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Journal of Organometallic Chemistry 690 (2005) 371–382
Journal of Organometallic Chemistry
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On the behaviour of Ru(I) and Ru(II) carbonyl acetates in the presence of H_2 and/or acetic acid and their role in the catalytic hydrogenation of acetic acid

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Received 9 September 2003; accepted 21 September 2004

Abstract

The reactivity of phosphine substituted ruthenium carbonyl carboxylates $Ru(CO)_2(MeCOO)_2(PBu_3)_2$, $Ru_2(CO)_4(\mu\text{-}MeCOO)_2(PBu_3)_2$, $Ru_4(CO)_8(\mu\text{-}MeCOO)_4(PBu_3)_2$ with H_2 and/or acetic acid was investigated by IR and NMR spectroscopy to clarify their role in the catalytic hydrogenation of acetic acid. Evidences were collected to suggest hydride ruthenium complexes as the catalytically active species. Equilibria among ruthenium hydrides and carboxylato complexes take place in the presence of hydrogen and acetic acid, that is in the conditions of the catalytic reaction. Nevertheless the presence of acetic acid reduces the rate of the formation of hydrides. Working at a very high temperature (180°C) polynuclear phosphido hydrides such as $[Ru_6(\mu\text{-}H)_6(CO)_{10}(\mu\text{-}PHBu)(\mu\text{-}PBu_2)_2(PBu_3)_2(\mu_6\text{-}P)]$ were formed. These phosphido clusters are suggested as the resting state of the catalytic system.

Furthermore the bi- or tetranuclear Ru(I) carboxylato complexes react with acetic acid giving a mononuclear ruthenium complex $Ru(CO)_2(MeCOO)(\mu\text{-}MeCOO)(PBu_3)$, containing a monodentate and a chelato acetato ligands. This complex was spectroscopically characterised. Its identity and structure were confirmed by its reactivity with stoichiometric amount of PPh_3 to give $Ru(CO)_2(MeCOO)_2(PBu_3)(PPh_3)$, a new mononuclear ruthenium carbonyl carboxylate containing two different phosphines, that was fully characterised.

Keywords: Ruthenium; Carbonyl carboxylates; Acetic acid; Hydrogenation

1. Introduction

The catalytic hydrogenation of carboxylic acids in homogeneous phase has been investigated in our laboratory for several years [1]. This reaction was achieved using ruthenium complexes such as $Ru_4H_4(CO)_8(PBu_3)_4$ (**1**) and $Ru_4H_4(CO)_8[(-)\text{-DIOP}]_2$ [2] as catalytic precursors.

Ruthenium carbonyl carboxylates $Ru(CO)_2(MeCOO)_2(PBu_3)_2$ (**2**), $Ru_2(CO)_4(\mu\text{-}MeCOO)_2(PBu_3)_2$ (**3**), $Ru_4(CO)_8(\mu\text{-}MeCOO)_4(PBu_3)_2$ (**4**), were detected in the crude of the hydrogenation of acetic acid in the presence of (**1**) as catalytic precursor [2a,3]. These carboxylato complexes (**2**)–(**4**) are catalytically active in the hydrogenation of acetic acid [1b].

The behaviour of (**1**)–(**4**) with hydrogen has been studied [1d,1e,1h] in order to understand their role in the catalytic hydrogenations. The ruthenium carboxylato complexes (**2**) and (**3**) react with hydrogen at low temperature (50 and 100 °C, respectively) to give the hydrido complexes $RuH_2(CO)_2(PBu_3)_2$ (**5**), $Ru_4H_4(CO)_9(PBu_3)_3$ (**6**) and (**1**) [1h]. At higher temperature (over 140 °C), the phosphido ruthenium clusters

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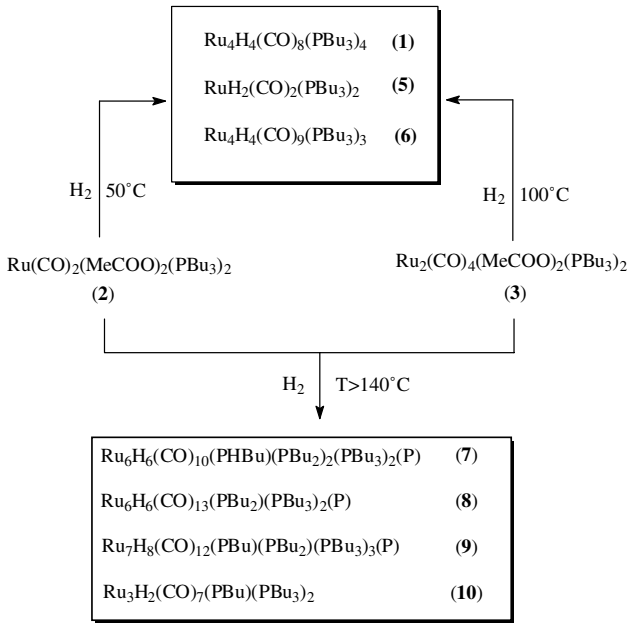
doi:10.1016/j.jorganchem.2004.09.048



Scheme 1.

$[Ru_6(\mu\text{-}H)_6(CO)_{10}(\mu\text{-}PHBu)(\mu\text{-}PBu_2)_2(PBu_3)_2(\mu_6\text{-}P)]$ (**7**), $[Ru_6(\mu\text{-}H)_6(\mu\text{-}CO)(CO)_{12}(\mu\text{-}PBu_2)(PBu_3)_2(\mu_6\text{-}P)]$ (**8**), $[Ru_7(\mu\text{-}H)_8(CO)_{12}(\mu_3\text{-}PBu)(\mu\text{-}PBu_2)(PBu_3)_2(\mu_6\text{-}P)]$ (**9**), $[Ru_3(\mu\text{-}H)_2(CO)_7(\mu_3\text{-}PBu)(PBu_3)_2]$ (**10**) are formed [1d,1e] (Scheme 1).

To get more information on the role played by the complexes (**2**–**4**) in the catalytic hydrogenation of acetic acid we have now investigated the behaviour of these complexes in the presence of acetic acid or acetic acid and H_2. The reactions were monitored by "in situ" HP-IR spectroscopy, using a cell directly connected to the reaction vessel. Samples of the solutions were also analysed by glc and glc-ms to identify the organic products formed. The new ruthenium complexes were characterised by IR and NMR spectroscopy.

Some reactions were also monitored by ^{31}P NMR spectroscopy.

At the end of this investigation, the hydrogenating activity of $[Ru_6(\mu\text{-}H)_6(CO)_{10}(\mu\text{-}PHBu)(\mu\text{-}PBu_2)_2(PBu_3)_2(\mu_6\text{-}P)]$ (**7**) has been tested in order to evaluate the role played by the phosphido clusters in the catalytic hydrogenation of acetic acid.

2. Results and discussion

2.1. Reactivity of ruthenium carbonyl carboxylates with acetic acid

2.1.1. $Ru_2(CO)_4(\mu\text{-}MeCOO)_2(PBu_3)_2$ (3)

2.1.1.1. IR study. $Ru_2(CO)_4(\mu\text{-}MeCOO)_2(PBu_3)_2$ (**3**), in *n*-heptane as solvent, reacted with acetic acid (Ru/CH_3COOH = 1:30) at 40 °C giving a new complex $Ru(CO)_2(MeCOO)(\mu\text{-}MeCOO)(PBu_3)$ (**11**) as evidenced by new bands at 2060(ff), 1990(ff) and 1575(m) cm^{-1}. After 48 h traces of (**3**) were still present. A quantitative conversion of (**3**) into (**11**) was reached after 70 h.

No other transformations were observed increasing the temperature up to 120 °C. At this temperature part of the acetic acid was present in vapour phase decreasing its concentration in solution. As a consequence the reaction was reversed and (**3**) returned to be the main complex present in the solution (Scheme 2). A further increase of temperature (150 °C) reduced further the concentration of acetic acid in solution and the amount of (**11**).

The process is reversible because when the vessel was cooled to room temperature and the concentration of acetic acid restored to its initial value, the amount of (**11**) increases: after 48 h (**11**) was the sole ruthenium complex present in solution.

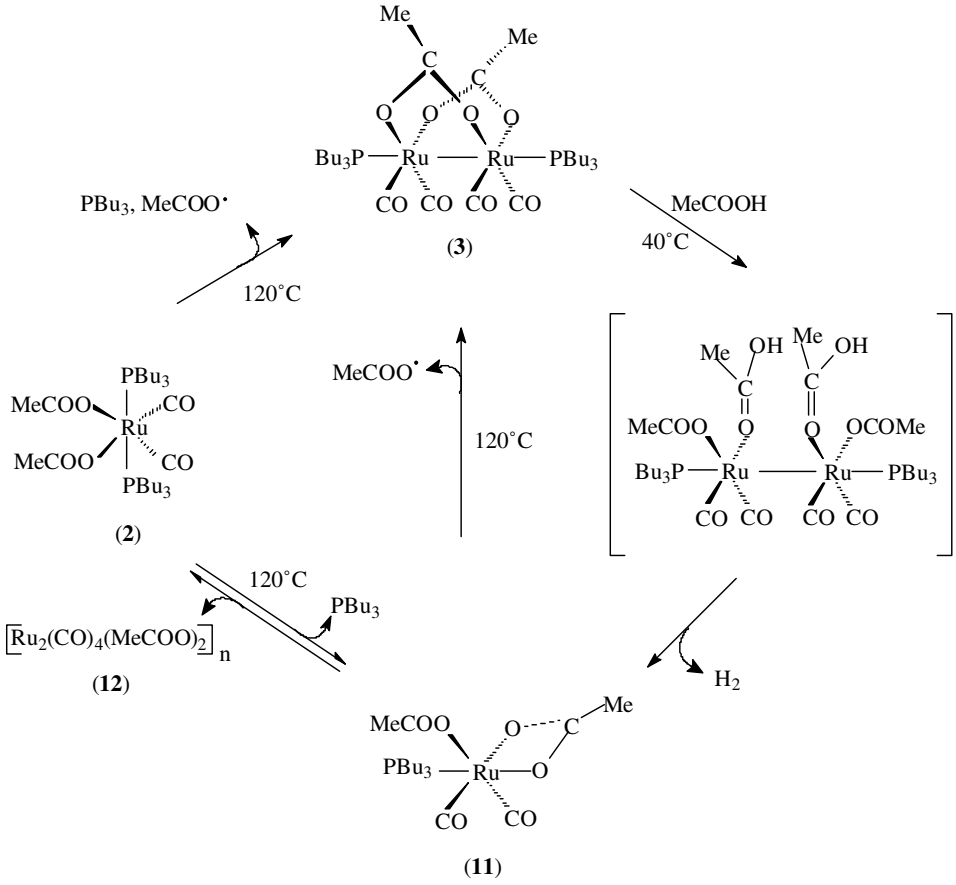
In the residue obtained removing the solvent and the acetic acid at reduced pressure and low temperature (10 °C), the complexes (**11**) and (**2**) were evidenced by IR spectroscopy using *n*-pentane as solvent. However, the IR spectrum of the same residue in a *n*-heptane/acetic acid solution showed the presence of (**11**) as the sole complex in solution because the absorptions of (**2**) in acetic acid are shifted and overwhelmed by those of (**11**).

Complex (**11**) showed a low stability in a hydrocarbon solution in the absence of acetic acid.

2.1.1.2. NMR study. The reactivity of (**3**) with acetic acid was also carried out in an NMR sample tube using C_6D_6 as solvent. After an hour at room temperature a singlet at 43.5 ppm (11.7%) attributable to (**11**) and a singlet at 17.2 ppm (1.2%) due to (**2**) were present in the ^{31}P NMR spectrum. Complex (**2**) was not easily identified in the IR spectrum performed in a C_6D_6/acetic acid solution when (**11**) was the main ruthenium complex because the absorptions of (**2**) in the presence of acetic acid are overwhelmed by those of (**11**). However, if the acetic acid was removed and the residue dissolved in *n*-pentane, the presence of (**11**) and (**2**) might be easily evidenced (see above).

A total conversion of (**3**) was reached after 56 h at 40 °C [70.4% of (**11**) and 29.6% of (**2**)]. No other signals were present in the ^{31}P NMR spectrum.

The ^{31}P-, ^{1}H-, and ^{13}C NMR spectra (C_6D_6 as solvent) of the residue after elimination of the acetic acid confirmed the presence of (**11**) and (**2**). The NMR resonances were shifted with respect to those collected from the solution containing acetic acid. The presence of (**2**) was confirmed by its characteristic resonances. The complex (**11**) showed resonances due to PBu_3 (a broad singlet at 44.4 ppm in the ^{31}P NMR spectrum) and CO ligands (195.9 (m) ppm in the ^{13}C NMR spectrum), two inequivalent MeCOO groups (174.5 and 183.0 ppm in the ^{13}C NMR spectrum attributable to a mono- and a bidentate acetato ligand, respectively). These attributions are in agreement with the resonance of the



Scheme 2.

monodentate acetato group in (**2**) (175.9 ppm) and the bidentate acetato ligand in Ru(μ-MeCOO)$_2$[(*S*)-BINAP] (188.1 ppm) [4], respectively. The broad signal in the ^{31}P NMR spectrum may be due to a rapid intramolecular rearrangement between the acetato ligands. Several complexes containing both mono- and bidentate carboxylato ligands are reported, such as Ru(CO)(RCOO)(μ-*O*,*O*′-RCOO)(PPh$_3$)$_2$ (R = Me, *p*-C$_6$H$_4$Cl, *p*-C$_6$H$_4$NO$_2$, CF$_3$, C$_2$F$_5$, C$_6$F$_5$) [5]. A rapid intramolecular exchange between mono- and bidentate carboxylato ligands was observed by NMR studies on these complexes (R = Me, CF$_3$, C$_2$F$_5$, C$_6$F$_5$) [6] at variable temperature.

The fluxional structure of the complex (**11**) was confirmed by the ^{1}H NMR spectrum. The broad resonance at 2.02 ppm, attributed to the methyl group of the acetato ligands, suggests a fast intramolecular rearrangement of the two acetato ligands. An analogous broad signal in the ^{1}H NMR spectrum is reported by Spencer and Wilkinson [5a] for the non-rigid Ru(MeCOO)(μ-MeCOO)(CO)(PPh$_3$)$_2$ complex.

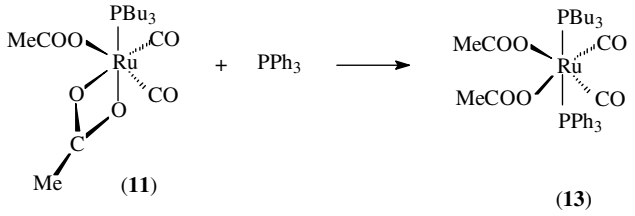
The low stability of (**11**) in the absence of acetic acid was confirmed by several signals present in the ^{31}P NMR spectrum recorded after 24 h.

The formation of (**11**) is rationalised in Scheme 2. Acetic acid is added to (**3**) breaking the acetato bridge and giving an intermediate complex [Ru$_2$(CO)$_4$(MeCOO)$_2$(MeCOOH)$_2$] containing two monodentate carboxylato ligands. An analogous process involving the formation of a Ru$_2$(MeCOO)$_2$(CO)$_6$(PBu$_3$)$_2$ containing monodentate acetato ligands has been suggested in the reaction of (**3**) with CO [1f] as a preliminary step of the formation of Ru(CO)$_4$(PBu$_3$).

The complexes that we are now proposing are closely related to those previously isolated by Rotem et al. [7], containing acetic acid units directly bound to the metal.

This intermediate Ru(I) complex gives the mononuclear Ru(II) complex (**11**) and H$_2$ (Scheme 2). A similar reactivity of the coordinated acetic acid was reported to explain the synthesis of (**2**) from [Ru$_2$(CO)$_4$(μ-MeCOO)$_2$]$_n$ (**12**) [8]. Ruthenium (I) was oxidised by the coordinated acetic acid and molecular hydrogen was formed. Fachinetti et al. [9] also suggest an analogous oxidation of Ru(0) to Ru(I) in the presence of CF$_3$COOH.

The partial transformation of (**11**) into (**2**) was observed by IR and NMR spectroscopy of the solution while the contemporary formation of (**12**), the ruthenium species without phosphinic ligands, was identified through IR spectroscopy (KBr pellets) on the yellow residue present in the NMR sample tube.



Scheme 3.

When the reaction was prolonged for a long time at 120 °C the Ru(II) complexes, (**11**) and (**2**), were reduced to the Ru(I) complex (**3**) (Scheme 2). An acetato radical may be involved. It reacted with *n*-heptane giving acetic acid and heptenes as showed by glc. No Ru(0) species were detected. The rearrangement of (**2**) into (**3**) at 120 °C was previously reported [1d] and attributed to a thermal transformation. On the contrary a disproportionation of a polymetallic Ru(I) complex into Ru(0) and Ru(II) species was reported by Fachinetti et al. [9,10].

*2.1.1.3. Synthesis and structure of $Ru(CO)_2(MeCOO)_2(PBu_3)(PPh_3)$ (**13**).* Complex (**11**) reacted at room temperature with a stoichiometric amount of PPh_3 giving $Ru(CO)_2(MeCOO)_2(PBu_3)(PPh_3)$ (**13**) (Scheme 3), a ruthenium carbonyl carboxylate containing two different phosphines. This new complex was isolated and spectroscopically characterised.

The data collected are in agreement with an octahedral structure containing a tributylphosphine *trans* to a triphenylphosphine, two *cis* carbonyl groups and two *cis* acetato ligands (Fig. 1(a)).

The other possible structures (b)–(f) (Fig. 1) have been ruled out according to the following considerations: the ^{31}P NMR spectrum shows an AB spin system

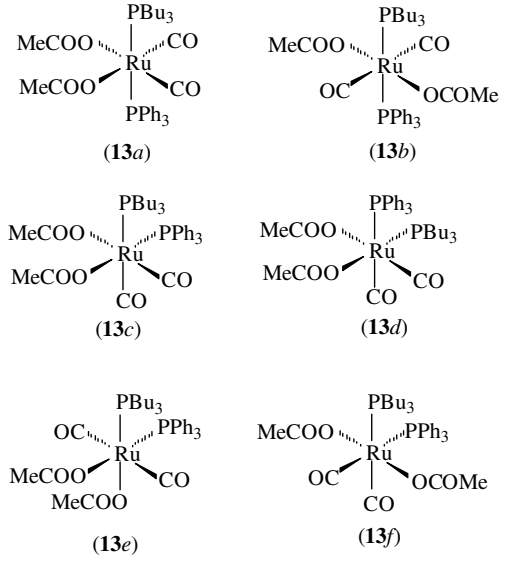


Fig. 1.

with resonances at 23.9 (d, 1P, PBu_3, J_{PP} = 311.6 Hz) and 30.5 (d, 1P, PPh_3, J_{PP} = 311.6 Hz) ppm. The J_{PP} value is in agreement with a *trans* coupling between the two phosphine [11]. The pattern of this NMR spectrum has been well simulated using the data above reported. The ^1H- and ^{13}C NMR spectra are in agreement with two equivalent acetato ligands ruling out the structures (**13c**), (**13d**) and (**13e**). The pseudo triplet at 198.8 ppm in the ^{13}C NMR spectrum may be ascribed to the carbon atoms of two equivalent carbonyl groups coupled with two *cis* phosphines. As a consequence the structures (**13c**), (**13d**) and (**13f**) showing two non-equivalent carbonyl groups must be excluded. The structures (**13b**) and (**13e**) containing the carbonyl groups in a *trans* position must be also discarded because two bands of equal intensity are present in the carbonyl stretching region of the IR spectrum.

The MS spectrum shows a pattern of peaks centred at *m/z* 740 in agreement with the $Ru(CO)_2(MeCOO)_2(PBu_3)(PPh_3)$ formulation of (**13**).

The elemental analysis confirm the reported formulation.

The synthesis of (**13**) from (**11**) and PPh_3 confirms also the structure attributed to (**11**).

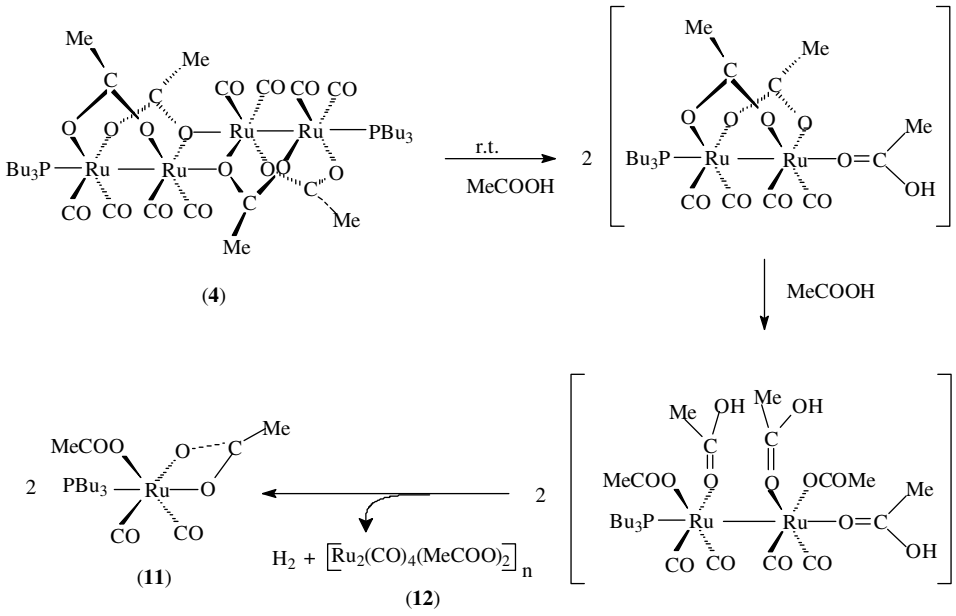
*2.1.2. $Ru_4(CO)_8(\mu\text{-}MeCOO)_4(PBu_3)_2$ (**4**)*

2.1.2.1. IR study. The complex (**4**), in *n*-heptane as solvent, reacted at room temperature with an excess of acetic acid (Ru/CH_3COOH = 1:23) giving (conversion 60% after 24 h) a mixture of ruthenium complexes. The new bands at 2060 and 1990 cm^{-1} were attributed to (**11**) while a band at 1999(w) cm^{-1} suggests the presence of a trace of another unidentified product. A broadband was also present in the carboxylato region at 1580 cm^{-1} suggesting the presence of an acetato complex. A reasonable mechanistic pathway for the conversion of (**4**) into (**11**) is proposed in Scheme 4 taking into account the reactivity of (**4**) with CO [1f]. A preliminary coordination of acetic acid is followed by a cleavage of the oxygen bridges between two Ru atoms giving the complex $[Ru_2(CO)_4(\mu\text{-}MeCOO)_2(MeCOOH)(PBu_3)]$ (Scheme 4). In a subsequent step this complex reacts with acetic acid giving the complexes (**11**) and (**12**). This last complex was identified as a yellow residue after cooling the vessel.

At higher temperature (120 °C after 24 h) (**11**) was the sole complex present in the solution as shown by the IR spectrum.

2.1.2.2. NMR study. The reaction of (**4**) with acetic acid was also carried out in a NMR sample tube (C_6D_6 as solvent) and monitored by ^{31}P NMR spectroscopy.

At room temperature (**11**) was formed (conversion 24.5% after 1 h) together with trace of two phosphinic compounds (singlet at 13.4 and 38.8 ppm in the ^{31}P



Scheme 4.

NMR). After 8 days (**11**) was the main complex (75.6%) present in the solution and (**4**) was still present (12.3%). A yellow insoluble product was also formed and identified by IR spectroscopy as (**12**).

The conversion of (**4**) was complete after 15 days at room temperature and (**11**) was the main product in the solution (87.2%) together with an unidentified product having a singlet at 38.8 ppm (12.8%) in the ^{31}P NMR.

The IR and NMR spectra of the residue obtained after distillation of the solvent and acetic acid at low temperature and reduced pressure showed (**11**) as the main ruthenium species. This solution was employed to perform the spectroscopic characterisation of (**11**) (see Section 4).

2.1.3. $Ru(CO)_2(MeCOO)_2(PBu_3)_2$ (2)

Complex (**2**) did not react with acetic acid at room temperature in a *n*-heptane solution (Ru/CH_3COOH = 1:30). Only a shift of the carbonyl stretchings of (**2**) to higher frequencies was due to the presence of acetic acid. This behaviour is reversible: if the liquids were removed and the residue dissolved in *n*-heptane the starting spectrum of (**2**) was restored. In the same way the resonances of (**2**) were shifted when the ^{1}H-, ^{31}P- and ^{13}C NMR spectra were recorded in a $MeCOOH/C_6D_6$ solution (Table 1). The multiplicity and the coupling constants remain unchanged in all cases.

A temperature of 140 °C was required to observe the conversion of (**2**) into traces of (**3**); the amount of (**3**) increased after heating at 150 °C, as expected, according to the thermal stability of (**2**) [1d].

2.2. Reactivity of ruthenium carbonyl carboxylates with hydrogen and acetic acid

The reaction of ruthenium complexes (**2**–**4**) with hydrogen and acetic acid, that is in the conditions employed for the hydrogenation of acetic acid, was tested by IR spectroscopy. The organic products were identified and quantified by glc and glc-ms analyses.

2.2.1. $Ru_2(CO)_4(\mu\text{-}MeCOO)_2(PBu_3)_2$ (3)

The complex (**3**), in a *n*-heptane solution, did not react with acetic acid (Ru/CH_3COOH = 1:30) and hydrogen (100 atm) at room temperature after a long time (15 days).

The IR spectrum of (**3**) was unchanged even if the solution was heated up to 140 °C; however in these conditions ethyl acetate was formed through the hydrogenation of acetic acid.

Only at 180 °C after 24 h (**3**) was transformed into the hydrido clusters (**7**), (**9**) and (**10**). The same ruthenium complexes were formed at lower temperature from (**3**) and hydrogen (50 atm) [1e]. The presence of acetic acid reduces the rate of the transformation of (**3**) into phosphido ruthenium clusters.

This behaviour supports the hypothesis that intermediate hydrido ruthenium complexes must be involved in these transformations [1h]. The presence of acetic acid decreases the rate of the hydrogenolysis of the acetato group in (**3**) because this reaction involves the formation of ruthenium hydrides and acetic acid. Furthermore, the presence of hydrogen hinders the formation of (**11**) by reaction of (**3**) and acetic acid, in agreement with the mechanism reported in Scheme 2.

Table 1
Spectroscopic data of $Ru(CO)_2(MeCOO)_2(PBu_3)_2$[a]: influence of acetic acid

Solvent	IR ν (cm^{-1})	Solvent	^{31}P NMR (ppm)	^{1}H NMR (ppm)	^{13}C NMR (ppm)
n-Heptane	2041(vs) 1971(vs) 1628(m)	C_6D_6	17.4	0.86 (t, 18H, CH_3CH_2, J_{HH} = 7.3 Hz), 1.28 (q, 12H, CH_3CH_2, J_{HH} = 7.3 Hz), 1.50 (m, 12H, CH_2CH_2P), 1.86 (m, 12H, CH_2 P), 2.25 (s, 6H, CH_3COO)	13.8 (s, CH_3CH_2), 23.7 (s, CH_3COO), 23.9 (t, CH_2P, J_{CP} = 12.7 Hz), 24.8 (t, CH_3CH_2, J_{CP} = 6.3 Hz), 25.4 (s, CH_2CH_2 P), 175.9 (s, CH_3COO), 199.0 (t, CO, J_{CP} = 10.9 Hz)
n-Heptane/MeCOOH	2049(vs) 1988(vs) 1575(m)	C_6D_6/MeCOOH	17.2	0.85 (t, 18H, CH_3CH_2, J_{HH} = 7.3 Hz), 1.28 (q, 12H, CH_3CH_2, J_{HH} = 7.3 Hz), 1.42 (m, 12H, CH_2CH_2P), 1.81 (m, 12H, CH_2P), 2.27 (s, 6H, CH_3COO)	14.1 (s, CH_3CH_2), 23.6 (s s, CH_3COO), 24.1 (t, CH_2 P, J_{CP} = 12.7 Hz), 25.0 (t, CH_3CH_2, J_{CP} = 6.3 Hz), 25.6 (s, CH_2CH_2 P), 179.3 (s, CH_3COO), 198.7 (t, CO, J_{CP} = 10.9 Hz t)

[a] NMR data are partially reported [1a].

2.3. $Ru_4(CO)_8(\mu\text{-}MeCOO)_4(PBu_3)_2$ (**4**)

The complex (**4**), in *n*-heptane as solvent, reacted in the presence of acetic acid (Ru/CH_3COOH = 1:23) and hydrogen (100 atm at room temperature) at 60 °C giving (**3**) (traces after 72 h) as reported in Scheme 5. The complex (**12**), formed as a concomitant product, was recovered as a yellow solid and identified by IR spectroscopy.

The same reaction takes place in a large extent at 60 °C in the presence of only hydrogen [1f] or through a thermal rearrangement of (**4**) at 150 °C [8,12].

These data support the hypothesis that the phosphine redistribution also takes place through hydride intermediates, formed in an undetectable amount. The formation of ruthenium hydrides is reduced by the presence of acetic acid and consequently the phosphine redistribution is very low. It was necessary to heat (**4**) at 140 °C for 20 h to obtain a (**4**)/(**3**) molar ratio of 3:2.

The complex (**4**), heated at 160 °C for 25 h, was almost completely transformed into (**3**) and (**12**). Ethyl acetate was also present in the solution collected at this temperature and analysed by glc.

2.4. $Ru(CO)_2(MeCOO)_2(PBu_3)_2$ (**2**)

The complex (**2**), in a *n*-heptane solution, did not react with acetic acid (Ru/CH_3COOH = 1:30) and hydrogen (100 atm) at room temperature. Only a shift of the bands in the IR spectrum was shown as observed under nitrogen.

Heating this solution for 24 h at 80 °C the complexes (**5**) [1d] and $RuH(CO)_2(MeCOO)(PBu_3)_2$ (**14**) [13] [conversion of (**2**) 56%; (**5**)/(**14**) = 1/1 molar ratio] were formed. Traces of (**3**) were also formed after 48 h at this temperature.

The conversion of (**2**) increased when the solution was heated at higher temperature; the dihydride (**5**) was the main ruthenium complex (49%) after 24 h at 100 °C [conversion 79%; (**5**)/(**14**) = 1.6 molar ratio] and (**5**) became 65% at 140 °C after 24 h [conversion 94%; (**5**)/(**14**) = 2.2 molar ratio].

At 180 °C, (**5**) (78%) and (**14**) (22%) were present together with traces of (**2**) and (**3**): at this temperature ethyl acetate was also formed by reduction of acetic acid.

The rate of the transformation of (**2**) into (**5**) was reduced by the presence of acetic acid according to the equilibria reported in Scheme 6.

The formation of (**14**) as intermediate of the reaction of (**2**) with hydrogen has been previously reported working at low temperature (50 °C) in the presence of Na_2CO_3 [1h].

The presence of an excess of acetic acid reduce the rate of the formation of (**5**) and, as a consequence, increases the amount of (**14**).

$$\underset{(\mathbf{4})}{Ru_4(CO)_8(\mu\text{–}MeCOO)_4(PBu_3)_2} \rightleftharpoons \underset{(\mathbf{3})}{Ru_2(CO)_4(\mu\text{–}MeCOO)_2(PBu_3)_2} + 1/n\,\underset{(\mathbf{12})}{[Ru_2(CO)_4(\mu\text{–}MeCOO)_2]_n}$$

Scheme 5.

$$\underset{(\mathbf{2})}{Ru(CO)_2(MeCOO)_2(PBu_3)_2} + H_2 \rightleftharpoons \underset{(\mathbf{14})}{RuH(CO)_2(MeCOO)(PBu_3)_2} + MeCOOH$$

$$\underset{(\mathbf{14})}{RuH(CO)_2(MeCOO)(PBu_3)_2} + H_2 \rightleftharpoons \underset{(\mathbf{5})}{RuH_2(CO)_2(PBu_3)_2} + MeCOOH$$

Scheme 6.

Table 2
Hydrogenation of unsaturated organic substrates in the presence of ruthenium complexes

Catalyst	Code	Hydrogenation of (yield %)			
		Cyclohexene[a]	Tiglic acid[b]	Acetophenone[c]	Acetic acid[d]
$Ru_4H_4(CO)_8(PBu_3)_4$	(**1**)	47.1	21.7	9.6	40.7
$Ru(CO)_2(MeCOO)_2(PBu_3)_2$	(**2**)	2.0	15.4	45.8	16.5
$Ru_2(CO)_4(\mu\text{-}MeCOO)_2(PBu_3)_2$	(**3**)	22.2	98.2	65.7	34.4
$Ru_4(CO)_8(\mu\text{-}MeCOO)_4(PBu_3)_2$	(**4**)	88.3	79.1	14.3	29.9
$[Ru_6(\mu\text{-}H)_6(CO)_{10}(\mu\text{-}PHBu)(\mu\text{-}PBu_2)_2(PBu_3)_2(\mu_6\text{-}P)]$	(**7**)	0.4	0.3	1.0	2.9

Catalyst: 0.018 mmol Ru, substrate: 42.5 mmol, $p(H_2) = 130$ atm, reaction time 22 h.
[a] $T = 60$ °C, hydrogenated product: cyclohexane.
[b] Solvent: 20 ml, toluene/ethanol (1:1), $T = 100$ °C, hydrogenated product: 2-methylbutanoic acid.
[c] $T = 120$ °C, hydrogenated product: 1-phenylethanol.
[d] Catalyst: 0.139 mmol Ru, substrate 433 mmol, $T = 180$ °C, reaction time 48 h, hydrogenated product: ethyl acetate.

2.5. Catalytic activity of $[Ru_6(\mu\text{-}H)_6(CO)_{10}(\mu\text{-}PHBu)(\mu\text{-}PBu_2)_2(PBu_3)_2(\mu_6\text{-}P)]$ (7)

The phosphido clusters (**7**)–(**10**) were formed from the catalytic precursors (**1**–**4**) when heated at high temperature under hydrogen. The catalytic activity of (**7**), the main cluster formed, was correlated with those of its precursors (**1**–**4**) to evaluate the role of phosphido clusters in the hydrogenations performed in the presence of the ruthenium complexes (**1**–**4**) as catalytic precursors.

Different substrates were hydrogenated in the presence of (**7**) and the ruthenium precursors (**1**)–(**4**) (Table 2).

Complex (**7**) was catalytically active in the hydrogenation of the substrates tested even if its activity was lower than that of the other catalysts. Furthermore the cluster (**7**) was recovered unaltered at the end of these hydrogenations.

The low catalytic activity of (**7**) suggests the formation of phosphido clusters as the cause of the gradual loss of activity of (**1**)–(**4**) in the course of the reduction of acetic acid at 180 °C.

3. Conclusions

The phosphine substituted ruthenium carbonyl carboxylates (**3**) and (**4**) react, at low temperature (25–40 °C) with a large excess of acetic acid to form new complexes containing monodentate acetato ligands. Further reaction of these intermediates leads to the formation of hydrogen and a mononuclear ruthenium (II) complex (**11**) containing a chelato and a monodentate acetato ligand. The same reactivity may be involved in the synthesis of (**2**) from (**12**) in the presence of acetic acid and a stoichiometric amount of PBu_3 [8].

The complex (**11**) is stable in the presence of acetic acid but easily reacts at room temperature with PPh_3 giving a new complex containing two different phosphinic ligands (**13**).

The reactivity of ruthenium complexes (**3**) and (**4**) changes when hydrogen and acetic acid are both present: (**3**) does not react up to 180 °C while (**4**) gives (**3**) and (**12**) at 60 °C. The high hydrogen pressure (100 atm) hinders the formation of (**11**) from (**3**) or (**4**) in agreement with a process involving the formation of molecular hydrogen (Schemes 2 and 4).

Hydride ruthenium complexes (**1**), (**5**)–(**10**) and (**14**) are formed in the reactions of (**2**)–(**4**) with hydrogen and acetic acid but the presence of acetic acid reduces the rates of these reactions. These results confirm the hypothesis that hydride ruthenium complexes are the active species in the catalytic hydrogenation of acetic acid [1h] and suggest equilibria among H–Ru and CH_3COO–Ru species. In the presence of a large amount of acetic acid these equilibria are shifted towards the ruthenium carboxylates (**2**), (**3**) and (**4**).

The hydrogenation of acetic acid to ethyl acetate takes place at 140 °C in the presence of (**3**), at 160 °C with (**4**) and at 180 °C with (**2**). In these conditions (**3**) is always formed even if in different amounts from (**4**) or (**2**) depending on the ruthenium precursor and reaction temperature employed. These results support the hypothesis that the same catalytically active intermediate is formed from (**2**)–(**4**) in the course of acetic acid

hydrogenation. Furthermore the hydride species are transformed into phosphido ruthenium cluster complexes such as (**7**) in the course of the reaction.

The polynuclear ruthenium complex (**7**) shows a catalytic activity lower than the precursors (**1**)–(**4**). As a consequence the loss of catalytic activity shown by the ruthenium complexes (**1**)–(**4**) in the reduction of acetic acid may be ascribed to this transformation [1b]. Other authors attribute the deactivation of catalytic systems to the partial loss of the alkyl groups of the phosphine ligands with formation of phosphido clusters [14].

4. Experimental

4.1. Instruments

Gas chromatographyc analyses (glc) were performed with a Perkin–Elmer Sigma 1 system coupled with a Perkin–Elmer Sigma 10 computer or using a Shimadzu GC-14A chromatographic system coupled with a Shimadzu C-R4A computer. Both systems were equipped with a FID detector.

The following packed columns (2 m) were used: PPG (''Polypropylenglicol'' 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%).

The conversion of acetic acid to ethyl acetate was evaluated using a calibration curve.

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

A Perkin–Elmer SCIEX API 365, a turbo ion spray system, was employed to obtain the MS spectra of the ruthenium complex.

Infrared spectra were recorded, at room temperature and pressure, with a Perkin–Elmer model 1760-X FTIR spectrophotometer. Liquid products and solutions were analysed using KBr or CaF_2 cells having 0.1 mm path. Solid samples were mulled with KBr. The IR spectra collected at high pressure and temperature were recorded with a Perkin–Elmer spectrophotometer mod. 580B Data System using the cell previously described [1d].

Multinuclear NMR spectra were registered using a Varian VXR300 spectrometer operating at 299.944 MHz for ^{1}H, at 75.429 MHz for ^{13}C and at 121.421 MHz for ^{31}P NMR; tetramethylsilane was used as external standard for ^{1}H- 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.

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

Tlc separations were performed on silica gel (thickness 2 mm) or alumina (thickness 1.5 mm) chromatographic plate (Merck) with fluorescent indicator F_{254}.

4.2. Test procedure

4.2.1. Reactivity of ruthenium complexes by IR spectroscopy

All tests were performed in a stainless steel autoclave (125 ml) equipped with two stopcocks and a high-pressure gauge. Air was evacuated from the vessel, the solution of reactants was introduced by suction then the gas (nitrogen or hydrogen) was transferred from a cylinder up to the pressure required.

The vessel was connected through a stainless-steel low volume (2 ml) coil to the IR cell, equipped with NaCl windows, capable of withstanding high pressure (200 atm), which could be heated up to 200 °C. The coil was kept at the same temperature of the system. The solution present in the autoclave was transferred into the IR cell under reaction conditions and examined by IR spectroscopy. All spectra were recorded after abundant flushing of both coil and IR cell with the solution present in the vessel. The solvent (*n*-heptane) bands were compensated using a variable-path IR cell.

4.2.2. Catalytic hydrogenation experiments

A solution containing the catalytic precursor, solvent, substrate and hydrogen was introduced into an evacuated stainless steel autoclave (150 ml) containing a steel cylinder (72 ml) to reduce the free volume. The tests of acetic acid hydrogenation were carried out in a ''Hastelloy C'' stainless steel rocking autoclave (125 ml). The vessel was placed in a thermostatic oil bath set at the desired temperature (±1 °C) and rocked for the prefixed time. The amounts of catalytic precursor, solvent, substrate and hydrogen are reported in Table 2.

At the end of the reaction, the reactor was cooled, the gases vented and the solution analysed by glc. The identity of the products was confirmed by glc-ms analysis.

4.3. Materials

All preparations and manipulations were routinely performed under dry nitrogen using Schlenk tube techniques.

Reagents and solvents were purified and dried as reported. Acetic acid was distilled under nitrogen (bp 118 °C). Cyclohexene was eluted through activated Al_2O_3 (70–230 mesh) and rectified under nitrogen (bp 83 °C). Acetophenone was distilled prior to use (bp 82 °C/15 mmHg). Toluene was refluxed on sodium metal, then 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%), dried on anhydrous $CaCl_2$, refluxed on sodium and distilled on $LiAlH_4$. Methanol, dried as reported by Vogel [15], had bp 65 °C. Tri-*n*-butylphosphine was distilled under nitrogen prior to use (bp 158–160 °C/60 mmHg).

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

4.3.1. Synthesis of ruthenium complexes

Complexes $Ru_4H_4(CO)_8(PBu_3)_4$ (**1**) [16], $Ru(CO)_2(MeCOO)_2(PBu_3)_2$ (**2**) [8], $Ru_2(CO)_4(\mu\text{-}MeCOO)_2(PBu_3)_2$ (**3**) [17], $Ru_4(CO)_8(\mu\text{-}MeCOO)_4(PBu_3)_2$ (**4**) [12], $RuH_2(CO)_2(PBu_3)_2$ (**5**) [1d], $Ru_4H_4(CO)_9(PBu_3)_3$ (**6**) [16], $[Ru_6(\mu\text{-}H)_6(CO)_{10}(\mu\text{-}PHBu)(\mu\text{-}PBu_2)_2(PBu_3)_2(\mu_6\text{-}P)]$ (**7**) and $[Ru_2(CO)_4(\mu\text{-}MeCOO)_2]_n$ (**12**) [17] were prepared as described in the literature. The ^{1}H-, ^{31}P- and ^{13}C NMR spectra of (**1**)–(**4**) and (**6**) were performed using the same solvents (C_6D_6) employed in experimental tests with the aim to facilitate their identification in the course of the reactions (Table 3).

4.4. Reactivity of ruthenium complexes in the presence of acetic acid: IR study

A solution of the system under examination was introduced in the autoclave, then N_2 (5 atm) was added.

IR spectra were recorded under reaction conditions after heating the solution at the pre-fixed temperature for the selected time.

4.4.1. $Ru_2(CO)_4(\mu\text{-}MeCOO)_2(PBu_3)_2$ (3) with MeCOOH

A solution of (**3**) (120 mg, 0.144 mmol) and acetic acid (0.5 ml, 8.734 mmol) in *n*-heptane (60 ml) was heated under nitrogen (5 atm at 20 °C) in the temperature range 40–150 °C.

The reaction was followed as reported in the general procedure.

4.4.2. $Ru_4(CO)_8(\mu\text{-}MeCOO)_4(PBu_3)_2$ (4) with MeCOOH

A solution of (**4**) (119 mg, 93.8 μmol) and acetic acid (0.5 ml, 8.734 mmol) in *n*-heptane (60 ml) was heated under nitrogen (5 atm at 20 °C) in the temperature range 20–140 °C.

The reaction was followed as reported in the general procedure.

The solution recovered at the end of the experiment was evaporated to dryness, the residue dissolved in C_6D_6 and analysed by IR, ^{1}H- and ^{31}P NMR. Several singlets were present in the ^{31}P NMR spectrum besides the signals at 43.5 ppm due to (**11**), at 17.4 (**2**), 38.5, 43.1, 44.6, 45.4, 53.3 ppm.

4.4.3. $Ru(CO)_2(MeCOO)_2(PBu_3)_2$ (2) with MeCOOH

A solution of (**2**) (190 mg, 0.279 mmol) and acetic acid (0.5 ml, 8.734 mmol) in *n*-heptane (60 ml) was heated under nitrogen (5 atm at 20 °C) in the temperature range 20–150 °C.

The reaction was followed as reported in the general procedure.

A sample of the solution was collected after heating at 40 °C. After evaporation of the solvent and acetic acid under reduced pressure the residue was dissolved in *n*-heptane and analysed by IR spectroscopy: only the bands at 2041(vs), 1971(vs) and 1628(m) cm^{-1} attributable to the starting complex were present. The ^{1}H-, ^{31}P- and ^{13}C NMR spectra were recorded on the residue dissolved in C_6D_6 or in C_6D_6 containing the same concentration of MeCOOH used for the reactivity tests. The absorptions are reported in Table 1.

4.5. Reactivity of ruthenium complexes in the presence of acetic acid: NMR study

4.5.1. $Ru_2(CO)_4(\mu\text{-}MeCOO)_2(PBu_3)_2$ (3) with MeCOOH

A solution of (**3**) (24 mg, 0.029 mmol) and acetic acid (0.1 ml, 1.747 mmol) in C_6D_6 (1 ml) was introduced, under nitrogen, into a NMR sample tube.

After 56 h at 40 °C two singlet at 43.5 (70.4%) and 17.2 ppm (29.6%) were present in the ^{31}P NMR spectrum while broad bands at 2060(vs), 1990(vs), 1950(vw) and 1575(w) cm^{-1} were present in the IR spectrum.

The solution was evaporated to dryness and the residue dissolved in C_6D_6: a broad singlet was present in the ^{31}P NMR spectrum at 44.4 ppm (70.4%), attributed to (**11**), together with a singlet at 17.4 ppm (29.6%), attributed to (**2**).

In the ^{1}H NMR spectrum (C_6D_6) signals attributed to (**11**) were present at δ 0.77 (m, 9H, CH_3, PBu_3), 1.16 (m, 6H, CH_3CH_2, PBu_3), 1.30 (m, 6H, $EtCH_2$, PBu_3), 1.63 (m, 6H, PCH_2, PBu_3), 2.06 (s broad, 6H, CH_3COO) ppm and other resonances attributed to (**2**) at δ 0.90 (t, 18H, CH_3, PBu_3, J_{HH} = 7.1 Hz), 1.30 (m, 12H, CH_3CH_2, PBu_3), 1.53 (m, 12H, $EtCH_2$, PBu_3), 1.87 (m, 12H, PCH_2, PBu_3), 2.27 (s, 6H, CH_3COO) ppm.

The ^{13}C NMR spectrum (C_6D_6) showed signals attributed to (**11**) at δ 13.4 (s, CH_3, PBu_3), 20.1 (s, μ-CH_3COO), 23.5 (s, CH_3COO), 24.1 (m, PCH_2, PBu_3), 24.3 (s, CH_3CH_2, PBu_3), 24.9 (m, $EtCH_2$, PBu_3), 174.5 (s, COO), 183.0 (s, μ-COO), 195.9 (m, CO) ppm and other resonances attributed to (**2**) at δ 13.8 (s, CH_3, PBu_3), 23.7 (s, CH_3COO), 23.9 (t, PCH_2, PBu_3, J_{PC} = 12.7 Hz), 24.8 (t, CH_3CH_2, PBu_3, J_{PC} = 6.3 Hz), 25.4 (s, $EtCH_2$, PBu_3), 175.9 (s, COO), 199.0 (t, CO, J_{PC} = 10.9 Hz) ppm.

The IR spectrum of the same sample dissolved in *n*-pentane showed the bands of the complex (**11**) at 2057(vs), 1987(vs), 1603(w), 1563(vw) cm^{-1} and those of the complex (**2**) at 2041(s), 1971(s), 1628(vw) cm^{-1}.

The sample kept for 24 h at room temperature in a C_6D_6 solution, without acetic acid, was transformed in

Table 3
NMR data of ruthenium complexes in C_6D_6 as solvent

Complex	^{31}P NMR	^{1}H NMR	^{13}C NMR
(**1**)[a]	16.6	−16.60 (qt,4H, HRu, J_{HP} = 6.0 Hz) 0.91 (t, 36H, CH_3, J_{HH} = 7.3 Hz) 1.34 (q, 24H, CH_3 CH_2, J_{HH} = 7.3 Hz) 1.52 (m, 24H, CH_2CH_2P) 1.86 (m, 24H, CH_2 P)	14.0 (s, CH_3) 24.9 (t, CH_3CH_2, J_{CP} = 6.0 Hz) 26.6 (s, CH_2CH_2P) 31.7 (t, CH_2P, J_{CP} = 10.4 Hz) 202.2 (m, CO)
(**3**)[b]	8.3	0.89 (t, 18H, CH_3CH_2, J_{HH} = 6,8 Hz) 1.35 (q, 12H, CH_3CH_2, J_{HH} = 6.8 Hz) 1.56 (m, 12H, CH_2CH_2 P) 1.81 (m, 12H, CH_2P) 1.85 (s, 6H, CH_3COO)	13.8 (s, CH_3CH_2) 23.4 (s, CH_3COO) 24.6 (t, CH_2P, J_{CP} = 7.9 Hz) 24.8 (t, CH_3CH_2, J_{CP} = 5.6 Hz) 25.6 (s, CH_2CH_2P) 186.3 (t, COO, J_{CP} = 7.9 Hz) 208.3 (m, CO)
(**4**)[c]	6.1	0.85 (t, 18H, CH_3CH_2, J_{HH} = 6,8 Hz) 1.28 (q, 12H, CH_3CH_2, J_{HH} = 6,8 Hz) 1.43 (m, 12H, CH_2CH_2P) 1.67 (m 12H, CH_2P) 2.12 (s, 12H, CH_3COO)	13.8 (s, CH_3CH_2) 23.5 (s, CH_3COO) 23.8 (d, CH_2P, J_{CP} = 12.7 Hz) 24.7 (d, CH_3CH_2, J_{CP} = 6.5 Hz) 25.4 (s, CH_2CH_2P) 185.3 (d, COO, J_{CP} = 6.5 Hz) 203.5 (d, CO, J_{C-P} = 10.9 Hz) 205.4 (d, CO, J_{C-P} = 10.9 Hz)
(**6**)[a]	20.7 22.7	−16.85 (m, 4H, HRu) −16.69 (m, 4H, HRu) 0.97 (t, 27H, CH_3, J_{HH} = 7,3 Hz) 1.43 (m, 18H, CH_3CH_2) 1.60 (m, 18H, CH_2CH_2P) 1.89 (m, 18H, CH_2P)	n.d.
(**11**)	44.4[d]	0.77 (m, 9H, CH_3, PBu_3), 1.16 (m, 6H, CH_3CH_2, PBu_3), 1.30 (m, 6H, EtCH_2, PBu_3), 1.63 (m, 6H, PCH_2, PBu_3), 2.06 (s broad, 6H, CH_3COO)	13.4 (s, CH_3, PBu_3), 20.1 (s, μ-C_3COO), 23.5 (s, C_3COO), 24.1 (m, PC_2PBu_3), 24.3 (s, $CH_3C_2PBu_3$), 24.9 (m, EtC_2PBu_3), 174.5 (s, COO), 183.0 (s, μ-COO), 195.9 (m, CO)
(**13**)	23.0 (A*B*, 1P, J_{PP} = 317.4 Hz, P^nBu_3), 29.7 (*A*B, 1P, J_{PP} = 317.4 Hz, PPh_3)	0.82 (t, 9H, CH_3CH_2, J_{HH} = 7.3 Hz), 1.24 (q, 6H, CH_3CH_2, J_{HH} = 7.3 Hz), 1.49 (m, 6H, CH_2CH_2P), 1.88 (s, 6H, CH_3COO), 1.94 (m, 6H, CH_2P), 7.02 (m, 3H, H_p, PPh_3), 7.10 (m, 6H, H_m, PPh_3), 7.96 (m, 6H, H_o, PPh_3)	13.5 (s, CH_3CH_2), 23.2 (s, CH_3COO), 24.0 (d, CH_2P, J_{CP} = 22.6 Hz), 24.5 (d, CH_3CH_2, J_{CP} = 11.3 Hz), 25.1 (s, CH_2CH_2P), 130.3 (s, C_m, PPh_3), 131.4 (s, C_p, PPh_3), 132.3 (d, C_i, PPh_3, J_{CP} = 11.3 Hz), 134.6 (d, C_o, PPh_3, J_{CP} = 9.0 Hz), 175.8 (s, CH_3COO), 198.8 (pt, CO, J_{CP} = 11.3 Hz)

[a] NMR data are partially reported [16].
[b] NMR data are reported in $CDCl_3$ as solvent [17,18].
[c] NMR data are partially reported [12].
[d] 43.5 in the presence of acetic acid.

several compounds as shown by various singlets present in the ^{31}P NMR spectrum as above reported.

*4.5.2. $Ru_4(CO)_8(\mu$-MeCOO$)_4(PBu_3)_2$ (**4**) with MeCOOH*

A solution of (**4**) (18.4 mg, 0.014 mmol) and acetic acid (0.1 ml, 1.747 mmol) in C_6D_6 (1 ml) was introduced, under nitrogen, into a NMR sample tube. After 1 h at room temperature new singlets were present in the ^{31}P NMR spectrum at 43.5 (**11**), 38.8 and 13.4 ppm.

The conversion of (**4**) was 24.5% after 1 h and 100% after 15 days at room temperature. The singlet of (**11**) at 43.5 ppm was the main resonance (87.2%) and a yellow residue was present in the sample tube. The solid was separated and the IR spectrum recorded as nujol mull showed bands at 2055(s), 1995(vs), 1970(vs), 1910(s) and 1555(vs) cm^{-1} attributable to (**12**).

The solution was evaporated to dryness and the residue dissolved in C_6D_6 and spectroscopically character-

ised as complex (**11**). NMR data are reported in Table 2.

In the IR spectrum (*n*-pentane) were present bands at 2057(vs), 1987(vs), 1563(vw, broad) cm^{-1} due to (**11**).

4.6. Synthesis of $Ru(CO)_2(MeCOO)_2(PBu_3)(PPh_3)$ (**13**)

Triphenylphosphine (15.21 mg, 0.058 mmol) was added to the solution containing (**11**) in C_6D_6 (PPh_3/Ru = 1/1, molar ratio) at room temperature and the mixture monitored by ^{31}P NMR.

After 3 h a second-order AB spin system with resonances at δ 23.9 (d, 1P, PBu_3, J_{PP} = 311.6 Hz) and 30.5 (d, 1P, PPh_3, J_{PP} = 311.6 Hz) ppm was present in the ^{31}P NMR spectrum while the intensity of the singlet attributable to (**11**) was very low. The conversion was 90% after 5 h.

The solvent was evaporated and the new complex, recrystallized from *n*-pentane at 0 °C as white crystals and spectroscopically characterised.

The IR spectrum of (**13**) (*n*-pentane), in the 2200–1500 cm^{-1} region, showed bands at 2044(vs), 1982(vs) and 1626(m) cm^{-1}.

In the ^1H NMR spectrum of (**13**) (C_6D_6) signals were present at δ: 0.79 (t, 9H, CH_3, PBu_3, J_{HH} = 7.3 Hz), 1.21 (q, 6H, CH_3CH_2, PBu_3, J_{HH} = 7.3 Hz), 1.46 (m, 6H, $EtCH_2$, PBu_3), 1.84 (s, 6H, CH_3COO), 1.91 (m, 6H, PCH_2, PBu_3), 7.02 (m, 6H, PPh_3), 7.70 (m, 3H, PPh_3), 7.93 (m, 6H, PPh_3) ppm.

In the ^{13}C NMR spectrum of (**13**) (C_6D_6) signals were present at δ: 13.5 (s, CH_3, PBu_3), 23.2 (s, CH_3COO), 24.0 (d, PCH_2, PBu_3, J_{CP} = 22.6 Hz), 24.5 (d, CH_3CH_2, PBu_3, J_{CP} = 11.3 Hz), 25.1 (s, $EtCH_2$, PBu_3), 130.3 (s, C_m, PPh_3), 131.4 (s, C_p, PPh_3), 132.3 (d, C_{ipso}, PPh_3, J_{CP} = 11.3 Hz), 134.6 (d, C_o, PPh_3, J_{CP} = 9.0 Hz), 175.8 (s, COO), 198.5 (m, CO) ppm.

MS spectrum of (**13**) *m*/*z* (%): 740 (10) $[M]^+$, 712 (2) $[M–CO]^+$, 681 (100) $[M–CH_3COO]^+$, 653 (20) $[M–CH_3COO–CO]^+$, 622 (5) $[Ru(PPh_3)(PBu_3)(CO)_2]^+$ (centres of each ruthenium cluster peaks are reported)

Elemental analysis of (**13**), for $C_{36}H_{48}O_6P_2Ru$: % C 58.3 (58.45), % H 6.6 (6.54).

4.7. Reactivity of ruthenium complexes with acetic acid and hydrogen

A *n*-heptane solution of each ruthenium complex and acetic acid was introduced in the autoclave under dry nitrogen, then H_2 (100 atm) was added.

IR spectra were recorded in the reaction conditions after heating the solution at the pre-fixed temperature for the selected time.

Samples of the solution examined by IR spectroscopy, were collected and analysed by glc using a FFAP column kept at 50 °C for 7 min, then heated up to 130 °C at a rate of 30 °C/min and kept at this temperature for 10 min. The peaks due to acetic acid and ethyl acetate were identified and quantified.

4.7.1. $Ru_2(CO)_4(\mu\text{-}MeCOO)_2(PBu_3)_2$ (**3**)

A solution of (**3**) (120 mg, 0.144 mmol) and acetic acid (0.5 ml, 8.734 mmol) in *n*-heptane (60 ml) under hydrogen (100 atm at 20 °C) was heated in the temperature range 20–180 °C.

The reaction was followed as reported in the general procedure.

At the end of the reaction the vessel was cooled to room temperature, the solvent evaporated under reduced pressure and the solid recovered and separated by preparative tlc on alumina using *n*-hexane as eluant. Traces of hydride clusters (**7**), (**9**) and (**10**) were obtained.

4.7.2. $Ru_4(CO)_8(\mu\text{-}MeCOO)_4(PBu_3)_2$ (**4**)

A solution of (**4**) (119 mg, 93.8 μmol) and acetic acid (0.5 ml, 8.734 mmol) in *n*-heptane (60 ml) under hydrogen (100 atm at 20 °C) was heated in the temperature range 40–180 °C.

The reaction was followed as reported in the general procedure.

4.7.3. $Ru(CO)_2(MeCOO)_2(PBu_3)_2$ (**2**)

A solution of (**2**) (190 mg, 0.279 mmol) and acetic acid (0.5 ml, 8.734 mmol) in *n*-heptane (60 ml) under hydrogen (100 atm at 20 °C) was heated in the temperature range 20–180 °C.

The reaction was followed as reported in the general procedure.

4.8. Catalytic hydrogenation experiments: analyses of the hydrogenation products

The experimental conditions and the results are reported in Table 2.

The products present at the end of the hydrogenation were analysed by glc and their identities confirmed by glc-ms.

The solvent, the starting substrate and the reaction products were separated and quantified using the following conditions:

- *Cyclohexene:* a PPG column was kept at 40 °C for 25 min.
- *Tiglic acid:* a FFAP column was kept at 140 °C per 15 min.
- *Acetophenone:* a CW column was kept at 60 °C for 5 min, then heated up to 160 °C at a rate of 20 °C/min and kept at this temperature for 10 min.
- *Acetic acid:* a FFAP column was kept at 50 °C for 7 min, heated up to 130 °C at a rate of 30 °C/min and kept at this temperature for 10 min.

In the hydrogenation of acetic acid the yields were evaluated using calibration curves obtained from mixtures of ethyl acetate, ethanol and acetic acid of known composition. In all other tests conversions were evaluated without response factors corrections.

Acknowledgements

The authors thank the University of Florence and the Ministero della Istruzione, Università e Ricerca (M.I.U.R.), Programmi di Ricerca Scientifica di Notevole Interesse Nazionale, Cofinanziamento 2003–04, for financial support. We also thank Prof. Mario Bianchi for stimulating suggestions and discussions.

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