohexene was chosen as substrate to avoid problems due to the formation of isomers (Table 2).

The main products were cyclohexylmethanol and cyclohexane together with low amount of cyclohexylformaldehyde (Scheme 1). Trace of the acetal resulting from the reaction between the alcohol and the aldehyde was also detected. The alcohol/alkane ratio is lower than 1 using a $p(\text{CO})$ of 9 bar (0.43–0.65) while it is increased to 1.51–1.84 working in the presence of 20 bar of CO. Increasing the CO pressure the

Table 4
Hydroformylation of cyclohexene in the presence of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (1)–(3) and $\text{Co}_2(\text{CO})_8$ (4) as catalysts

Run no.	X	Co/Ru (molar ratio)	$p(\text{H}_2)$ (bar)	$p(\text{CO})$ (bar)	Induction time (min)	Reaction time ^a (min)	Reaction products composition (%)			Selectivity ^b (%)
							Alkane	Alcohol	Aldehyde	
10	Cl	2.5	107	11	14	206	12.0	85.0	3.0	88.0
11	Br	2.5	107	11	13	120	21.0	78.1	0.9	79.0
12	I	2.5	107	11	13	101	13.5	83.0	2.5	85.5
13	Cl	5	107	11	12	320	10.0	85.0	5.0	90.0
14	Cl	3	101	42	20	310	4.0	89.0	7.0	96.0

Cyclohexene 98.7 mmol; toluene 30 ml; $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ 11.5 mmol; T 150 °C.

^a Time required to obtain a complete conversion of alkene.

^b Selectivity: mol hydroformylation products/mol total products.

selectivity towards alcohol improves while the reaction rate decreases.

The bromo derivative (**2**) (entry 5, Table 2) shows the highest catalytic activity in all experiments while the highest alcohol/alkane ratio is obtained using the iodo complex (**3**) (entry 6, Table 2).

3.2. Hydrogenation of cyclohexylformaldehyde in the presence of (**1**)–(**3**) as catalysts

The results reported in Table 2 show the ability of the catalysts (**1**)–(**3**) to hydroformylate an olefin although the selectivity towards hydroformylation products is low (among 32.4 and 67.5%) because a large amount of alkene is hydrogenated to alkane (67.6–32.5%). The direct formation of alcohol together with low amount of aldehyde suggests that these ruthenium complexes catalyze in a first step the hydroformylation of olefin to aldehyde. In a second step the aldehyde is hydrogenated to alcohol (Scheme 1). These data suggest that these complexes are able to hydrogenate a carbonylic compound in the presence of hydrogen and carbon monoxide. The catalysts (**1**)–(**3**) were tested in the hydrogenation of cyclohexylformaldehyde to confirm this hypothesis and to evaluate their ability to reduce a carbonylic compound. The reaction conditions were chosen in order to discriminate among the catalytic activity of the three catalysts: CO (20 bar) and hydrogen (100 bar) at 120 °C with a reaction time of 20 min (Table 3).

All catalysts hydrogenate cyclohexylformaldehyde but the best conversion and selectivity were obtained using the catalyst (**1**).

3.3. Direct synthesis of cyclohexylmethanol from cyclohexene through tandem catalysis in the presence of $\text{Co}_2(\text{CO})_8/[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).

The complexes $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), are catalytically active in the hydrogenation of cyclohexylformaldehyde in the presence of CO, especially the chloro derivative, but they have a low activity in the hydroformylation of alkene. To increase the rate of hydroformylation a tandem catalytic system was tested. $\text{Co}_2(\text{CO})_8$ was chosen as a very active and selective catalyst for the hydroformylation of cyclohexene and $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) as a catalyst able to hydrogenate the intermediate aldehyde formed. In this way it was possible to reduce the hydrogenation of cyclohexene and to realize the one-pot syntheses of primary alcohols from the corresponding olefins in high yield (Scheme 2).

The preliminary tests, reported in Table 4, show the possibility to realize the tandem catalysis obtaining a complete conversion of cyclohexene and an yield to cyclohexylmethanol of 78–85%. A few amount of cyclohexylformaldehyde (less than 5%) remained among the reaction products while the hydrogenation of cyclohexene to cyclohexane was in the range 12.0–21.0%. The best yield in cyclohexylmethanol was reached using the chloro derivative even if a higher reaction time is required to obtain a complete conversion of cyclohexene. Trying to optimize the reaction conditions we have also improved the Co/Ru

Table 5
Hydroformylation of olefins in the presence of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{Cl}_2]_2$ (**1**) and $\text{Co}_2(\text{CO})_8$ (**4**) as catalysts

Run no.	Olefin	Solvent	Co/Ru (molar ratio)	$p(\text{H}_2)$ (bar)	$p(\text{CO})$ (bar)	Induction time (min)	Reaction time ^a (min)	Reaction products composition (%)			Selectivity ^b (%)	S/B ^c ratio
								Alkane	Alcohol	Aldehyde		
14	Cyclohexene	Toluene	3.0	101	42	14	310	4.0	89.0	7.0	96.0	–
15	Pent-1-ene	Benzene	3.0	101	36	15	330	3.0	87.2	9.8	97.0	1.85
16	4-Methylpent-1-ene	Toluene	2.5	110	13	22	223	10.4	79.1	10.5	89.6	1.50
17	4-Methylpent-1-ene	Benzene	3.0	101	36	18	300	6.0	84.0	10.0	94.0	1.96
18	Oct-1-ene	Toluene	2.5	108	13	5	273	22.0	67.4	10.6	78.0	1.15
19	Oct-1-ene	Benzene	3.0	101	36	13	310	3.0	82.4	14.6	97.0	1.75
20	Pent-1-ene	Benzene	2.0	101	50	20	235	4.0	88.6	7.4	96.0	1.87
21	Cyclohexene	Toluene	2.0	101	50	34	235	5.5	88.5	5.0	94.5	–
22	Oct-1-ene	Benzene	2.0	101	50	30	235	5.0	85.2	9.8	95.0	1.80

Olefin 100.0 mmol; toluene 30 ml; $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ 11.5 mmol; T 150 °C.

^a Time required to obtain a complete conversion of the alkene.

^b Selectivity: mol hydroformylation products/mol total products.

^c S/B: straight/branched ratio of alcohols.

Table 6
Hydroformylation of cyclohexene in the presence of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{Cl}_2]_2$ (**1**) and $\text{Co}_2(\text{CO})_8$ (**4**) as catalysts

Run no.	Reaction time (min)	Conversion (%)	Reaction products composition (%)			Selectivity ^a (%)
			Alkane	Alcohol	Aldehyde	
23	20	85.5	3.8	10.3	71.4	95.6
24	94	100	4.0	27.0	69.0	96.0
14	310	100	4.0	89.0	7.0	96.0

Influence of the reaction time. Cyclohexene 98.7 mmol; toluene 30 ml; $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{Cl}_2]_2$ 11.5 mmol; Co/Ru (molar ratio) 3.0; $p(\text{H}_2)$ 101 bar; $p(\text{CO})$ 42 bar; T 150 °C.

^a Selectivity: mol hydroformylation products/mol total products.

and CO/H_2 ratios (Table 4). A high pressure of CO increased the yield of alcohol to 88% together with 7% of aldehyde and only 4% of alkane.

3.4. Direct synthesis of primary alcohols from olefins through tandem catalysis using a $\text{Co}_2(\text{CO})_8/[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{Cl}_2]_2$ system

Taking into account that the chloro derivative (**1**) gave better results than the other Ru complexes the subsequent tests were performed using this hydrogenation catalyst (Table 5).

Different olefins were chosen and the results of the one-pot synthesis of primary alcohols is reported in Table 5. Using pent-1-ene the yield of hexanols was 87.2% accomplished by a 9.8% of aldehydes and only 3% of alkene. Using phosphine or arsine substituted cobalt carbonyls [3f,3g] low yields to alcohols were obtained.

Increasing the molecular weight of the olefin, i.e. using oct-1-ene, a slightly lower alcohol yield was obtained (82.4%) together with 14.6% of aldehydes and only 3% of alkane. Lower yield are reported in the literature [3h]. A branched olefin such as 4-methylpent-1-ene gave a slightly low yield (83%) than pent-1-ene with a low increase of the resulting alkane (6%).

The straight/branched ratio (S/B) among the alcohols was as expected for the hydroformylation of the same alkenes [2c].

In all tests reducing the CO/H_2 ratio the amount of alcohol is reduced while the amount of alkane increases (Table 5).

In these reactions the syn gas was in large excess but initially in a CO/H_2 1:3 ratio. Considering that hydrogen was required for hydroformylation of the olefin and hydrogenation of the aldehyde, some experiments were carried out using the stoichiometric ratio CO/H_2 (1:2) (Table 5). The yield remains almost

unchanged (around 95% as hydroformylation products) but the reaction rate is higher and 235 min are required to obtain the complete conversion of the alkene.

The gas consumption was very rapid up to 2/3 of the theoretical amount, suggesting that the hydroformylation is faster than hydrogenation. This hypothesis was confirmed by the data reported in Table 6, where the reaction was quenched at different reaction time. After 20 min the olefin conversion was 85.5% and products were the aldehyde (71.4%) and the alcohol (10.3%). After 94 min the conversion was 100% but the aldehyde was reduced to 69.0% and the alcohol increased to 27.0%. Finally, after 310 min, the alcohol was 89.0% and the aldehyde only 7.0%.

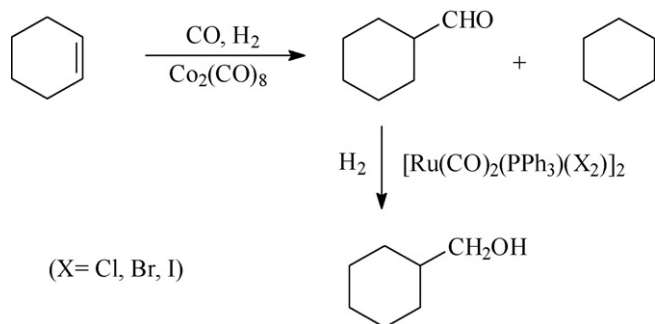
4. Conclusion

The results reported show that the complexes $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are catalysts able to transform an alkene in the alcohol having one more carbon atom through the hydroformylation of the olefin and its subsequent hydrogenation to the corresponding alcohol. A large part of the alkene is however hydrogenated to alkane especially if a CO/H_2 ratio was 1:10. In the course of this reaction the starting complexes $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\text{X}_2]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were converted into mononuclear specie $\text{Ru}(\text{CO})_3(\text{PPh}_3)\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) that may be recovered at the end of the reaction.

The hydrogenation activity of the catalysts (**1**)–(**3**) reduces the yield to alcohols because the alkene is partially hydrogenated to alkane even if carbon monoxide is present in the reaction medium. This last property is not very usual for hydrogenation catalysts. With the aim to improve the alcohol we have realized a tandem system coupling a catalyst able to hydroformylate the olefin at a high rate $[\text{Co}_2(\text{CO})_8]$ with the ruthenium complexes active in the hydrogenation of the carbonylic intermediate. By this way has been possible to realize the one-pot synthesis of primary alcohols from the corresponding olefins in high yields.

The initial gas consumption was very rapid (up to 2/3 of the theoretical amount), then decreases. This behaviour and the data reported in Table 6 confirm the reaction sequences reported in Scheme 2.

If we consider that residual aldehydes may be converted into alcohols when the reaction time is improved, the combination of the catalysts (**1**) and (**4**) in a tandem process gives primary alcohols from alkenes with very high yields.



Scheme 2.

Presumably in the course of the reaction the role of the two catalysts is independent. The starting complexes were modified at the end of the reaction as happen when the two catalyst are independently employed. However it must be remembered that $[\text{Co}(\text{CO})_4]^-$ formed under syngas conditions reacts with the $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ complex as reported by Joo and Alper [11] Further studies are in progress to evidence the specie involved in this tandem process.

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