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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 $Co_2(CO)_8$ complex for hydroformylation and different $[Ru(CO)_2(PPh_3)X_2]_2$ (X: Cl, Br, I) complexes for hydrogenation. The sole ruthenium(II) complexes $[Ru(CO)_2(PPh_3)X_2]_2$ (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%).

Keywords: Alcohol; Alkene; Hydroformylation; Tandem catalysis

1. Introduction

Primary alcohols are an important class of products that founds 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 $[Ru(CO)_2(PPh_3)X_2]_2/Co_2(CO)_8$ (X: Cl, Br, I). The sole $[Ru(CO)_2(PPh_3)X_2]_2$ (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 SP^{TM}-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, ^{13}C and ^{31}P NMR spectra were recorded using a Varian VXR300 spectrometer operating at 299.987 MHz for ^1H NMR, at 75.429 MHz for ^{13}C NMR and at 121.421 MHz for ^{31}P 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 ^{13}C NMR, and H_3PO_4 (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_2Cl_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_2Cl_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_2Cl_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_6D_6	2129 (s), 2072 (vs), 2034 (s)	C_6D_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_6D_6	2128 (s), 2071(s), 2036 (vs)	C_6D_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_6D_6	2113 (s), 2062 (vs), 2035 (s)	C_6D_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 ^{31}P NMR (signals reported as positive downfield to the standard). ^{13}C and ^{31}P 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/H_2 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 Al_2O_3 column, then dried by refluxing and distilling on Na.

2.2. *Synthesis of complexes*

The following complexes were prepared according to the literature: $[Ru(CO)_2(PPh_3)Cl_2]_2$ (**1**) [8], $[Ru(CO)_2(PPh_3)Br_2]_2$ (**2**) [8], $[Ru(CO)_2(PPh_3)I_2]_2$ (**3**) [8], $Co_2(CO)_8$ (**4**) [9]. Their spectroscopic characteristics are reported in Table 1.

The following complexes were also synthesised as reference compounds.

2.2.1. *Synthesis of* $Ru(CO)_3(PPh_3)Cl_2$ *(**5**)*

A solution of $[Ru(CO)_2(PPh_3)Cl_2]_2$ (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 $Ru(CO)_3(PPh_3)Cl_2$ (**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 ^{1}H, ^{13}C and ^{31}P NMR signals, in C_6D_6, are reported in Table 1. Elemental analysis for $C_{21}H_{15}Cl_2O_3PRu$ 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* $Ru(CO)_3(PPh_3)Br_2$ *(**6**)*

A solution of $[Ru(CO)_2(PPh_3)Br_2]_2$ (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 $Ru(CO)_3(PPh_3)Br_2$ (**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 ^{1}H, ^{13}C and ^{31}P NMR signals, in C_6D_6, are reported in Table 1. Elemental analysis for $C_{21}H_{15}Br_2O_3PRu$ 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* $Ru(CO)_3(PPh_3)I_2$ *(**7**)*

A solution of $[Ru(CO)_2(PPh_3)I_2]_2$ (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 $Ru(CO)_3(PPh_3)I_2$ (**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 ^{1}H, ^{13}C and ^{31}P NMR signals, in C_6D_6, are reported in Table 1. Elemental analysis for $C_{21}H_{15}I_2O_3PRu$ 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.