Novel dinuclear μ -carboxylatoruthenium complexes for the low pressure hydroformylation of terminal alkenes

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Abstract

A series of di- μ -carboxylatoruthenium complexes of general formula [Ru₂(μ -OOCR)₂(CO)₄L₂] were tested as precursors for the hydroformylation reaction of alkenes. It was shown that this reaction requires the CO/H₂ couple in the presence of small amounts of water in addition to the solvent. The more active system is represented by [Ru₂(μ -OAc)₂(CO)₄(PPh₃)₂] and a slight excess of triphenylphosphine (P/Ru=5) at 3 MPa. Although a modest reaction rate was noted (2.5 h⁻¹), aldehydes were selectively obtained, the linear aldehydes being recovered with 80% selectivity in the best conditions. In some cases, especially when the P/Ru ratio=1 or with the less basic ligands, some isomerization of the alkene was observed but hydrogenation of the substrate or of the aldehydes was never detected.

Introduction

Many efforts have been made to replace classical metals, *i.e.* cobalt and rhodium, in the hydroformylation reaction by ruthenium in order to have a less expensive metal of the second row which would give high levels of selectivity [1-4], and numerous papers have been published in this area [4].

Usually, even under high pressure, the rates remain low as compared to the rhodium system. For instance, the mononuclear complexes used by Wilkinson and coworkers such as $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ [5] or $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$ [1] gave low conversion rates. Similarly the system $\text{Ru}_3(\text{CO})_{12} + \text{PPh}_3$ affords conversions of ~85% and selectivities in aldehyde of 100%; however the selectivities in linear aldehyde remain low even under high pressure.

More recently, Taqui Khan [6] and coworkers have reported $[Ru(EDTA)(H_2O)]^-$ to be an excellent soluble catalyst precursor. The hydroformylation of hex-1-ene performed at 5 MPa (CO/H₂=1/1) and 130 °C in water—ethanol gave 100% conversion to heptanal with turnover frequencies of 0.2 min⁻¹.

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The complexes $\text{Ru}_3(\text{CO})_{12}$ as well as $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ transform propene into butanal under a partial CO pressure of 2.8 MPa ($P(\text{C}_3\text{H}_6) = 1.2$ MPa) at 100 °C with aqueous triethylamine in excess to afford oxo compounds (TOF=10 h⁻¹) in addition to hydrogen produced by the water-gas shift reaction [7, 8].

Süss-Fink and Schmidt [9, 10] have reported high selectivities obtained with the anionic cluster $[HRu_3(CO)_{11}]^-$ which allows 97% of linear compounds to be obtained; however poor rates were observed except for ethylene, even under pressure.

Using mixtures of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$, a synergetic effect between the two metals was shown (TOF=230 h⁻¹) during the hydroformylation of pentene [11].

Experimental

Materials

Octene, toluene, water and tetrahydrofuran were distilled and stored under nitrogen. The phosphine and phosphite ligands as well as the acetic, benzoic and pivalic acids were of commercial origin. $\text{Ru}_3(\text{CO})_{12}$ was obtained according to the literature [23].

Different synthetic methods to obtain the $[Ru_2(\mu-OOCR)_2(CO)_4L_2]$ complexes are described in the literature [16–18]. However, we preferred to start from $Ru_3(CO)_{12}$. Aliphatic and aromatic carboxylic acids were reacted with $Ru_3(CO)_{12}$ to afford the carboxylato complexes which are polymeric or dimetallic carbonyl species [19–22]. Various adaptations were carried out starting from the synthesis of $[Ru_2(\mu-OOCCH_3)_2(CO)_4(PPh_3)_2]$ described in the literature. These preparations are detailed below.

Acetato complexes

The orange polymeric solid $[\text{Ru}(\mu\text{-OOCCH}_3)(\text{CO})_2]_n$, resulting from the heating of dodecarbonyl triruthenium (1 g, 1.57 mM) and acetic acid (15 ml, 252 mM) at 100 °C for 20 h, filtration, washing with acetic acid (5 ml), then diethyl ether (2×5 ml) and drying *in vacuo*, was dissolved in a solution containing triphenylphosphite (9.3×10⁻⁴ M) in 20 ml of toluene. The mixture was refluxed for 24 h. The yellow solution was evaporated and the powder washed with hexane (yield 414 mg; 85%). IR and NMR see Table 1.

For the preparation of $[Ru_2(\mu$ -OOCCH₃)₂(CO)₄(P(OMe)₃)]₂ the procedure remained the same (yield: 65%) IR and NMR see Table 1.

Trifluoroacetato complex $[Ru_2(\mu \text{-OOCCF}_3)_2(CO)_4(PPh_3)_2]$

A mixture of dodecarbonyl triruthenium (200 mg, 3×10^{-4} M) and trifluoroacetic acid (2×10^{-3} M) in toluene (20 ml) was heated at 90 °C for 24 h. The white polymer obtained (yield 40%) was washed with toluene, then dissolved in diethyl ether and stirred with two equivalents of triphenylphosphine (1.2×10^{-4} M) at room temperature for 24 h (yield 89%).

Complex	IR <i>v</i> (CO) (cm ⁻¹)	region ^a			RMN ³¹ P (ppm)
$[\operatorname{Ru}(\mu\operatorname{-OOCCH}_3)(\operatorname{CO})_2]_n$	2053(s)	1994(s)	1963(s)	1949(s)	
$[\operatorname{Ru}(\mu\operatorname{-OOCCH}_3)(\operatorname{CO})_2(\operatorname{PPh}_3)]_2$	2017(vs)	1977(s)	1942(vs)		s: 15.08 ^b
$[\operatorname{Ru}(\mu\operatorname{-OOCCH}_3)(\operatorname{CO})_2(\operatorname{P(OPh)}_3)]_2$	2043(vs)	1994(s)	1972(vs)		s: 118.1 s: 96.98 ^b
$[\operatorname{Ru}(\mu\operatorname{-OOCCH}_3)(\operatorname{CO})_2(\operatorname{P(OMe)}_3)]_2$	2031(vs)	1982(s)	1948(vs)		m: 135.7 ^b
$[\operatorname{Ru}(\mu\operatorname{-OOCPh})(\operatorname{CO})_2]_n$	2048(s)	2006(m)	1988(s)	1973(vs)	
$[Ru(\mu-OOCPh)(CO)_2(PPh_3)]_2$	2020(vs)	1975(s)	1950(vs)	1917(w)	s: 16.76°
$[\operatorname{Ru}(\mu\operatorname{-OOCCF}_3)(\operatorname{CO})_2]_n$	2153(vs)	2085(vs)	2001(s)	1969(s)	
$[Ru(\mu-OOCCF_3)(CO)_2(PPh_3)]_2$	2136(vs)	2056(s)	1985(vs)	1966(s)	s: 35.68 s:21.34 ^b
$[Ru(\mu-OOCCMe_3)(CO)_2(Me_3CCOOH)]_2$	2043(vs)	1986(s)	1950(vs)	1924(w)	
$[Ru(\mu-OOCCMe_3)(CO)_2(PPh_3)]_2$	2022(vs)	1975(s)	1945(vs)	1921(w)	s: 13.75°

TABLE 1 Infrared and ³¹P NMR data of the diruthenium precursors

*As KBr pellets.

^bIn d⁸-toluene.

^cIn d⁶-benzene.

 $[Ru_2(\mu$ -OOCCF₃)₂(CO)₄(PPh₃)₂] was washed with diethyl ether. For IR, NMR data see Table 1.

Benzoato complexes $[Ru_2(\mu \text{-OOCPh})_2(CO)_4(PPh_3)_2]$

Benzoic acid (290 mg, 2.38×10^{-3} M) and dodecacarbonyl triruthenium (500 mg, 0.78 mM), dissolved in toluene (20 ml), were heated at 100 °C for 20 h to give an orange polymer characterized as $[\text{Ru}(\mu\text{-OOCPh})(\text{CO})_2]_n$. This complex was washed with dicthyl ether (yield: 326 mg, 50%), and dried under reduced pressure. IR data see Table 1.

The polymer thus obtained was suspended in diethyl ether with triphenylphosphine (307 mg, 1.17×10^{-3} M) and stirred for 72 h at room temperature to give a precipitate identified as $[\text{Ru}_2(\mu\text{-OOCPh})_2(\text{CO})_4(\text{PPh}_3)_2]$ (yield 600 mg, 95%).

Pivalato complexes $[Ru_2(\mu - OOCCMe_3)_2(CO)_4(PPh_3)_2]$

Dodecarbonyl triruthenium (350 mg; 0.55 mM) and pivalic acid (1.67 mg, 1.65 mM) in benzene were refluxed for 24 h. The orange solution was evaporated and the resulting solid $[Ru_2(\mu\text{-OOCCMe}_3)_2(CO)_4(Me_3CCOOH)_2]$ washed with diethyl ether and dried *in vacuo* (yield: 177 mg, 30%).

This dimeric complex was reacted with triphenylphosphine (130 mg, 4.96×10^{-4} M), in hexane 15 ml. The $[\text{Ru}_2(\mu\text{-OOCCMe}_3)_2(\text{CO})_4(\text{PPh}_3)_2]$ obtained (yield 276.3 mg, 90%) was characterised by NMR and IR, see Table 1.

Analytical procedure

Gas phase chromatography was performed on a Carlo Erba MFC 500 apparatus equipped with a 20 m \times 0.5 mm macrobore column fitted with Carbowax 20M(RSL) and a flame ionisation detector, hydrogen was used as

carrier gas. The identification of the reaction products was checked by GC/MS. All the GPC analyses were performed with anisole as internal standard, the overall error being around 5% according to the dispersion of the results and to the total mass-balance.

General procedure for the catalytic runs Hydroformylation of alkene

An amount of 10^{-4} mol ruthenium complex, possibly in the presence of an excess of phosphine, was added to a nitrogen-saturated mixture of THF (30 ml), water (2 ml) and oct-1-ene (32 mM) in a Schlenck tube. The mixture was stirred for 5 min and introduced by suction into the stainless steel autoclave previously purged with nitrogen and then placed under vacuum. The mixture was stirred with a magnetic bar and the double envelope autoclave heated to 80 °C. When the temperature of the reactor was stabilized, the pressure was elevated to 3 MPa of CO/H₂, 1/1. After 20 h of reaction, the autoclave was cooled to room temperature, then slowly depressurized. The yellow solution was collected under nitrogen and transferred into a Shlenck tube.

Results and discussion

The high selectivity shown by the cluster of Süss-Fink and Schmidt puzzled us [9, 10]. As at least two ruthenium atoms are involved in this catalysis, our attention was drawn towards the selective addition of acetic acid on an alkyne occurring cleanly on the two ruthenium centers of the complex $[\operatorname{Ru}_2(\mu\operatorname{-OOCCH}_3)_2(\operatorname{CO})_4(\operatorname{alkyne})]$ described by Rotem and Shvo [12]. We anticipated that this diruthenium complex, in which the two acetato bridges seem to maintain the integrity of the dinuclear framework, could be reminiscent of the selectivity exhibited by the $[\operatorname{HRu}_3(\operatorname{CO})_{11}]^-$ cluster.

The $[\operatorname{Ru}_2(\mu\operatorname{-OOCCH}_3)_2(\operatorname{CO})_4(\operatorname{PPh}_3)_2]$ complex was used as precursor for the hydroformylation reaction (eqn. 1) under mild conditions (1 to 3 MPa, 80 °C) of oct-1-ene. Using syn-gas as usual, no reaction was noted at all. Similar ruthenium complexes were already reported in the literature to catalyze the water-gas shift reaction (eqn. 2) [13, 14].

$$R \longrightarrow H_2 + CO \longrightarrow R \longrightarrow CHO + (branched isomer)$$
 (1)

$$CO + H_2O \xrightarrow{CO_2} CO_2 + H_2$$
(2)

However this WGS reaction did not occur, even on adding a basic promoter such as NEt₃ or KOH to assist the reaction, the diruthenium complex being recovered unchanged after the test. Surprisingly, we observed that the combination of the two experiments $(CO/H_2, H_2O + KOH)$ led to the conversion of oct-1-ene into the corresponding aldehydes. At 1 MPa conversions remain quite low but at 3 MPa, as shown in Table 2, ~18% yield was reached (run 4). All the following tests were carried out at 3 MPa.

Run	1	8	e	4	ъ	9	7	æ	6
[complex] (mol)	10-4	10-4	10-4	10-4	2×10-4	10-4	10-4	10-4	10-4
PPha/Ru	1	-	ទ	ŋ	ß	ũ	ນ	ۍ	6
KOH	0	0	0	10-4	0	3×10^{-4}	0	0	10^{-4}
H ₂ O (ml)	0 or 2×10^{-3}	2	7	2	2	2	0	2	0
MeOH (ml)	0	0	0	0	0	0	63	0	0
alkene (mM)	32	32	32	32	16	32	32	20	40
time (h)	20	20	20	20	20	5×20	20	20	20
vield ^b (%)	0	21.4	15.8	18.7	43	67	0.5	25	1.5
nonanal	I	16.4	11.9	14.1	32.1	50.3	linear	18.9	1.4
							ester		
methyl-2-octanal	ı	5	4	4.6	10.9	26.8	I	6.1	0.1
n/n+i (%)	1	76.6	75	75.5	74.7	75	1	75.7	97
oct-2-ene	I	1.8	I	I	0	0	1	0	23.1
octane	0	0	0	0	0	0	0	0	41.6
-					0				

*Each run was performed with $[Ru_2(\mu-OOCCH_3)_2(CO)_4(PPh_3)_2]$, except run 9 with $[HRu_3CO_{11}]^-$. ^bYield in aldehyde.

Search for the best conditions of catalysis

TABLE 2

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of this particular reaction was undertaken. Table 2 shows the effects of the parameters investigated. In fact, water itself without promoter is sufficient for the system to catalyze the reaction (run 2) since $\sim 21\%$ yield was obtained; some isomerization to oct-2-ene was noted. Addition of an excess (P/Ru = 5) of triphenylphosphine prevents this isomerization phenomenon of the terminal alkene and the conversion in aldehyde is slightly lowered, from 21% (run 2) to 16% (run 3). As shown irrcolumn 4, addition of water, triphenylphosphine and potassium hydroxide increases to a slight extent but not significantly the yield from 16% to 19%, showing that KOH does not contribute the major promoting effect, if any.

Thus, it is essential that water be present in the reaction medium in order for the hydroformylation of oct-1-ene to be started. In run 2 no CO_2 was detected in the gaseous phase, reinforcing the fact that the WGS reaction (*i.e.* in the presence of $CO+H_2O$ only) is not catalyzed by the present ruthenium species. Moreover, we have performed an experiment in which water is replaced by methanol; alkoxycarbonylation of the alkene occurred but with a very low yield. In both cases, H_2O and MeOH should generate a hydride species which is the active one in the catalytic cycle. However, the generation of this starting complex is not straightforward, since addition to $[Ru_2(\mu-OAc)_2(CO)_4(PPh_3)_2]$ of a stoichiometric quantity of H_2O does not induce any activation; our experiments show that a significant excess of water with regard to the ruthenium complex is necessary for reactivity.

Two different solvents were tested in order to determine roughly if a polar medium improves the reaction rate and/or the selectivity. In fact toluene and tetrahydrofuran did not lead to significant differences concerning the reactivity, except that the starting diruthenium complex is more easy to dissolve in THF.

In run **3** of Table 2, the 15.8% yield in aldehyde represents a turnover frequency of 2.5 h⁻¹ and is representative of the catalytic activity of the system, since no hydrogenation nor isomerization of the alkene was noted. After the catalytic test, the IR spectra as well as the ³¹P NMR spectra indicated that the starting complex of formula $[Ru_2(\mu-OOCCH_3)_2(CO)_4(PPh_3)_2]$ was recovered unchanged. In order to induce higher conversions we introduced in test **5** half the quantity of alkene and twice the quantity of diruthenium complex. After the same time as in run **3**, the yield reached 43% in aldehydes instead of 15.8%, *i.e.* not the 63% expected. Analysis of the complex after reaction revealed that large amounts of the dinuclear species are still present, but another complex was formed which presents a $\nu(CO)$ band at 1889 cm⁻¹ and is silent in ³¹P NMR. Presumably this species should be of very low activity and could be responsible for the slight deactivation. Investigations are in progress to determine the nature of this species.

Recently Süss-Fink and Schmidt reported the interesting catalytic performances shown by the anionic cluster $[HRu_3(CO)_{11}]^-$ for the hydroformylation of ethylene and propene [9, 10]. Under our conditions $Ru_3(CO)_{12}$ was not active at all; for oct-1-ene, $[NEt_4][HRu_3(CO)_{11}]$ used at 3 MPa instead of 4 MPa [9, 10] led to 65% conversion. However only 1.5% aldehyde was obtained. We found, as did Süss-Fink for terminal alkene, that the selectivity in linear aldehyde reaches 92%. The reaction produces large quantities of octane and internal octenes. Thus, the two systems appear to follow quite different catalytic routes, since the cluster is essentially characterized by a high linearity of aldehyde.

We have explored the effects on the catalytic course of the nature of the bridges as well as the phosphorus ligands. The results are listed on Table 3.

Generally (runs 2-4, 8) the absence of an excess of phosphorus ligand - triphenylphosphine or trimethyl- or triphenylphosphite - leads to significant amounts of oct-2-ene. The results in Table 2 show that it is necessary to introduce a slight excess of ligand to prevent this isomerization phenomenon and we chose arbitrarily a P/Ru=5 ratio. However, the most interesting results were obtained using triphenylphosphine, the phosphite ligands giving rise to poor yields. It is necessary to have a minimal electron density on the metal centers to have good catalytic activity. Indeed, substitution of the methyl group by an electron-withdrawing group on the carboxylato bridging ligand induced a dramatic decrease in the yields. This effect was also observed using the benzoato ligand (run 7). Moreover, steric hindrance plays an important role; indeed the presence of a pivalato bridging group (run 6) having a t-butyl group characterized by a + I effect, as well as of a triphenyl phosphine ligand should induced a yield comparable to that of run 1. In fact a very low yield was obtained; presumably the steric effect of both bridging and phosphine ligands could account for this low reactivity.

Variation of the bridging groups or the ligands does not afford significant increases in linear selectivity. Particularly, in the rhodium chemistry [15] addition of an excess of triphenylphosphine to the complex $[HRh(CO)(PPh_3)_3]$ induces a dramatic improvement in the linearity of the aldehyde produced;

Runª	R	L	P/Ru	Yield	Nonanal	2-methyl- octanal (%)	n/(n+i) (%)	Oct-2-ene (%)	Turnover frequency ^b (h ⁻¹)
1	Me	PPh ₃	5/1	15.8	11.9	4	75	0	2.5
2	Me	PPh ₃	1/1	23	16.4	5	76.8	1.9	3.4
3	Me	P(OPh) ₃	1/1	30	6.5	2.2	75	21	1.4
4	Ме	P(OMe) ₃	1/1	12	1.7	1.0	62	8.8	0.4
5	CF_3	PPh ₃	5/1	2	1.7	0.6	74	0	0.4
6	CMe ₃	PPh ₃	5/1	1	0.8	0.3	75	0	0.2
7	C.H.	PPh ₃	5/1	4	2.6	0.9	76.2	0	0.6
8	C_6H_5	PPh_3	1/1	24	4.7	1.3	79	18	1

TABLE 3 Hydroformylation of oct-1-ene with $[Ru_2(\mu-OOCR)_2(CO)_4L_2]$

^aRun conditions: total pressure 3 MPa ($H_2/CO = 1/1$) T = 85 °C, t = 20 h; each run is performed with 10^{-4} mol catalyst, 2 ml water and 32×10^{-3} mol alkene in 25 ml tetrahydrofuran. ^bWith regard to the production of aldehyde. it is admitted that the *trans* influence of the phosphorus ligand gives the M-H ligand a more hydridic character. In the diruthenium complexes of interest, the two phosphine ligands are *trans* to the metal-metal bond so that their *cis* influence on a hydrido ligand should be weak. In this case, for instance runs 1 and 2, a P/Ru=5 ratio induces a slight decrease in linearity. The same conclusion prevails for runs 7 and 8 where the bridge is the benzoato ligand. Moreover the nature of the substituent group on the carboxylato framework does not play a significant role, presumably because the hydrido ligand is largely influenced by the oxygen atom of the carboxylato ligand which lies in the *trans* position.

Except for the formation of an inactive species in low yield during run **5**, we have no evidence of intermediate complexes which could provide information on the catalytic cycle. Collecting usually the starting material after catalysis seems to be in agreement with the hypothesis of retention of the dinuclear framework of the ruthenium complex. In our opinion, water leads via direct attack on a CO ligand or after an oxidative addition reaction to a hydridocarbonylruthenium species $Ru-COOH^-$, which loses a CO_2 equivalent to produce a $Ru-H^-$ species. At the present time the hypothesis of an active species being $[(CO)_2(PPh_3)Ru(\mu-OOCMe)_2RuH(CO)L]^-$ sounds reasonable, where L is PPh₃, alkene or CO.

Conclusion

The $[\operatorname{Ru}_2(\mu\operatorname{-OOCR})_2(\operatorname{CO})_2\operatorname{L}_2]$ precursors present a high level of selectivity for the hydroformylation of terminal alkenes to the corresponding aldehydes under mild conditions of pressure (1 to 3 MPa). The reaction requires the simultaneous presence of water and syn gas $\operatorname{CO}/\operatorname{H}_2$ in order to achieve the catalytic transformation. Modest turnover frequencies were obtained. The best precursor is the complex $[\operatorname{Ru}_2(\mu\operatorname{-OAc})_2(\operatorname{CO})_4(\operatorname{PPh}_3)_2]$ in the presence of a slight excess of triphenylphosphine. Presumably water affords an anionic species which is active for the hydroformylation reaction with $\operatorname{CO}/\operatorname{H}_2$. Study of the mechanism is under investigation.

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