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The role of functionalized phosphines in the hydrogenation of carboxylic acids in the presence of phosphine substituted hydrido ruthenium complexes

Antonella Salvini, Piero Frediani, Mario Bianchi, Franco Piacenti *, Leonardo Pistolesi, Luca Rosi

Dipartimento di Chimica Organica della Università di Firenze, via Gino Capponi, 9, I-50121 Firenze, Italy

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Abstract

Hydrido ruthenium carbonyl complexes substituted by functionalized phosphines such as $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ have been synthesized and tested as catalysts in the hydrogenation of carboxylic acids. These complexes are more active than those reported previously, containing trialkyl- or triarylphosphines. On the basis of their behavior, their different activity has been explained in terms of an involvement of the phosphine ligand in the catalytic cycle. The ester group present in the phosphine $P(CH_2OCOR)_3$ is hydrogenated to produce an alcohol (RCH_2OH) and a $P(CH_2OH)$ group which, in turn, reacts with the free acid present in solution to restore the $P(CH_2OCOR)$ group. This hypothesis has been confirmed by the reactivity of the possible intermediate $H_4Ru_4(CO)_8[P(CH_2OH)_3]_4$ with acetic acid. Another support to this statement is the almost equal catalytic activity, displayed by $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ complexes, whatever the R group present, in the phosphine ligand, in the hydrogenation of carboxylic acids. These complexes, on the other hand, are less active than the corresponding tributylphosphine substituted ones in the hydrogenation of alkenes and ketones. Finally when the phosphine ligand is $P(CH_2CH_2COOCH_3)_3$ the ester group is not reduced and consequently the catalytic activity of this complex in the hydrogenation of carboxylic acids is very low.

Keywords: Carboxylic acids; Functionalized phosphines; Catalytic activity; Hydrogenation

1. Introduction

The hydrogenation of free carboxylic acids in homogeneous phase was first achieved using ruthenium complexes such as $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ and $H_4Ru_4(CO)_8[P(CH_2CH_2CH_2CH_3)_3]$ [1]. Several investigations on this catalytic reaction have been made in order to elucidate its mechanism [2].

The influence of the phosphine ligand on the catalytic activity of the ruthenium complex in this reaction is certainly relevant. We have thought interesting to investigate the role played by the phosphine if it contains a functional group.

We have described recently [3] the synthesis, characterization and the reaction with hydrogen of hydridocarbonyl ruthenium clusters substituted with functionalized phosphines $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ [$R = CH_3$–(**1**), C_2H_5–(**2**), $(CH_3)_2CH$–(**3**), $(CH_3)_3C$–(**4**), (S)–$C_2H_5CH(CH_3)$–(**5**)]. These complexes are potential catalysts for the homogeneous hydrogenation of unsaturated organic compounds. The eventual presence of chiral carbon atoms in the alkyl substituent of the phosphine (i.e. **5**) might lead to stereoselective hydrogenations.

The acyl groups in the phosphinic ligand of **1**–**5** react with hydrogen at moderate temperatures (100–130°C) with formation of the corresponding alcohol and free hydroxy groups in the phosphine ligand (Scheme 1) [3].

The free hydroxy groups present in the phosphine may act as new activation sites for carboxylic acids (Scheme 2) in addition to the one operative in the complexes containing trialkylphosphines such as $P(CH_2CH_2CH_2CH_3)_3$ [1,2a].

* Corresponding author. Tel.: +39-055-2757648; fax: +39-055-2757660.

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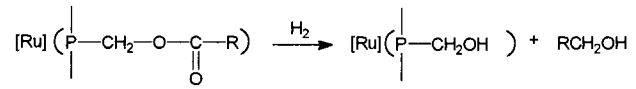
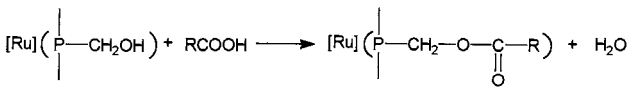
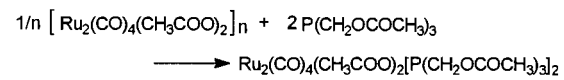


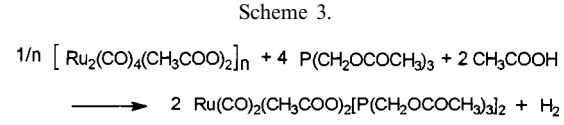
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

This hypothesis has been checked by testing the catalytic activity of complexes **1**–**5** in the hydrogenation of simple monocarboxylic acids (CH_3COOH, CH_3CH_2COOH, $CH_3CH_2CH(CH_3)COOH$, $CH_3CH_2CH_2CH_2COOH$) and comparing the results obtained with those provided by the corresponding $P(CH_2CH_2CH_2CH_3)_3$ substituted complex, $H_4Ru_4(CO)_8[P(CH_2CH_2CH_2CH_3)_3]_4$ (**6**).

The catalytic activity of analogous ruthenium complexes containing functionalized phosphines having a different steric and electronic situation [$P(CH_2OCOR)_3$ or $P(CH_2CH_2COOCH_3)_3$] have been compared.

Ruthenium carbonyl carboxylates are present generally in the crude of the catalytic hydrogenation of carboxylic acids performed in the presence of $H_4Ru_4(CO)_8[P(CH_2CH_2CH_2CH_3)_3]_4$ [1,2b]. We have therefore synthesized and characterized $Ru_2(CO)_4(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (**7**) and $Ru(CO)_2(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (**8**), in order to detect their presence in the reaction crude. The catalytic activity of **7** has also been tested and compared with that of **1**.

The catalytic activity of **5** was also tested in the hydrogenation of C=C and C=O groups.

2. Results

2.1. Synthesis and characterization of rutheniumcarbonyl complexes

Complexes $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ (**1**–**5**) were synthesized as reported previously [3]. The new complexes employed were prepared as described below:

2.1.1. $Ru_2(CO)_4(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (7)

Was prepared as described by Crooks et al. [4] for the analogous tributylphosphine derivative (Scheme 3).

$[Ru_2(CO)_4(CH_3COO)_2]_n$ and $P(CH_2OCOCH_3)_3$ in toluene were refluxed for 10 h. By crystallization from methanol at -20°C yellow needles were obtained.

Only one singlet at 8.7 ppm is present in the ^{31}P-NMR spectrum, attributable to two magnetically equivalent phosphine ligands. In the ^{1}H-NMR spectrum a singlet at 1.85 ppm is attributable to the methyl proton of the acetato ligand in agreement with the ^{1}H-NMR spectrum of analogous tributylphosphino complex [4,5]. The other resonances in the spectrum may be attributed to the $P(CH_2OCOCH_3)_3$ ligand: 2.07 (s, 18H, CH_3COOCH_2), 4.78 (s, 12H, CH_2O) ppm. In the ^{13}C-NMR spectrum the singlet at 23.0 ppm and the triplet at 187.0 ($J_{CP} = 9.0$ Hz) ppm are attributable to the carbon atom of the methyl group and to the carbon atom of the carboxylato group of the acetato ligand, in keeping with the ^{13}C-NMR spectrum of the analogous tributylphosphino complex [6]. The other resonances in the spectrum may be attributed as follows: signals at 20.3 (s, CH_3COOCH_2), 56.3 (t, CH_2, $J_{CP} = 10.4$ Hz) and 170.1 (s, PCH_2COO) are attributable to the $P(CH_2OCOCH_3)_3$ ligand and the triplet at 203.8 ($J_{CP} =$ 4.5 Hz) ppm, in agreement with the spectroscopic data of the analogous tributylphosphino complex [6], is assigned to carbonyl ligands.

The IR spectrum, in the range 2200–1500 cm^{-1}, shows absorptions at 2032 (vs), 1987 (m), 1961 (vs) cm^{-1} due to terminal carbonyls, a band at 1757 (s) cm^{-1} attributable to the ester groups and a band at 1573 (m) cm^{-1} due to the carboxylato ligands.

These data suggest for **7** a structure similar to that reported for $Ru_2(CO)_4(CH_3COO)_2(PR_3)_2$ with R = $-CH(CH_3)_2$, $-CH_2CH_2CH_2CH_3$, $-C(CH_3)_3$ [7].

2.1.2. $Ru(CO)_2(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (8)

Was prepared as described by Bianchi et al. [8] for the tributylphosphine substituted analogue (Scheme 4).

Polymeric $[Ru_2(CO)_4(CH_3COO)_2]_n$ was reacted with $P(CH_2OCOCH_3)_3$ in acetic acid under reflux for 90 h. An oily residue was obtained after elimination of the solvent under reduced pressure.

An octahedral structure containing two phosphine molecules in *trans* position and two carboxylato and two carbonyl groups in *cis* position may be attributed to **8** on the basis of its spectroscopic data. In fact the singlet at 26.7 ppm in the ^{31}P-NMR spectrum is indicative of two equivalent phosphine ligands; the presence of two *cis* carbonyl ligands is in keeping with two carbonyl stretching bands of equal intensity in the IR spectrum, at 2067 (vs), 2008 (vs) cm^{-1} and, in the ^{13}C-NMR spectrum, with the presence of only one triplet at 193.2 ppm ($J_{CP} = 12.7$ Hz). A singlet at 2.04 in the ^{1}H-NMR spectrum and two singlets at 22.2 and 178.5 ppm in the ^{13}C-NMR spectrum are attributable to two equivalent acetato ligands.

The spectroscopic data of **8** are in keeping with those reported in the literature for analogous ruthenium complexes [5,8]. On standing at room temperature the complex turns into a new ruthenium species not yet well characterized.

2.1.3. $H_4Ru_4(CO)_8[P(CH_2CH_2COOCH_3)_3]_4$ (9)

Was prepared by reacting $H_4Ru_4(CO)_{12}$ with $P(CH_2CH_2COOCH_3)_3$ in *n*-heptane (Scheme 5) as described by Piacenti et al. [9] for the analogous tributylphosphine substituted derivative

The ^{1}H-, ^{31}P-, ^{13}C-NMR and IR spectra are in keeping with those reported [5,9,10] for analogous ruthenium complexes. Only one singlet at 19.2 ppm is present in the ^{31}P-NMR spectrum, attributable to four magnetically equivalent phosphine ligands. At the same time the presence of only one quintet at -17.05 ppm ($J_{HP} = 6.5$ Hz) in the hydrido region of the ^{1}H-NMR spectra is in agreement with four equivalent hydrides coupling with four equivalent phosphine ligands. The other resonances in the spectrum may be attributed as follows: 3.40 (s, 36H, CH_3O), 2.53 (m, 24H, CH_2CO), 2.25 (m, 24H, PCH_2) ppm. The resonances in the ^{13}C-NMR spectrum may be attributed as follows: 199.9 (m, RuCO), 172.0 (t, $J_{PC} = 7.2$ Hz, COO), 51.6 (s, OCH_3), 28.1 (s, CH_2CO), 25.3 (t, $J_{PC} = 10.9$ Hz, PCH_2). The attributions of the ^{13}C- and ^{1}H-NMR spectra are confirmed by an HETCOR spectrum. These attributions are also in agreement with the statement of Pregosin [11] that the carbon atoms in α and γ positions couple with the phosphorous atom.

The IR spectrum, in the carbonyl stretching region, shows three absorptions at 2006 (vs), 1966 (m), 1946 (s) cm^{-1} characteristic for these complexes [9,10].

These data support the hypothesis of a structure similar to that of $H_4Ru_4(CO)_{12}$ [12], based on a tetrahedral ruthenium cluster, containing one phosphine per ruthenium atom.

2.1.4. $H_4Ru_4(CO)_8[P(CH_2OH)_3]_4$ (10)

Was prepared by reacting $H_4Ru_4(CO)_{12}$ with $P(CH_2OH)_3$ in butan-2-ol (Scheme 6) as described by Piacenti et al. [9] for the analogous tributylphosphine substituted derivative.

The residue, after distillation of the solvent was washed with *n*-pentane, benzene and methylene chloride. Due to the very low solubility in all the solvents tested it is not possible to crystallize it, to determine its molecular weight and to collect its ^{13}C-NMR spectrum. The ^{1}H- and ^{31}P-NMR spectra (D_2O or DMSO as solvent) are in keeping with those reported [5,9,10] for analogous ruthenium complexes. Only one singlet at 44.2 ppm, present in the ^{31}P-NMR spectrum, is attributable to four magnetically equivalent phosphine ligands. The presence of only one multiplet at -21.55 ppm in the hydrido region of the ^{1}H-NMR spectrum is in agreement with the presence of four equivalent hydrides.

The IR spectrum (KBr pellets) shows in the carbonyl stretching region two broad bands at 2048 (vs) and 1975 (vs) cm^{-1}.

The elemental analysis supports the formulation proposed.

$$H_4Ru_4(CO)_{12} + 4\ P(CH_2CH_2COOCH_3)_3 \longrightarrow H_4Ru_4(CO)_8[P(CH_2CH_2COOCH_3)_3]_4 + 4\ CO$$

Scheme 5.

$$H_4Ru_4(CO)_{12} + 4\ P(CH_2OH)_3 \longrightarrow H_4Ru_4(CO)_8[P(CH_2OH)_3]_4 + 4\ CO$$

Scheme 6.

2.2. Hydrogenation experiments

The hydrogenation experiments were performed on carboxylic acids, ketones and orefins. No optimization of the yield was attempted.

2.2.1. Hydrogenation of carboxylic acids

Series of hydrogenation tests of acetic acid (Table 1) were carried out in the presence of hydrido ruthenium complexes **1**–**4**, **9**, scanning the 80–130°C temperature range, under 130 atm of hydrogen with a substrate/catalyst molar ratio of 3.53×10^3 and a reaction time of 48 h. Samples were collected at the end of each test and analyzed by GC and GC-MS. The residual catalyst was also recovered from the crude after distillation of the liquid at reduced pressure and examined by IR spectroscopy.

No hydrogenation of the carboxylic group took place at temperatures lower then 100°C.

In the presence of catalysts **1**–**4** the product formed at the lowest reaction temperature is ethyl acetate while ethanol is present at higher temperatures ($\geq$120°C).

Conversions were 14–16% with hydrides **1**–**4** while only ca. 4% was reached working with **9** (Table 1).

Comparative tests, performed at 130°C using **2, 9** and $H_4Ru_4(CO)_8[P(CH_2CH_2CH_2CH_3)_3]_4$ (**6**) as catalysts, showed a decrease of the catalytic activity in the order **2** > **6** > **9** (Table 2).

The IR analysis of the solid residue recovered from the crude of the tests performed at 130°C (Table 1) in the presence of complexes **1**–**4** shows the disappearance of the starting $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ complex and the presence, in the carbonyl stretching region, of two broad bands at 2045 (vs) and 1975 (vs) cm^{-1} attributable to a mixture of ruthenium carbonyl complexes. Other bands at 1750 (s) and 1600 (w) cm^{-1} may be attributed, respectively, to the ester group of the phosphinic ligands and to carboxylato ligands.

The catalytic activity of the carboxylato complex **7** in the hydrogenation of acetic acid is almost the same of **1** at all temperatures tested (Table 3).

The hydrogenation of propionic acid was performed, at temperatures between 130 and 150°C, in the presence of hydrido ruthenium complexes **2, 3, 6**, and **9** (Table 4). *n*-Propyl propionate was the main reaction product. The conversion reached 28% in the presence of **2** at 150°C. The catalytic activity of the complexes decreases in the order $\mathbf{2} \cong \mathbf{3} > \mathbf{6} > \mathbf{9}$.

n-Pentanoic and 2-methylbutanoic acids were also hydrogenated to the corresponding *n*-pentyl and 2-

Table 1
Hydrogenation of acetic acid in the presence of $H_4Ru_4(CO)_8(PR_3)_4$ catalysts [a]

Catalyst	T (°C)	Conv. (%)	Selectivity (%)	
			Ethyl acetate	Ethanol
$H_4Ru_4(CO)_8[P(CH_2OCOCH_3)_3]_4$ (**1**)	100	2.0	100	0
	110	5.0	100	0
	120	9.0	100	0
	130	16.0	94.0	6.0
$H_4Ru_4(CO)_8[P(CH_2OCOCH_2CH_3)_3]_4$ (**2**)	100	Trace	100	0
	110	3.9	100	0
	120	7.4	94.0	6.0
	130	16.0	91.7	8.3
$H_4Ru_4(CO)_8[P(CH_2OCOCH(CH_3)_2)_3]_4$ (**3**)	100	Trace	100	0
	110	2.0	100	0
	120	6.8	~100	Trace
	130	14.3	92.2	7.8
$H_4Ru_4(CO)_8[P(CH_2OCOC(CH_3)_3)_3]_4$ (**4**)	100	Trace	100	0
	110	2.9	100	0
	120	6.3	93.7	6.3
	130	14.0	90.1	9.9
$H_4Ru_4(CO)_8[P(CH_2CH_2COOCH_3)_3]_4$ (**9**)	100	0	0	0
	110	Trace	100	0
	120	1.8	100	0
	130	3.6	100	0

[a] Influence of temperature. Tests performed by heating the system in subsequent steps at the temperatures indicated. Substrate 5.24 ml (91.6 mmol), catalyst 30.0 μmol, p(H_2) 130 atm at 20°C, reaction time 48 h at each temperature.

Table 2
Hydrogenation of acetic acid in the presence of $H_4Ru_4(CO)_8(PR_3)_4$ catalysts [a]

Catalyst	Conv. (%)	Selectivity (%)	
		Ethyl acetate	Ethanol
$H_4Ru_4(CO)_8[P(CH_2OCOCH_2CH_3)_3]_4$ (**2**)	10.1	92.1	7.9
$H_4Ru_4(CO)_8[P(CH_2CH_2COOCH_3)_3]_4$ (**9**)	1.8	100	0
$H_4Ru_4(CO)_8[P(CH_2CH_2CH_2CH_3)_3]_4$ (**6**)	6.1	100	0

[a] Influence of the phosphine ligand. Substrate 45.8 mmol (2.62 ml), catalyst 15.0 μmol, $T = 130$°C, $p(H_2)$ 130 atm at 25°C, reaction time 48 h.

Table 3
Hydrogenation of acetic acid in the presence of $Ru_2(CO)_4(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (**7**): influence of temperature [a]

Catalyst	T (°C)	Conv. (%)	Selectivity (%)	
			Ethyl acetate	Ethanol
$Ru_2(CO)_4(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (**7**)	100	2.3	100	0
	110	5.8	100	0
	120	9.5	100	0
	130	15.7	94.0	6.0

[a] Tests performed by heating the system in subsequent steps at the temperatures indicated. Substrate 5.24 ml (91.6 mmol), catalyst 60.0 μmol, $p(H_2)$ 130 atm at 20°C, reaction time 48 h at each temperature.

Table 4
Hydrogenation of propionic acid in the presence of $H_4Ru_4(CO)_8(PR_3)_4$ catalysts [a]

Catalyst	T (°C)	R.t. [b] (h)	Conv. (%)	Selectivity (%)	
				n-Propyl propionate	Propanol
$H_4Ru_4(CO)_8[P(CH_2OCOCH_2CH_3)_3]_4$ (**2**)	130	48	15.6	95.9	4.1
	150	24	28.0	98.6	1.4
$H_4Ru_4(CO)_8[P(CH_2OCOCH(CH_3)_2)_3]_4$ (**3**)	130	48	14.1	98.2	1.8
	150	24	27.0	99.2	0.8
$H_4Ru_4(CO)_8[P(CH_2CH_2COOCH_3)_3]_4$ (**9**)	130	48	2.2	100	0
	150	24	4.4	100	0
$H_4Ru_4(CO)_8[P(CH_2CH_2CH_2CH_3)_3]_4$ (**6**)	130	48	5.2	100	0
	150	24	23.2	99.1	0.9

[a] Catalyst 15.0 μmol, substrate 3.41 ml (45.8 mmol), $p(H_2)$ 130 atm at 25°C.
[b] R.t.: reaction time.

Table 5
Hydrogenation of 2-methylbutanoic and *n*-pentanoic acid to the corresponding esters (2-methylbutyl 2-methylbutanoate and *n*-pentyl *n*-pentanoate, respectively) in the presence of (+)(*S*)-$H_4Ru_4(CO)_8\{P[CH_2OCOCH(CH_3)CH_2CH_3]_3\}_4$ (**5**) or $H_4Ru_4(CO)_8[P(CH_2CH_2CH_2CH_3)_3]_4$ (**6**) [a]

Substrate	Catalyst	14 h at 130°C		48 h at 150°C		116 h at 150°C	
		Conversion (%)	Selectivity [b] (%)	Conversion (%)	Selectivity [b] (%)	Conversion (%)	Selectivity [b] (%)
2-Methylbutanoic acid	(**5**)	0.4	100	8.6	98.8	16.5	97.6
2-Methylbutanoic acid	(**6**)	0.2	100	2.9	100	6.9	~100
n-Pentanoic acid	(**5**)	1.2	100	19.6	99.0	39.4	99.2
n-Pentanoic acid	(**6**)	0.3	100	4.1	100	11.0	99.0

[a] Catalytic precursor 15 μmol, substrate 45.8 mmol, $p(H_2)$ 130 atm at 20°C neat.
[b] Selectivity to ester, the other product is the corresponding alcohol.

methylbutyl esters in the presence of **5** and **6** at temperatures higher than 130°C. The conversions reached in the presence of **5** were higher than those found with **6** (Table 5).

Trace of the $RCOOCH_3$ esters were detected in the crude when working at 130°C with long reaction times or at higher temperatures, indicative of some hydrogenolysis in a low extension of the P–C bond of the phosphine ligand. This reactivity had not been observed in a previous investigation on the behavior of $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ complexes with hydrogen [3]. This new finding may be ascribed to the more severe conditions adopted in the present work.

2.2.2. Hydrogenation of olefins and ketones

The results of the hydrogenation tests on C=C (cyclohexene, tiglic acid) and C=O double bonds (acetophenone) in the presence of **5** and **6** are reported in Table 6. In all cases **6** provides higher conversions than **5**. Complex **5** provides a very low enantioface discrimination in the hydrogenation of prochiral substrates.

2.3. Reaction of rutheniumcarbonyl complexes with acetic acid

The reactivity of $H_4Ru_4(CO)_8[P(CH_2OH)_3]_4$ (**10**) with acetic acid has been evaluated in order to confirm that the $P(CH_2OH)$ group formed in the catalytic experiments reacts with the free acid to restore the $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ complex. We wanted also to test if hydrido ruthenium complexes react with acetic acid to give ruthenium carbonyl carboxylates containing the same phosphine ligands.

2.3.1. $H_4Ru_4(CO)_8[P(CH_2OH)_3]_4$ (**10**)

$H_4Ru_4(CO)_8[P(CH_2OH)_3]_4$ is transformed partially, at reflux temperature in acetic acid for 24 h, into a new specie containing the $P(CH_2OCOCH_3)_3$ ligand (band at 1756 (vs) cm^{-1} in the IR spectrum and absence of bands due to the CH_2OH group).

After heating at reflux temperature for 72 h in acetic acid and evaporation of the unreacted acid, a carboxylato ruthenium complex is present, containing a phosphine in which the initial CH_2OH groups is

Table 6
Hydrogenation of unsaturated organic substrates in the presence of (+)(*S*)-$H_4Ru_4(CO)_8\{P[CH_2OCOCH(CH_3)CH_2CH_3]_3\}_4$ (**5**) or $H_4Ru_4(CO)_8[P(CH_2CH_2CH_2CH_3)_3]_4$ (**6**) [a]

Substrate		Catalyst		*T* (°C)	R.t. [b] (h)	Conv. (%)	Product	O.P. [c] (%)
	mmol	Code	μmol					
Acetophenone	41.6	**5**	23	120	14	7.6	(+)(*S*)-1-Phenylethanol	0.04
Acetophenone	41.6	**6**	23	120	14	14.0	1-Phenylethanol	
Tiglic acid [d]	49.9	**5**	23	100	48	9.6	(+)(*S*)-2-Methylbutanoic acid	5.7
Tiglic acid [d]	49.9	**6**	23	100	48	96.4	2-Methylbutanoic acid	
Cyclohexene	42.5	**5**	4.5	60	22	1.8	Cyclohexane	
Cyclohexene	42.5	**6**	4.5	60	22	47.1	Cyclohexane	

[a] Neat, $p(H_2)$ 130 atm.
[b] R.t.: reaction time.
[c] O.P.: optical purity (%)
[d] Solvent: 10 ml toluene/ethanol (1:1).

transformed into an ester group (band at 1754 (vs) cm^{-1} in the IR spectrum). The stretching at 1559 (w) cm^{-1} indicates the presence of the carboxylato ligand; the hydride resonances in the ^{1}H-NMR spectrum are absent.

However the complex is not one of the ruthenium carbonyl acetato complexes, $Ru_2(CO)_4(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (**7**) or $Ru(CO)_2(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (**8**), but it has the same spectroscopic characteristics of one of the products obtained by reacting $H_4Ru_4(CO)_8[P(CH_2OCOCH_3)_3]_4$ with acetic acid (signal in the ^{31}P-NMR spectrum at 35.7 ppm) (see below).

2.3.2. $H_4Ru_4(CO)_8[P(CH_2OCOCH_3)_3]_4$ (*1*)

When heating **1** in acetic acid at reflux temperature for 48 h, the starting complex is still the main product (91.2%, evaluated by ^{31}P-NMR spectroscopy) while a small amount of **7** (2.3%) and of another complex (signal at 26.4 in the ^{31}P-NMR spectrum, 6.5%) are formed. In the IR spectrum of the solution new bands appear at 2070 (w), 2011 (sh) and 1559 (w, broad) cm^{-1}. These spectroscopic data (IR and ^{31}P-NMR spectra) are in agreement with the presence of the same product formed by reacting **7** with acetic acid at 40°C (see below).

Compound **1** is transformed completely when refluxed in acetic acid for 192 h: two new complexes are present in the reaction crude, having signals at 26.4 (s, 55.3%) and 35.7 (s, 44.7%) ppm in the ^{31}P-NMR spectrum.

In the usual working up the complex giving the signal at 26.4 ppm decomposes and a mixture of products is present in solution (signals in the ^{31}P-NMR spectrum at 35.7, 51.4, 64.0, 82.4 ppm).

2.3.3. $Ru_2(CO)_4(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (*7*)

$Ru_2(CO)_4(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ slowly reacts in the presence of acetic acid at room temperature; heating for 3 h at 40°C a colorless solution is obtained. After elimination of acetic acid under reduced pressure at a temperature non-exceeding 0°C, a residue is obtained containing only one phosphine-substituted complex having one signal at 26.4 ppm in the ^{31}P-NMR spectrum.

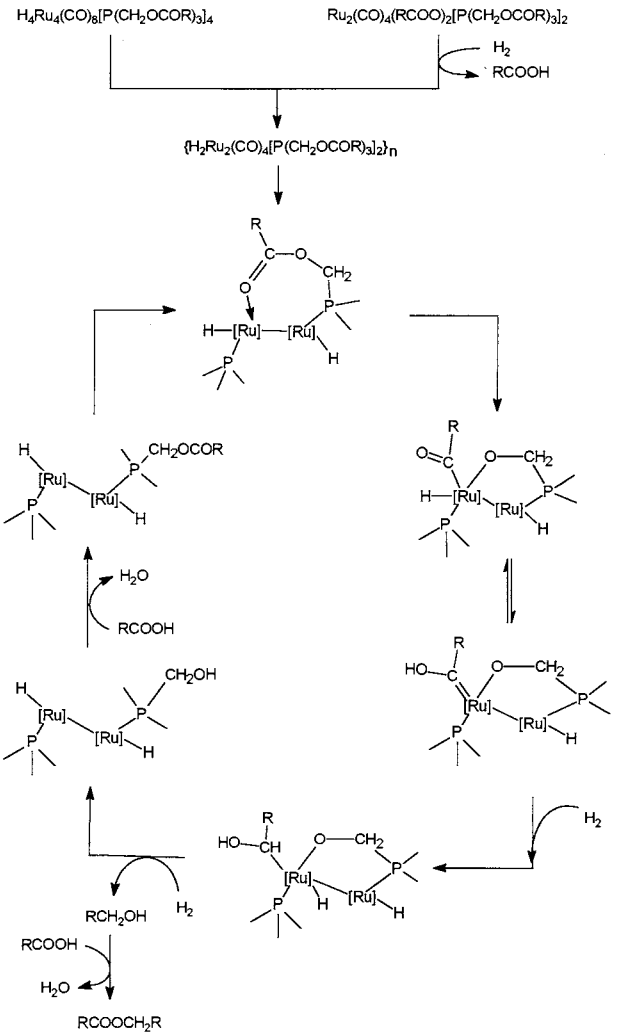
The spectroscopic data are in agreement with the presence of a carboxylato ligand but a complete characterization of this complex has not yet been possible due to its rapid decomposition.

3. Discussion

The results of the hydrogenation tests show that the catalytic activity of the ruthenium complexes **1**–**5**, containing a functionalized phosphine such as $P(CH_2OCOR)_3$, is different from that of **6**, the $P(CH_2CH_2CH_2CH_3)_3$ substituted analogue. This difference may be summarized as follows:

1. In the hydrogenation of carboxylic acids the hydrido ruthenium complexes **1**–**5** are catalytically more active than **6** at all the temperatures tested (100–150°C) (Tables 2, 4 and 5). A low activity is displayed by **1**–**4**, even below 130°C, while at the same temperature **6** is not active (Table 1).
2. The catalytic activity of the $P(CH_2OCOR)_3$ substituted ruthenium complexes in the hydrogenation of C=C or C=O double bonds (Table 6) is lower than that one of **6**.

The nature of the catalytic species in the hydrogenation of carboxylic acids is rather intriguing. $H_4Ru_4(CO)_8[P(CH_2OCOCH_3)_3]_4$ and some carboxylato derivatives containing the same phosphine ligand (like **7** and **8**) could be involved in the catalytic cycle as found in the hydrogenation catalyzed by $H_4Ru_4(CO)_8[P(CH_2CH_2CH_2CH_3)_3]_4$ [1,2b]. Tributylphosphine substituted hydridoruthenium carbonyls have in fact been shown to react easily with carboxylic acids, even at



Scheme 7.

room temperature, in the absence of hydrogen, to give phosphine substituted ruthenium carbonyl carboxylates. Moreover, the catalytic activity shown by the carboxylato complex **7** is very similar to that of **1**.

The higher activity of the ruthenium complexes containing functionalized phosphines **1**–**5**, **7** (Tables 1–5) in the hydrogenation of carboxylic acids may tentatively be explained through the involvement of the phosphine ligand in the activation of the substrate as shown in the reaction pattern reported in Scheme 7. This path can not be operative when **6** is the catalyst. The almost equal catalytic activity shown by complexes $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ (**1**–**4**) in the hydrogenation of acetic acid (Table 1) suggests moreover the formation of the same catalytic intermediates. The same species containing the $P(CH_2OCOCH_3)_3$ ligand may in fact be formed from all precursors **1**–**4** if the reactions reported in Scheme 7 ($R = CH_3$) are operative.

The hydrogenation of free carboxylic acids can involve the reaction path previously reported for complexes **1**–**5** with hydrogen [3]. The formation of the same hydrido cluster from the binuclear carboxylato complex **7** is also suggested in consideration of almost the same catalytic activity. The activation of the ester moiety of the phosphine takes place by co-ordination of its carbonyl group to a ruthenium atom of the cluster. Activation of substrates by the breaking of a Ru–Ru bond in cluster complexes has been reported by Lugan [13]. The higher catalytic activity of the binuclear ruthenium carboxylato complexes compared with that of the mononuclear derivatives is in agreement with the involvement of a Ru–Ru bond in the catalytically active intermediate [2c]. This consideration suggests that the ruthenium atom which became coordinated to the carbonyl group of the ester is not the same to which the phosphine is bonded. The oxidative addition of the ester group gives rise to the formation of an acyl and an alkoxy ruthenium complex. The hydride moves then on the oxygen of the acyl group forming a carbene derivative that is hydrogenated to the alcohol and a ruthenium complex with a $P(CH_2OH)$ group. Esterification of this $P(CH_2OH)$ group restore the starting complex while reaction of the substrate (RCOOH) with the alcohol formed (RCH_2OH) gives the corresponding carboxylic acid ester. This hypothesis is supported by the fact that $H_4Ru_4(CO)_8[P(CH_2OH)_3]_4$, a model complex bearing a hydroxylated phosphine, reacts easily with acetic acid at 120°C (the temperatures adopted in the catalytic hydrogenation) yielding ruthenium complexes containing the $P(CH_2OCOCH_3)_3$ ligand (Scheme 2). Working in harsh conditions the expected carboxylato complexes $Ru_2(CO)_4(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (**7**) and $Ru(CO)_2(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (**8**), have not however been detected among the reaction products in agreement with the behaviour of the acetato ruthenium carbonyl **7** with acetic acid. This complex in fact, in the presence of acetic acid, give rise to new labile complexes not yet characterised completely, whose spectroscopic properties are identical to those shown by the products formed from $H_4Ru_4(CO)_8[P(CH_2OCOCH_3)_3]_4$ and acetic acid (see Experimental).

Surprisingly not only a free carboxylic acid but also the ester group of the phosphino ligand are reduced at a low temperature, if compared with that necessary for the reduction of an ester, using the trialkylphosphino derivative **6** [1a]. Analogous $H_4Ru_4(CO)_8(PR_3)_4$ complexes containing tri(propyl)phosphine have been reported to improve the catalytic activity of these clusters in the reduction of dimethyl oxalate to methyl glycolate [6], but the reduction of the monoester, however, can be obtained only at higher temperature (180°C). Other ruthenium complexes have been reported as efficient catalysts in the reduction of carboxylic acid esters in mild conditions [14,15].

Another observation supports the suggestion that a different path is operative in the hydrogenation of

carboxylic acids at low temperature in the presence of **1**–**5**. The $P(CH_2CH_2COOCH_3)_3$ substituted complex **9** shows a much lower catalytic activity than **1**–**5** in the hydrogenation of acetic and propionic acids, even lower than that of **6** (Tables 1, 2 and 4): In the conditions adopted in the catalytic tests the carbomethoxy groups in the phosphine ligand of **9** are not hydrogenated and therefore no new 'sites' for the possible engagement of the carboxylic acid are formed.

As a final consideration the mechanism suggested provides a justification of the insignificant enantioface discrimination provided by **5** in the hydrogenation of prochiral acids: the chiral center is in fact removed from the complex by hydrogenation and substituted by the prochiral acid used as substrate.

4. Experimental

4.1. Instruments

Elemental analyses were performed with a Perkin–Elmer 240 C system.

Gas chromatographic analyses (GC) were performed with a Perkin–Elmer–Sigma 1 system or a Shimadzu GC-14A chromatographic system coupled with a Shimadzu C-R4A computer; the packed columns (2 m) used were: PPG ('Polipropylenglycol' LB-550-X on Chromosorb W at 15%), FFAP ('free fatty acids phase' on Chromosorb G AW-DMCS at 5%), CW ('Carbowax 20M' on Chromosorb W at 15%). Both apparatuses were equipped with a FID.

Conversions of carboxylic acids to esters were evaluated by calibration curves.

GC-MS spectra were collected using a Shimadzu GC-MS-QP2000 instrument, or a Carlo Erba QMD 1000 GC-MS data system equipped with capillary columns: a SPB-1™ (a Supelco column, 30 m, internal diameter 0.25 mm) or a AT™-1 (Alltech column, 30 m, internal diameter 0.25 mm).

Infrared spectra were recorded with a Perkin–Elmer model 1760-X FTIR spectrophotometer. Liquid products and solutions were analyzed using KBr or CaF_2 cells having 0.1 mm path. Solid samples were mulled with KBr.

Multinuclear NMR spectra were registered using a Varian VXR300 spectrometer operating at 299.944 MHz for ^1H, at 75.429 MHz for ^{13}C and at 121.421 MHz for ^{31}P-NMR spectra, tetramethylsilane was used as external reference for ^1H- and ^{13}C-NMR spectra. In the ^{31}P-NMR spectra, downfield values from external H_3PO_4 (85%) were taken as positive. ^{13}C- and ^{31}P-NMR spectra were recorded as proton decoupled spectra.

Optical rotations were measured with a Perkin–Elmer model 241 polarimeter.

4.2. Materials

Reagents and solvents were purified and dried as reported. Acetic acid was distilled under nitrogen (b.p. 118°C). Cyclohexene was eluted through activated Al_2O_3 (70–230 mesh) and rectified under nitrogen (b.p. 83°C). Acetophenone was distilled prior to use (b.p. 82°C/15 mmHg). Toluene was dried by refluxing on sodium metal, then was refluxed and distilled on $LiAlH_4$. *n*-Heptane was purified by treatment with conc. H_2SO_4, washed with a solution of $KMnO_4$ in H_2SO_4 (10%), then dried on anhydrous $CaCl_2$, refluxed on sodium and distilled on $LiAlH_4$. Methanol, dried as reported by Vogel [16], had b.p. 65°C.

2-Methylbutyl 2-methylbutanoate was synthesized by reacting 2-methylbutanol with 2-methylbutanoyl chloride prepared from 2-methylbutanoic acid as reported by Vogel [16] for analogous compounds and had b.p. 73–74°C/10 mmHg.

n-Pentyl *n*-pentanoate, synthesized and purified as reported by Vogel [16] for analogous compounds, had b.p. 102–103°C/23 mmHg.

$P(CH_2OH)_3$ [17,18], $P(CH_2OCOCH_3)_3$ [3], $P(CH_2OCOCH_2CH_3)_3$ [3], $P[CH_2OCOCH(CH_3)_2]_3$ [3] $P[CH_2OCOC(CH_3)_3]_3$ [3], $(-)(S)$-$[P(CH_2OCOCH(CH_3)CH_2CH_3)_3]$ [3] and $P(CH_2CH_2COOCH_3)_3$ [19,20] were synthesized as reported in the literature.

Complexes $H_4Ru_4(CO)_{12}$ [9], $H_4Ru_4(CO)_8[P(CH_2CH_2CH_2CH_3)_3]_4$ (**6**) [9], $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ [R = CH_3–(**1**), C_2H_5–(**2**), $(CH_3)_2CH$–(**3**), $(CH_3)_3C$–(**4**), (S)–$C_2H_5CH(CH_3)$–(**5**)] [3] and $[Ru_2(CO)_4(CH_3COO)_2]_n$ [4] were prepared as described in the literature.

All other solvents and chemicals were reagent grade and used without further purification.

All reactions and manipulations were performed under dry nitrogen by the Schlenk tube technique.

4.3. Synthesis of ruthenium complexes

4.3.1. $Ru_2(CO)_4(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (7)

$[Ru_2(CO)_4(CH_3COO)_2]_n$ (302 mg, 1.398 mmol Ru) and $P(CH_2OCOCH_3)_3$ (350 mg, 1.4 mmol) in toluene (10 ml) were refluxed for 10 h. The solution was then evaporated to dryness and the residue crystallized from methanol at −20°C. A yellow crystalline product (396 mg, 61% yield) was recovered.

Anal. Calc. for $C_{26}H_{36}O_{20}P_6Ru_4$: C, 33.48; H, 3.89. Found: C, 33.09; H, 3.88.

The IR spectrum (toluene) shows, in the 2200–1500 cm^{-1} region, bands at 2032 (vs), 1987 (m), 1961 (vs), 1757 (s), 1573 (m) cm^{-1}.

The ^1H-NMR spectrum ($CDCl_3$) shows signals at 1.85 (s, 6H, CH_3COORu), 2.07 (s, 18H, CH_3COOCH_2), 4.78 (s, 12H, CH_2O) ppm.

The ^{31}P-NMR spectrum ($CDCl_3$) shows a singlet at 8.7 ppm.

The ^{13}C-NMR spectrum ($CDCl_3$) shows resonances at 20.3 (s, CH_3COOCH_2), 23.0 (s, CH_3COORu), 56.3 (t, CH_2, $J_{CP} = 10.4$ Hz), 170.1 (s, PCH_2COO), 187.0 (t, COORu, $J_{CP} = 9.0$ Hz), 203.8 (t, Ru–CO, $J_{CP} = 4.5$ Hz) ppm.

4.3.2. $Ru(CO)_2(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (**8**)

$[Ru_2(CO)_4(CH_3COO)_2]_n$ (165 mg, 0.75 mmol Ru) was treated with $P(CH_2OCOCH_3)_3$ (380 mg, 1.51 mmol) in acetic acid (5 ml) and the mixture refluxed for 90 h. The colorless solution was evaporated to dryness and the residue analyzed spectroscopically.

The IR spectrum (CH_2Cl_2) shows, in the 2200–1500 cm^{-1} region, bands at 2067 (vs), 2008 (vs), 1754 (vs), 1619 (m) cm^{-1}.

The ^{1}H-NMR spectrum ($CDCl_3$) shows signals at 2.04 (s, 6H, CH_3COORu), 2.09 (s, 18H, CH_3COOCH_2), 4.80 (s, 12 H, CH_2O) ppm.

The ^{31}P-NMR spectrum (CD_2Cl_2) shows a singlet at 26.4 ppm.

The ^{13}C-NMR spectrum ($CDCl_3$) shows resonances at 20.0 (s, CH_3COOCH_2), 22.2 (s, CH_3COORu), 55.7 (t, CH_2, $J_{CP} = 18.0$ Hz), 170.0 (s, PCH_2COO), 178.5 (s, COORu), 193.2 (t, Ru–CO, $J_{CP} = 12.7$ Hz) ppm.

Prolonged standing in solution causes its transformation into a new product with a singlet in the ^{31}P-NMR spectrum (CD_2Cl_2) at 35.7 ppm; its IR spectrum (CH_2Cl_2) in the 2200–1500 cm^{-1} region, show bands at 2061 (vs), 1978 (broad), 1754 (vs), 1557 (m) cm^{-1}.

4.3.3. $H_4Ru_4(CO)_8[P(CH_2CH_2COOCH_3)_3]_4$ (**9**)

In a 25 ml round bottom flask $H_4Ru_4(CO)_{12}$ (0.200 g, 0.204 mmol), $P(CH_2CH_2COOCH_3)_3$ (0.355 g, 1.21 mmol) and *n*-heptane (12 ml) were introduced under dry nitrogen. The mixture was heated at 100°C for 12 h, removing the CO evolved by slowly bubbling nitrogen.

The course of the reaction was monitored by IR spectroscopy and TLC. After 12 h the IR spectrum of the solution showed the absorptions characteristic of the class of compounds expected: this pattern remained unaltered even after longer heating. The solvent was then distilled at reduced pressure and the residue dissolved in methanol and crystallized by cooling at −20°C. After two recrystallizations 0.385 g of product (77% yield) were obtained.

Anal. Calc. for $C_{56}H_{88}O_{32}P_4Ru_4$: C, 37.25; H, 4.92. Found: C, 37.28; H, 5.18.

The IR spectrum (CH_2Cl_2) shows, in the 2200–1500 cm^{-1} region, bands at 2006 (vs), 1966 (m), 1946 (s) and 1738 (vs) cm^{-1}.

The ^{1}H-NMR spectrum (C_6D_6) shows signals at −17.05 (qt, 4H, HRu, $J_{HP} = 6.5$ Hz), 2.25 (m, 24H, PCH_2), 2.53 (m, 24H, PCH_2CH_2) and 3.40 (s, 36 H, OCH_3) ppm.

The ^{31}P-NMR spectrum (C_6D_6) shows a singlet at 19.2 ppm.

The ^{13}C-NMR spectrum (DMSO-d_6) shows signals at 25.3 (t, PCH_2CH_2, $J_{CP} = 10.9$ Hz), 28.1 (s, PCH_2CH_2), 51.6 (s, CH_3O), 172.0 (t, COO, $J_{CP} = 72$ Hz) and 199.9 (m, RuCO) ppm.

4.3.4. $H_4Ru_4(CO)_8[P(CH_2OH)_3]_4$ (**10**)

$H_4Ru_4(CO)_{12}$ (190 mg, 0.255 mmol) was reacted with $P(CH_2OH)_3$ (200 mg, 1.61 mmol) in butan-2-ol (15 ml) by heating at 100°C for 48 h. A red solution was formed showing bands in the IR spectrum different from those of the starting complex. The solvent was evaporated and the solid residue washed with *n*-pentane, benzene and methylene chloride. The product recovered (173 mg, 0.153 mmol, 60% yield) has a low solubility in acetone, methanol, tetrahydrofurane and dimethylsulfoxide.

Anal. Calc. for $C_{20}H_{40}O_{20}P_4Ru_4$: C, 21.28; H, 3.57. Found: C, 21.28; H, 3.64.

The IR spectrum (KBr pellets) shows, in the 2200–1500 cm^{-1} region, bands at 2048 (vs), 1975 (vs) cm^{-1}.

The ^{1}H-NMR spectrum (D_2O) shows signals at −21.55 (m, 4H, Ru–H) and 4.01 (d, 2H, PCH_2, $J_{HP} = 3$ Hz) ppm

The ^{31}P-NMR spectrum (DMSO) shows a singlet at 44.2 ppm.

4.4. Reactivity of ruthenium complexes

4.4.1. Behavior of **9** under hydrogen

A total of 57.3 mg (0.032 mmol) of complex **9**, dissolved in 5 ml benzene, were introduced under dry nitrogen in a glass vial placed in a stainless steel autoclave (150 ml) and hydrogen was added up to 130 atm. The autoclave was then rocked and heated up to 130°C. Samples of the solution were monitored by GC (using PPG column heated to 40°C for 50 min) and IR techniques. Methanol and methyl propionate were not detected. The IR spectrum of the final solution was identical to the initial one (bands at 2006 (vs), 1966 (m), 1946 (s) and 1738 (vs) cm^{-1}).

4.4.2. Reaction of **10** with acetic acid

$H_4Ru_4(CO)_8[P(CH_2OH)_3]_4$ (24 mg, 0.021 mmol) was refluxed for several hours in acetic acid (5 ml). The reaction was monitored by IR spectroscopy.

A sample of the solution collected after 24 h was distilled to dryness and the residue dissolved partially in methylene chloride. The IR spectrum of the solution showed a band at 1756 (vs) cm^{-1} attributable to the $P(CH_2OCOCH_3)$ group and a band at 1557 (w) cm^{-1} attributable to the carboxylato group [$Ru(OCOCH_3)$]. Other absorptions at 2058 (s) and 1990 (s) cm^{-1} were also present. No bands due to the CH_2OH group were evident.

The IR spectrum of the solid residue (KBr pellets), showed a band at 3430 (vs) cm^{-1} attributable to the presence of CH_2OH groups. Other absorptions were at 2051 (vs), 1980 (vs), 1735 (s), 1663 (s), 1559 (m) cm^{-1}.

The residue obtained after refluxing for 72 h and evaporation of the acetic acid was soluble completely in methylene chloride. The spectroscopic data of this residue were in agreement with the presence of only one phosphino complex.

The IR spectrum (CH_2Cl_2) shows, in the 2200–1500 cm^{-1} region, bands at 2064 (vs), 1993 (vs, broad), 1754 (vs), 1559 (w) cm^{-1}.

The ^{1}H-NMR spectrum (CD_2Cl_2) shows characteristic signals attributable to $P(CH_2OCOCH_3)$ group at 2.09 (s, CH_3COOCH_2) and 4.53 (d, CH_2O, $J_{HP} = 5$ Hz) ppm.

The ^{31}P-NMR spectrum (CD_2Cl_2) shows a singlet at 35.7 ppm.

The ^{13}C-NMR spectrum (CD_2Cl_2) shows resonances attributable to the $P(CH_2OCOCH_3)$ group at 16.7 (s, CH_3), 54.0 (t, CH_2, $J_{CP} = 80.1$ Hz) and 166.3 (s, PCH_2COO) ppm.

4.4.3. Reaction of **1** with acetic acid

$H_4Ru_4(CO)_8[P(CH_2OCOCH_3)_3]_4$ (45 mg, 0.028 mmol) in acetic acid (5 ml) was refluxed for several hours and the reaction monitored by IR and ^{31}P-NMR spectroscopy. After 48 h a sample of the solution was evaporated to dryness and the residue analyzed with spectroscopic methods: the starting complex was the main product present but in the IR spectrum (CH_2Cl_2) new bands were present at 2070 (w), 2011 (sh) and 1559 (w, broad) cm^{-1}. The ^{31}P-NMR spectrum (CD_2Cl_2) shows signals at 8.7 (s, **7**, 2.3%), 24.5 (s, **1**, 91.2%) and 26.4 (s, n.d.; 6.5%) ppm.

The solution was further refluxed for 144 h. The ^{31}P-NMR spectrum (CD_2Cl_2) of a sample of the solution, after the usual work up, showed signals at 26.4 (s, 55.3%) and 35.7 (s, 44.7%) ppm.

On standing at room temperature the signal at 26.4 ppm decreases rapidly while there is an increase in intensity of the signal at 35.7 ppm and the appearance of new weak signals at 51.4, 64.0, 82.4 ppm.

The IR solution of the residue dissolved in CH_2Cl_2 show bands at 2060 (vs, broad), 1998 (vs, broad), 1755 (vs) and 1559 (w) cm^{-1}.

4.4.4. Reaction of **7** with acetic acid

$Ru_2(CO)_4(CH_3COO)_2[P(CH_2OCOCH_3)_3]_2$ (26 mg, 0.028 mmol) in acetic acid (5 ml) was stirred for 24 h at room temperature. A sample of the pale yellow solution was evaporated to dryness. The IR spectrum of the residue, dissolved in CH_2Cl_2, shows the bands of the starting complex and new bands at 2066 (w) and 2011 (sh) cm^{-1}.

The solution after heating for 3 h at 40°C becomes colorless. This solution was evaporated to dryness at 0°C and the residue was analyzed spectroscopically.

The IR spectrum (CH_2Cl_2) shows, in the 2200–1500 cm^{-1} region, bands at 2070 (vs), 2011 (vs), 1758 (vs), 1562 (m) cm^{-1}.

The ^{1}H-NMR spectrum ($CDCl_3$) shows signals at 2.04 (s, CH_3COORu), 2.09 (s, CH_3COOCH_2), 2.12 (s, CH_3COORu), 4.81 (s, CH_2O) ppm.

The ^{31}P-NMR spectrum (CD_2Cl_2) shows a singlet at 26.4 ppm.

The ^{13}C-NMR spectrum ($CDCl_3$) shows resonances at 17.6 (s, CH_3COOCH_2), 19.9 (s, CH_3COORu), 26.9 (s, CH_3COORu), 53.2 (t, CH_2, $J_{CP} = 16.9$ Hz), 167.0 (s, PCH_2COO), 175.5 (s, COORu), 182.3(s, COORu), 190.7 (m, Ru–CO) ppm.

The complex decomposes rapidly. Its complete characterization is therefore difficult.

4.5. Catalytic hydrogenation

4.5.1. General procedure

The catalytic experiments were carried out in a glass vial placed in a 'Hastelloy C' stainless steel rocking autoclave (125 ml). Air was evacuated from the vessel and replaced by dry nitrogen. The catalytic precursor, the selected substrate and the solvent (when necessary) were then introduced. The autoclave was then sealed and hydrogen introduced up to the pressure required. The autoclave was placed in a thermostatic oil bath set at the desired temperature ($\pm$ 1°C) and rocked for the prefixed time. The amount and the identity of the organic products in the crude were obtained by GC and GC-MS analysis.

Working conditions and results are reported in Tables 1–5.

4.5.2. Analyses of the hydrogenation products

In the hydrogenation of acetic, propanoic, 2-methylbutanoic and *n*-pentanoic acid conversions were evaluated by GC analyses using calibration curves obtained from mixtures of known composition. In all other tests conversions were determined without response factors correction.

The GC analyses were performed using the following conditions:

Acetic acid: a FFAP column kept at 50°C for 7 min, then heated up to 130°C at a rate of 30°C min^{-1}, and kept at this temperature for 20 min.

Propanoic acid: a FFAP column kept at 50°C for 10 min, then heated up to 100°C at a rate of 5°C min^{-1}, and kept at this temperature for 30 min.

2-Methylbutanoic acid: a FFAP column kept at 45°C for 10 min, then heated up to 140°C at a rate of 10°C min^{-1}, and kept at this temperature for 30 min.

n-Pentanoic acid: a FFAP column kept at 45°C for 10 min, then heated up to 140°C at a rate of 10°C min^{-1}, and kept at this temperature for 30 min.

Cyclohexene: a PPG column kept at 40°C for 25 min.

Acetophenone: a CW column kept at 60°C for 5 min, then heated up to 160°C at a rate of 20°C min^{-1}, and kept at this temperature for 10 min. The hydrogenation product, (+)(*S*)-1-phenylethanol, was recovered and purified by distillation. Its optical purity was determined by polarimetry. When the catalytic precursor was **5** the hydrogenated product had $[\alpha]^{25}_{D(max)} + 0.017°$ (neat). Its optical purity was 0.04% based on $[\alpha]^{25}_{D(max)} + 43.6°$ (neat) [21,22].

Tiglic acid: a FFAP column kept at 45°C for 10 min, then heated up to 140°C at a rate of 10°C min^{-1}, and kept at this temperature for 30 min. The hydrogenated acid was recovered as follows: the reaction mixture was neutralized using a saturated aqueous solution of sodium carbonate. After extraction with diethyl ether, the organic acid was recovered from the aqueous layer by acidification with sulfuric acid followed by extraction with diethyl ether. The hydrogenation product, (+)(*S*)-2-methylbutanoic acid, was recovered and purified by distillation: bp 76–77°C/16 mmHg. When the catalytic precursor was **5** the hydrogenated product had $[\alpha]^{25}_{D(max)} + 1.128°$ (neat); Optical purity 5.7%, based on $[\alpha]^{25}_{D(max)} + 19.8°$ [23].

4.6. Recovery of the catalyst from hydrogenation experiments

From the hydrogenation crude of acetic acid in the presence of $H_4Ru_4(CO)_8[P(CH_2OCOCH_2CH_3)_3]_4$ (Table 2) the residual substrate and the other volatile materials were removed by distillation at reduced pressure. The residue was analyzed by IR spectroscopy (CH_2Cl_2 as solvent). A complex pattern (2045(vs, broad), 1975(vs, broad), 1750(s) cm^{-1}) is present, in the 2200–1500 cm^{-1} range, attributable to several ruthenium complexes containing $P(CH_2OCOR)_3$ and $(PCH_2OH)_3$ groups, together with bands at 1610, 1580 and 1558 cm^{-1} due to carboxylato ligands.

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