

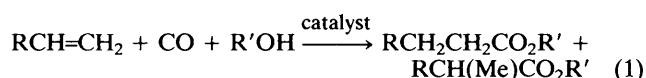
## Direct Hydroesterification of Ethylene with Methyl Formate with the New System RuCl<sub>3</sub>-NR<sub>4</sub>I-NR<sub>3</sub>: an Example of Catalytic Activation of the CH Bond of Methyl Formate?

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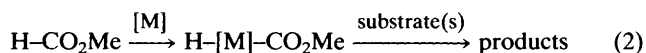
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Upon using the simple RuCl<sub>3</sub>-NR<sub>4</sub>I-NR<sub>3</sub> catalytic combination and dimethylformamide as solvent, an exceptionally reactive system is obtained for direct hydroesterification of ethylene with methyl formate (turnover frequency up to 2000 h<sup>-1</sup>) in the absence of carbon monoxide.

Catalytic olefin carbonylation in the presence of alcohols is of great potential interest for the synthesis of various carboxylic esters<sup>1</sup> [eqn. (1)].



Methyl formate, which can be considered as a liquid condensate of CO and MeOH<sup>2</sup>, CO and H<sub>2</sub><sup>3</sup> or as a precursor of methoxycarbonyl moieties *via* C-H activation [eqn. (2)], is also a convenient substrate for this reaction, as it could avoid the use of carbon monoxide.<sup>4</sup>



In this context, several reports have described this reaction with ethylene and other olefins using different catalysts [M] based on ruthenium,<sup>5</sup> iridium<sup>6</sup> or palladium.<sup>7</sup> However, the turnover frequencies (TOF) so far reported are generally low and/or the use of CO seems to be generally required.

We report here a simple and new, much more reactive catalytic system based on ruthenium, which does *not* require the presence of CO<sup>8</sup> [eqn. (3), Ru = ruthenium catalyst, R = alkyl or aryl]

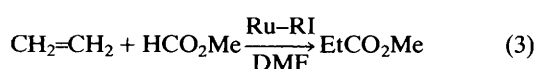


Table 1 compares typical results obtained in this reaction, using different transition-metal salts for the ethylene hydroes-

terification with methyl formate. In accordance with literature data, classical systems exhibit a very low activity (runs 1-4). In contrast, upon addition of 2 equivalents of covalent iodide or ammonium iodide to the ruthenium based system (RuCl<sub>3</sub>), and using dimethylformamide (DMF) as solvent, a drastic improvement of the catalytic activity was observed (TOF = 2300 h<sup>-1</sup>). However, this effect was not observed with the other metal salts used in this work (runs 2-4).

The nature of the ruthenium precursor used has no significant influence on the observed activities, apart from phosphorus derivatives (run 17) which completely inhibited the reaction.

Only covalent iodides RI or ammonium salts NR<sub>4</sub>I (R = alkyl or aryl) are efficient in amide type solvents. Alkali, alkaline-earth or phosphonium iodides are inefficient, and often lead to decarbonylation of HCO<sub>2</sub>Me (run 6).

With covalent iodides, an induction period of *ca.* 20-30 min

Table 2 CO pressure effect on hydroesterification of ethylene with methyl formate<sup>a</sup>

Run	P <sub>C<sub>2</sub>H<sub>4</sub></sub> /bar	P <sub>CO</sub> /bar	t/h	Conversion (%)	Ester Sel. mol. %	TOF/h <sup>-1</sup>
21	60	0	1	67	94	1500
22	60	3	1	37	85	760
23	30	30	1	45	12	130

<sup>a</sup> Experimental conditions as in Table 1; RuCl<sub>3</sub> 0.11 mmol, Me 0.22 mmol, HCO<sub>2</sub>Me = 266 mmol; runs 21-23: DMF 30 ml, 190 °C.

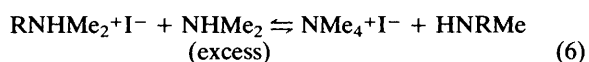
Table 1 Hydroesterification of ethylene with methyl formate<sup>a</sup>

Run	Catalyst	Promoter	Solvent	t/h	Conversion (mol %)	EtCO <sub>2</sub> Me Selectivity (mol %)	TOF <sup>b</sup> /h <sup>-1</sup>
1	Ru <sub>3</sub> (CO) <sub>12</sub>	None	None	10	30 <sup>c</sup>	0	—
2	PdCl <sub>2</sub>	MeI	DMF	3	5	2	1
3	Rh <sub>2</sub> Cl <sub>2</sub> (CO) <sub>4</sub>	MeI	DMF	2	50 <sup>c</sup>	2	10
4	IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub>	MeI	DMF	3	8	2	1
5	RuCl <sub>3</sub>	MeI	DMF	2	26 <sup>c</sup>	20	120
6	RuCl <sub>3</sub>	LiI	DMF	2	65 <sup>c</sup>	20	160
7	RuCl <sub>3</sub>	MeI	DMF	1	52	91	1170
8	RuCl <sub>3</sub>	EtI	DMF	1	61	93	1350
9	RuCl <sub>3</sub>	Bu <sup>n</sup> I	DMF	1	67	94	1500
10	RuCl <sub>3</sub>	HI	DMF	1	61	92	1300
11	RuCl <sub>3</sub>	HI	NMP	2	18	74	210
12	RuCl <sub>3</sub>	HI	DMA	1	44	79	850
13	RuCl <sub>3</sub>	NEt <sub>4</sub> I	DMF	0.5	24	98	2300
14	RuCl <sub>3</sub>	NEt <sub>4</sub> I	DMF	1	62	92	1300
15	RuCl <sub>3</sub>	PPh <sub>3</sub> MeI	DMF	2	15	0	—
16	[RuCl <sub>2</sub> (CO) <sub>3</sub> ] <sub>2</sub>	NEt <sub>4</sub> I	DMF	1	63	96	1400
17	RuHCl(CO)(PPh <sub>3</sub> ) <sub>2</sub>	MeI	DMF	2	15	22	50
18	RuCl <sub>3</sub>	MeI	γ-BL	3	5	20	30
19	RuCl <sub>3</sub>	NEt <sub>4</sub> I	γ-BL	1	7	80	150
20	RuCl <sub>3</sub>	NEt <sub>4</sub> I + NEt <sub>3</sub>	γ-BL	1	31	92	650

<sup>a</sup> All reactions were conducted in a stainless-steel autoclave (100 ml) with methyl formate (16 ml, 266 mmol) catalyst (0.11 mmol) promoter (0.22 mmol) 30 ml solvent, at 190 °C and P<sub>C<sub>2</sub>H<sub>4</sub></sub> = 60 bar, except run 10, catalyst (0.05 mmol) and promoter (0.10 mmol). <sup>b</sup> Turnover frequency for hydroesterification. <sup>c</sup> CO + MeOH are the major products.

is observed, which can be reduced to 10 min upon using the corresponding ammonium salt with triethylamine. This behaviour led us to look after the production of this type of compound during a reaction conducted with only covalent iodides as promoters. After evaporation of the solvent and products at the end of this catalytic reaction, a solid precipitate of  $\text{NMe}_4\text{I}$  was isolated, whatever the starting covalent iodide used.

The production of this salt can only be explained by partial decarbonylation of DMF followed by the reaction of the incipient dimethylamine with iodide. In the presence of an excess of dimethylamine, the exchange reaction leads to the production of tetramethylammonium iodide [eqns. (4)–(6)].

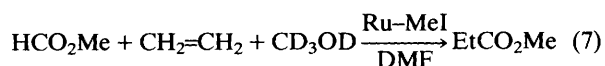


The contribution of the amine and its salt to the overall process is in agreement with the following features: (i) the induction period completely disappears when the reaction is performed upon using the  $\text{RuCl}_3\text{-NR}_3\text{-NR}_4\text{I}$  mixture (5 equiv. of amine to Ru). (ii) In the absence of amine, only solvents containing amide functionalities are suitable. (iii) With the  $\text{NR}_3\text{-NR}_4\text{I-RuCl}_3$  system, a fairly good activity can also be obtained with other polar solvents like  $\gamma$ -butyrolactone ( $\gamma$ -BL) (run 20, TOF =  $650 \text{ h}^{-1}$ ).

The inhibiting effect of carbon monoxide on the reaction is shown in Table 2; even for a low CO pressure (3 bar) the activity is half that observed in its absence.

Furthermore, under identical reaction conditions, the alkoxycarbonylation of ethylene with methanol and CO leads to much lower activities than with methyl formate alone ( $60 \text{ vs. } 350 \text{ h}^{-1}$  at  $150^\circ\text{C}$ ).

This observation seems to indicate that the reaction pathway involves a direct activation of methylformate rather than a decarbonylation process followed by alkoxycarbonylation. To confirm this hypothesis, a specific experiment has been performed using  $\text{HCO}_2\text{Me-CD}_3\text{OD}$  [eqn. (7)]: no deuterium was incorporated into the ester.



The absence of deuterium in the product gives further evidence for a direct activation of methylformate vs. its decarbonylation, followed by a classical alkoxycarbonylation process, which would lead to a  $\text{MeOD-MeOH}$  mixture and therefore to the production of deuterated methylpropionate.

The above results and the FAB mass spectrum of the residue obtained after evaporation† lead us to propose that the reaction mechanism involves an initial reaction of the

amine–ammonium mixture with the ruthenium salt which probably leads to anionic amido species<sup>9</sup> highly reactive towards the oxidative addition of methylformate via its C–H bond. Olefin coordination to this hydrido methoxycarbonyl intermediate, followed by insertion of the double bond into the metal hydride, could then produce a ruthenium ethylmethoxycarbonyl species which by reductive elimination would produce methylpropionate and regenerate the active species.

In conclusion we have discovered a new catalytic system comprising a ruthenium salt ammonium iodide and amine (1:2:5) which is particularly efficient for the direct hydroesterification of ethylene in the absence of carbon monoxide. This exceptional reactivity is certainly due to a direct activation of methylformate rather than a process involving decarbonylation into methanol and CO.

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### Footnote

† This residue was still reactive when subjected to another reaction conducted under the same conditions as in Table 1. The FAB MS data obtained in a 90/10 v/v 18-crown 6-tetraglyme solution, using a CONCEPT II H-H Spectrometer, Kratos Analytical Ltd.  $\{m/z$  229 (RuI), 273 [RuI(NMe<sub>2</sub>)], 303 [RuI(NMe<sub>2</sub>) (NMe)], 346 [RuI(NMe<sub>2</sub>)<sub>2</sub>(NMe)]} are consistent with the presence of amido type ligands, NMe<sub>2</sub>.

### References

- 1 *Organic Syntheses via Metal Carbonyls*, ed. I. Wender and P. Pino, Wiley, New York, 1977.
- 2 C. Legrand, Y. Castanet, A. Mortreux and F. Petit, *Tetrahedron Lett.*, 1992, **33**, 3753 and references therein.
- 3 T. Hiratami and S. Noziri, *Chem. Econ. Eng. Rev.*, 1985, **17**, 2.
- 4 W. Keim, *Pure Appl. Chem.*, 1986, **58**, 825.
- 5 P. Isnard, B. Denise, R. P. A. Sneeden, J. M. Cognion and P. Durual, *J. Organomet. Chem.*, 1983, **256**, 135; W. Ueda, T. Yokoyama, Y. Morikawa, Y. Moro-Oka and T. Ikawa, *J. Mol. Catal.*, 1988, **44**, 197; W. Keim and J. Becker, *J. Mol. Catal.*, 1989, **54**, 95; T. Kondo, S. Yoshii, Y. Tsuji and Y. Watanabe, *J. Mol. Catal.*, 1989, **50**, 31; M. Nahmed and G. Jenner, *J. Mol. Catal.*, 1990, **59**, 215; G. Lavigne, N. Lugan, P. Kalck, J. M. Soulié, O. Lerouge, J. Y. Saillard and J. F. Halet, *J. Am. Chem. Soc.*, 1992, **114**, 10669.
- 6 D. J. Drury and P. S. Williams, *Eur. Pat. Appl.*, 106656, 1984.
- 7 M. Mlekuz, F. Joo and H. Alper, *Organometallics*, 1987, **6**, 1591; I. J. B. Lin and H. Alper, *J. Chem. Soc., Chem. Commun.*, 1989, 248; B. El Ali and H. Alper, *J. Mol. Catal.*, 1992, **77**, 7.
- 8 C. Legrand, Y. Castanet, A. Mortreux and F. Petit, *Eur. Pat. Appl.*, 449 963A, 1991; *Fr. Demande FR*, 3805, 1990.