Ethene hydroformylation with CO/H_2O: nucleophilic attack by water on to a terminal CO of a Ru(II) acylcarbonyl complex†

Giuseppe Fachinetti,* Tiziana Funaioli* and Fabio Marchetti

Received (in Cambridge, UK) 3rd March 2005, Accepted 18th April 2005
First published as an Advance Article on the web 6th May 2005
DOI: 10.1039/b502998h

The reaction with water of acyldicarbonyl–Ru(II) complexes relevant to ruthenium catalysed ethene hydrocarbonylation with CO/H_2O is shown to consist of a nucleophilic attack and to proceed *via* coordination of propionate and CO to the Ru(II) species.

The metal–carbonyl catalyzed reactions of alkenes with CO/H_2O (commonly identified as Reppe's reactions) can consist of CO/H_2O addition to give carboxylic acids (hydrocarboxylation) or of a redox process yielding CO_2 and aldehydes (hydrocarbonylation). Acylcarbonyl complexes are believed to be the catalytic intermediates in both reactions, the carboxylic acid formation requiring the attack by H_2O or OH^- on to the activated carbon of an electrophilic acyl complex, while aldehyde formation is believed to derive from protonation by H_2O of an electron-rich, basic, acyl intermediate.[1] When the two reactions are competitive,[2] acyl intermediates of opposite electronic properties should be operating simultaneously.

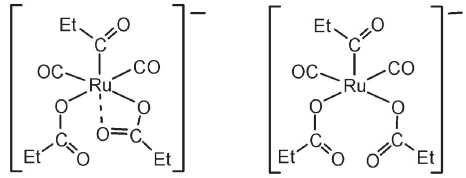
We have now found that $[Ru(C(O)Et)(H_2O)_3(CO)_2]^+$ (**1**), which was recognized as an intermediate for ethene hydrocarboxylation,[3] in the presence of propionate and CO becomes a precursor to ethene hydrocarbonylation, according to a mechanism proposed here by which aldehyde formation also originates from a nucleophilic attack.

While the hydrocarboxylation of ethene to propionic acid with **1** is selective in water at pH $\approx$ 1,[3] it has now been found that the hydrocarbonylation to propanal and CO_2, which is a side-reaction at the higher pH of a propionic acid/propionate buffer, becomes highly selective in diglyme containing 7% H_2O (by weight) in the presence of propionic acid/propionate. A TOF (EtCHO) = 20 h^{-1} [TOF (EtCHO) = (mol of propanal) $(\text{mol Ru})^{-1}$ h^{-1}] and a selectivity >90% were obtained under the following conditions: [Ru] = 0.025 M, P_{CO} = 30 atm, P_{ethene} = 20 atm, $[EtCOO^-]$ = 0.063 M, [EtCOOH] = 0.050 M and T = 140 °C. These findings conflict with the assumption of the protonolysis of an acyl as the aldehyde producing step,[1] since ethene hydrocarbonylation is suppressed at a low pH and is selective at low H_2O concentrations in diglyme as solvent. As shown later, the propionato base appears to be essential for the hydrocarbonylation to occur: under CO, it converts the acyldicarbonyl intermediate **1** for hydrocarboxylation to an acyltricarbonyl complex intermediate for hydrocarbonylation. Such a transformation is based on a delicate balance between the donor/acceptor properties of propionato and CO ligands as well as on the monodentate/bidentate binding mode of the propionato anion.

Three elementary steps can be recognized: (i) substitution of the three water ligands of **1** by two propionato ligands to give the anionic $[Ru(C(O)Et)(OOCEt)_2(CO)_2]^-$ (**2**), (ii) CO uptake by **2** to give the acyltricarbonyl derivative *mer*-$[Ru(C(O)Et)(OOCEt)_2(CO)_3]^-$ (**3**) and, (iii) nucleophilic attack by water on to a terminal CO group of **3**.

(i) Synthesis of **2**: IR spectroscopy in solution shows that on adding increasing amounts of sodium propionate to a 0.1 M solution of the triflate salt of **1** in diglyme containing 7% H_2O, the two IR carbonyl stretching vibrations of **1** (2051s and 1975vs cm^{-1}) are shifted to lower frequencies, and two bands at 2035s and 1954vs cm^{-1}, unaffected by further addition of propionate, appear for $[EtCOO^-]/[Ru]$ = 2. The pure sodium derivative of **2** was prepared.‡ The one-pot synthesis consists of reacting $[Ru(EtCOO)(CO)_2]_n$[4] with an excess of sodium propionate in wet diglyme under a pressure of CO and ethene. As a consequence of disproportionation of the Ru(I) derivative,[5] a Ru(0) and a Ru(II) complex are quantitatively formed. Oxidative addition of propionic acid to the Ru(0) species, and nucleophilic attack by water on to the tricarbonyl Ru(II) complex, followed by CO_2 elimination, results in a hydride complex which inserts ethene and CO giving **2**. The structure of **2**§ (as its sodium derivative) is shown in Figs. 1 and 2.

Two independent anions, containing the same five ligands around ruthenium, are assembled in a rather unusual geometry. While one of the anions may be considered to be hexacoordinated, the second one should be better described as pentacoordinated, the Ru(2)···O(11) distance being 2.61 Å.[6] The IR spectrum of the sodium salt of **2** in diglyme containing 7% H_2O shows the two absorptions at 2035s and 1954vs cm^{-1}, thus confirming **2** as the product of the substitution of water by propionato ligands. On the other hand, in spite of the increased electron density at the metal with respect to **1**, the acyl complex **2** fails to give aldehyde on protonation. Indeed, the addition of a twofold molar quantity of triflic acid to 0.1 M solution of **2** in



2a **2b**

Fig. 1 The two independent anions of **2**.

---

† Electronic supplementary information (ESI) available: Atomic coordinates file to allow viewing of the molecules using the CHIME plugin. See http://www.rsc.org/suppdata/cc/b5/b502998h/

*tiziana@dcci.unipi.it (Tiziana Funaioli)

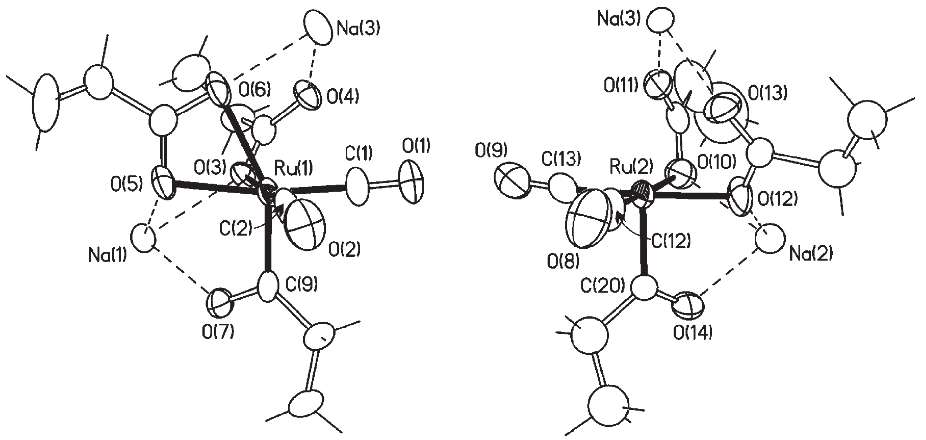


Fig. 2 Structures of the two independent anions $[RuC(O)Et)(OOCEt)_2(CO)_2]^-$ (**2**). Ellipsoids are at 30% probability. Only the most populated positions of the disordered ethyl groups have been represented. The interactions with the Na^+ ions are indicated by dashed lines. Interatomic distances (Å) around Ru: Ru(1)–C(1), 1.86(2); Ru(1)–C(2), 1.82(2); Ru(1)–C(9), 1.99(2); Ru(1)–O(3), 2.09(1); Ru(1)–O(5), 2.15(1); Ru(1)–O(6), 2.34(1); Ru(1)···O(4), 3.16(1); Ru(2)–C(12), 1.87(3); Ru(2)–C(13), 1.79(2); Ru(2)–C(20), 1.98(2); Ru(2)–O(10), 2.16(2); Ru(2)–O(12), 2.08(1); Ru(2)···O(11), 2.61(1); Ru(2)···O(13), 2.92(1).

diglyme containing 7% H_2O restores **1** (ν_{CO} = 2051s and 1975vs cm^{-1}) with propionic acid formation.

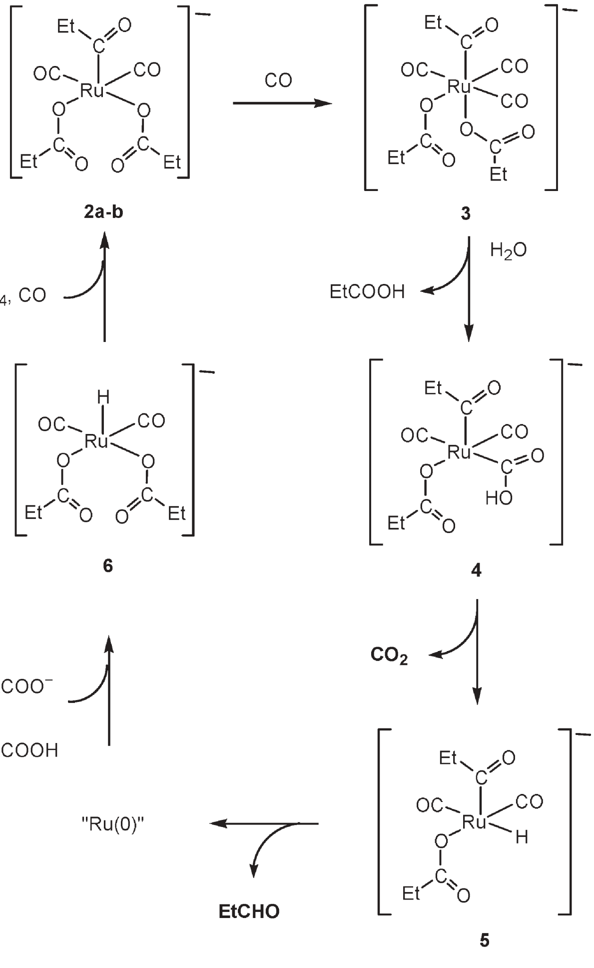
(ii) CO uptake by **2**: the increased electron density in **2**, together with some degree of unsaturation suggested by the solid-state findings, anticipates the CO uptake by **2**. The behaviour of **2** in anhydrous diglyme under increasing P_{CO} was investigated by IR spectroscopy: three terminal CO stretching absorptions at 2110m, 2042s and 1990s cm^{-1}, correspond to the reversible formation of the equatorial tricarbonyl complex *mer*-$[Ru(C(O)Et)(OOCEt)_2(CO)_3]^-$ (**3**), the high wavenumbers indicating its electrophilic character.[7]

(iii) Nucleophilic attack by water on to a terminal CO group of **3**: by injecting water into a solution of **3** in diglyme under a CO pressure of 40 atm at room temperature, the quantitative formation of propanal, CO_2 and $Ru(CO)_5$ was observed [eqn. (1)]: through the decarboxylation of the metallacarboxylic acid intermediate, a hydrido–acyl complex is formed which reductively eliminates aldehyde.¶

$$\textit{mer}\text{-}\underset{\mathbf{3}}{[Ru(C(O)Et)(OOCEt)_2(CO)_3]^-} \xrightarrow[H_2O]{CO} \\ EtCHO + CO_2 + Ru(CO)_5 + EtCOOH + EtCOO^- \qquad (1)$$

Reaction (1), unprecedented in the chemistry of acyl complexes, constitutes a step in the catalytic Reppe's ethene hydroformylation, where the Ru(0) labile intermediate oxidatively adds propionic acid, the resulting hydrido complex inserting ethene and CO to give back **2** (Scheme 1).

Evidence for the mechanism of Scheme 1 was gathered by studying the effect of P_{CO} on TOF (EtCHO) and the nature of the intermediates accumulating in the catalytic reaction.|| With [Ru] = 0.025 M, P_{ethene} = 20 atm, $[EtCOO^-]$ = 0.063 M, [EtCOOH] = 0.050 M and T = 140 °C, TOF (EtCHO) exhibits a maximum value (20 h^{-1}) at $P_{CO} \approx 30$ atm (Fig. 3). *In situ* IR spectroscopy shows that both **2** (2035s and 1954vs cm^{-1}) and $Ru(CO)_5$ (2042m and 1996vs cm^{-1}) accumulate under the conditions of maximum TOF. At lower P_{CO}, only **2** was detected as the accumulating species, thus indicating that the conversion of **2** into the tricarbonyl **3** is the slow step under these conditions. On the other hand, IR spectra at $P_{CO} > 30$ atm show only $Ru(CO)_5$, the oxidative addition of propionic acid to the Ru(0) species becoming the rate-determining step.



Scheme 1 Suggested mechanism for the Reppe's ethene hydroformylation catalyzed by $[Ru(C(O)Et)(OOCEt)_2(CO)_2]^-$ (**2**) in wet diglyme.

On the basis of these findings, the catalytic ethene hydrocarboxylation and hydrocarbonylation, promoted by Ru(II)

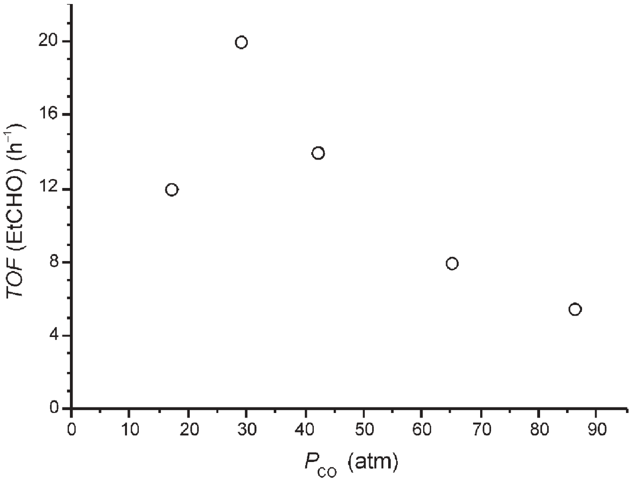


Fig. 3 Effect of P_{CO} on TOF (EtCHO) for the ethene Reppe's hydroformylation catalyzed by **2**. For experimental conditions, see text.

acyldicarbonyl complexes, appear to be strictly related. Concerning the formation of the acyl complex, both reactions require oxidative addition of propionic acid to the Ru(0) intermediate, followed by ethene and CO insertion (see Scheme 1). A nucleophilic attack by water on to an acyl intermediate has been demonstrated for both hydrocarbonylation and hydrocarboxylation. With water as an ancillary ligand, the site of the nucleophilic attack is the acyl group and **1** is the intermediate for hydrocarboxylation. The propionato ancillary ligands, by increasing the electron density in **2**, protect the acyl group against such an attack, but allow the coordination of a third CO group to give **3**. The competition by three CO ligands for the electron density in **3** results in their electrophilic character, thus bringing about attack by water (Scheme 1).

This work was supported by Ministero MIUR, Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 2004–2005.

Giuseppe Fachinetti,* Tiziana Funaioli* and Fabio Marchetti
Dipartimento di Chimica e Chimica Industriale dell'Università di Pisa, Via Risorgimento, 35, I-56126, Pisa, Italy. E-mail: tiziana@dcci.unipi.it; Fax: +39 0502219223; Tel: +39 0502219260

Notes and references

‡ A 200 mL rocking stainless-steel autoclave was charged with $[Ru(EtCOO)(CO)_2]_n$[4] (3.83 g, 16.6 mmol), sodium propionate (3.37 g, 35.1 mmol) and 50 mL of diglyme containing 7% H_2O by weight. The autoclave was pressurized with 30 atm of ethene and 60 atm of CO and heated in an oil-bath at 140 °C. After 2 h, the autoclave was cooled to room temperature and the gas was vented. The pale yellow solution was evaporated to dryness (70 °C, 0.1 mm Hg) and the solid residue was extracted with 150 mL of anhydrous THF. After concentration to 50 mL and addition of 300 mL of hexane, 4.14 g (10.8 mmol, 65% yield) of $Na[Ru(C(O)Et)(OOCEt)_2(CO)_2]$ were obtained as colourless crystals. IR (Nujol mull): ν_{CO} = 2043vs, 1969s and 1959s cm^{-1}. IR (diglyme containing 7% H_2O): ν_{CO} 2035s and 1954vs cm^{-1}.

§ *Crystal data* for $Na[Ru(C(O)Et)(OOCEt)_2(CO)_2]$: $C_{22}H_{30}Na_2O_{14}Ru_2$, $M = 766.58$, triclinic, space group $P\bar{1}$, $a = 10.672(6)$, $b = 12.450(4)$, $c = 14.069(6)$ Å, $\alpha = 73.26(3)$, $\beta = 75.03(4)$, $\gamma = 65.11(3)°$, $V = 1604(1)$ Å^3, $D_c = 1.588$ g cm^{-3}, $\mu = 1.028$ mm^{-1}, $Z = 2$, Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 296$ K. Two ethyl moieties of the Ru(2) anion are disordered: they were refined as statistically distributed in two limiting positions with isotropic thermal parameters for their carbon atoms. Programs used: SHELX97[8] and WINGX suite.[9] $R_1 = 0.0777$, $wR_2 = 0.1850$; GOF = 1.117 for 4143 unique reflections and 358 parameters. CCDC 211423. See http://www.rsc.org/suppdata/cc/b5/b502998h/ for crystallographic data in CIF or other electronic format.

¶ An alternative route to propanal could be the reduction of the acyl complex with H_2 formed by the water–gas-shift reaction. Hydrogen, however, was never detected in the gas phase.

|| Catalytic runs, product analyses and IR spectra were performed as described elsewhere.[3]

1 P. C. Ford and A. Rokicki, *Adv. Organomet. Chem.*, 1988, **28**, 139, and references therein.
2 A. Cabrera, P. Sharma, J. L. Garcia, L. Velasco, F. J. Perez, J. L. Arias and N. Rosas, *J. Mol. Catal.*, 1997, **118**, 167; K. Murata and A. Matsuda, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 245; A. J. Pardey, A. B. Rivas, C. Longo, T. Funaioli and G. Fachinetti, *J. Coord. Chem.*, 2004, **57**, 871.
3 T. Funaioli, C. Cavazza, F. Marchetti and G. Fachinetti, *Inorg. Chem.*, 1999, **38**, 3361.
4 G. R. Crooks, B. F. G. Johnson, J. Lewis and I. G. Williams, *J. Chem. Soc. A*, 1969, 2761.
5 G. Fachinetti, T. Funaioli, L. Lecci and F. Marchetti, *Inorg. Chem.*, 1996, **35**, 7217.
6 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
7 T. Y. Luth, *Coord. Chem. Rev.*, 1984, **60**, 255.
8 G. M. Sheldrick, SHELX (Rel. 97-2), *Programs for Crystal Structure Analysis*, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
9 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.