

# On the behaviour of Ru(I) and Ru(II) carbonyl acetates in the presence of H<sub>2</sub> 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  $\text{Ru}(\text{CO})_2(\text{MeCOO})_2(\text{PBU}_3)_2$ ,  $\text{Ru}_2(\text{CO})_4(\mu\text{-MeCOO})_2(\text{PBU}_3)_2$ ,  $\text{Ru}_4(\text{CO})_8(\mu\text{-MeCOO})_4(\text{PBU}_3)_2$  with H<sub>2</sub> 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  $[\text{Ru}_6(\mu\text{-H})_6(\text{CO})_{10}(\mu\text{-PHBu})(\mu\text{-PBU}_2)(\text{PBU}_3)_2(\mu_6\text{-P})]$  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  $\text{Ru}(\text{CO})_2(\text{MeCOO})(\mu\text{-MeCOO})(\text{PBU}_3)$ , 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<sub>3</sub> to give  $\text{Ru}(\text{CO})_2(\text{MeCOO})_2(\text{PBU}_3)(\text{PPh}_3)$ , a new mononuclear ruthenium carbonyl carboxylate containing two different phosphines, that was fully characterised.

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**Keywords:** Ruthenium; Carbonyl carboxylates; Acetic acid; Hydrogenation

## 1. Introduction

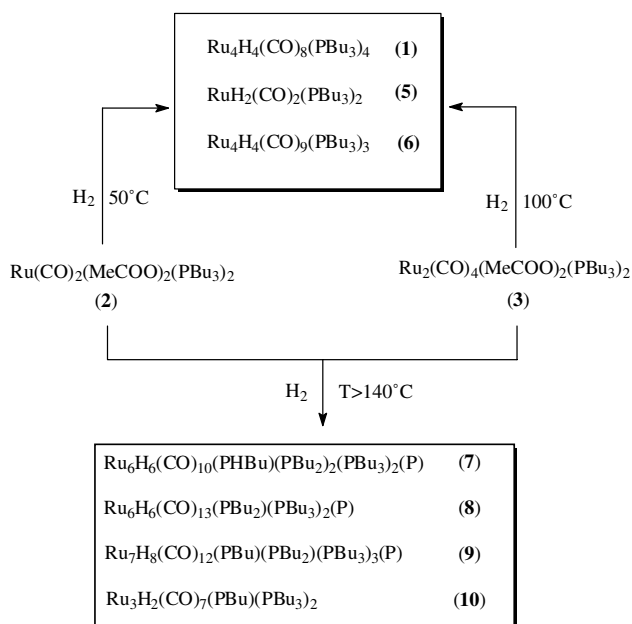
The catalytic hydrogenation of carboxylic acids in homogeneous phase has been investigated in our laboratory for several years [1]. This reaction was achieved using ruthenium complexes such as  $\text{Ru}_4\text{H}_4(\text{CO})_8(\text{PBU}_3)_4$  (1) and  $\text{Ru}_4\text{H}_4(\text{CO})_8(-)\text{-DIOP}]_2$  [2] as catalytic precursors.

Ruthenium carbonyl carboxylates  $\text{Ru}(\text{CO})_2(\text{MeCOO})_2(\text{PBU}_3)_2$  (2),  $\text{Ru}_2(\text{CO})_4(\mu\text{-MeCOO})_2(\text{PBU}_3)_2$  (3),

$\text{Ru}_4(\text{CO})_8(\mu\text{-MeCOO})_4(\text{PBU}_3)_2$  (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  $\text{RuH}_2(\text{CO})_2(\text{PBU}_3)_2$  (5),  $\text{Ru}_4\text{H}_4(\text{CO})_9(\text{PBU}_3)_3$  (6) and (1) [1h]. At higher temperature (over 140 °C), the phosphido ruthenium clusters

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Scheme 1.

[ $\text{Ru}_6(\mu\text{-H})_6(\text{CO})_{10}(\mu\text{-PHBu})(\mu\text{-PBu}_2)_2(\text{PBu}_3)_2(\mu_6\text{-P})$ ] (7), [ $\text{Ru}_6(\mu\text{-H})_6(\mu\text{-CO})(\text{CO})_{12}(\mu\text{-PBu}_2)(\text{PBu}_3)_2(\mu_6\text{-P})$ ] (8), [ $\text{Ru}_7(\mu\text{-H})_8(\text{CO})_{12}(\mu_3\text{-PBu})(\mu\text{-PBu}_2)(\text{PBu}_3)_3(\mu_6\text{-P})$ ] (9), [ $\text{Ru}_3(\mu\text{-H})_2(\text{CO})_7(\mu_3\text{-PBu})(\text{PBu}_3)_2$ ] (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  $\text{H}_2$ . 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  $^{31}\text{P}$  NMR spectroscopy.

At the end of this investigation, the hydrogenating activity of [ $\text{Ru}_6(\mu\text{-H})_6(\text{CO})_{10}(\mu\text{-PHBu})(\mu\text{-PBu}_2)_2(\text{PBu}_3)_2(\mu_6\text{-P})$ ] (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. $\text{Ru}_2(\text{CO})_4(\mu\text{-MeCOO})_2(\text{PBu}_3)_2$ (3)

2.1.1.1. IR study.  $\text{Ru}_2(\text{CO})_4(\mu\text{-MeCOO})_2(\text{PBu}_3)_2$  (3), in *n*-heptane as solvent, reacted with acetic acid ( $\text{Ru}/\text{CH}_3\text{COOH} = 1:30$ ) at 40 °C giving a new complex  $\text{Ru}(\text{CO})_2(\text{MeCOO})(\mu\text{-MeCOO})(\text{PBu}_3)$  (11) as evidenced

by new bands at 2060(ff), 1990(ff) and 1575(m)  $\text{cm}^{-1}$ . 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  $\text{C}_6\text{D}_6$  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  $^{31}\text{P}$  NMR spectrum. Complex (2) was not easily identified in the IR spectrum performed in a  $\text{C}_6\text{D}_6$ /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  $^{31}\text{P}$  NMR spectrum.

The  $^{31}\text{P}$ -,  $^1\text{H}$ -, and  $^{13}\text{C}$  NMR spectra ( $\text{C}_6\text{D}_6$  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  $\text{PBu}_3$  (a broad singlet at 44.4 ppm in the  $^{31}\text{P}$  NMR spectrum) and CO ligands (195.9 (m) ppm in the  $^{13}\text{C}$  NMR spectrum), two inequivalent MeCOO groups (174.5 and 183.0 ppm in the  $^{13}\text{C}$  NMR spectrum attributable to a mono- and a bidentate acetato ligand, respectively). These attributions are in agreement with the resonance of the

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