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Journal of Organometallic Chemistry 498 (1995) 187–197

Journal of Organometallic Chemistry

Ruthenium carbonyl carboxylate complexes with nitrogen-containing ligands III. ☆ Catalytic activity in hydrogenation

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Received 23 December 1994

Abstract

Several mononuclear and dinuclear ruthenium carbonyl acetate complexes containing bipyridine or phenanthroline have been tested as catalysts in the hydrogenation of alkenes, alkynes and ketones. They are active in polar solvents and in water and the nitrogen-containing ligands are unaltered at the end of the hydrogenation.

Keywords: Ruthenium: Carbonyl complexes; *N*-donors; Hydrogenation; Catalysis; Homogeneous

1. Introduction

The catalytic activity of phosphine-substituted ruthenium and cobalt carbonyl complexes in the hydroformylation and hydrogenation of organic unsaturated substrates [2–4] is limited by the experimental conditions necessary to perform these reactions. When the temperature exceeds 120–130°C, the catalytic activity of these systems often declines abruptly and cleavage of a P–C bond in the phosphine takes place, accompanied by the formation of inactive metal clusters of high nuclearity, containing phosphido ligands [5–8].

In order to eliminate this inconvenience we decided to prepare analogous ruthenium carbonyl carboxylate complexes with ligands containing sp^2-hybridized nitrogen atoms in an aromatic system and to evaluate their activity as hydrogenation catalysts. The donor–acceptor bonds formed by nitrogen atoms are in general somewhat stronger than those formed by phosphorus donors [9]. The ligands chosen are water soluble and may therefore improve the solubility of the complexes containing them in water or polar solvents. It was therefore also of interest to evaluate the catalytic activity in water-containing solvents.

Ruthenium complexes with nitrogen donors are catalysts for a number of reactions such as the water–gas shift reaction [10–13], the reduction [14] or carbonylation of nitrobenzene [15], CO_2 reduction [16–18], the chemoselective degradation of aromatic compounds to carboxylic acids [19], the Michael addition of nitromethane to α,β-unsaturated ketones, [20] and the direct formation of ethylene glycol from synthesis gas [21].

2. Results and discussion

We have already reported the synthesis of ruthenium complexes of the types $[Ru_2(CO)_4(CH_3COO)(N\text{–}N)_2]^+$ and $[Ru(CO)_2(CH_3COO)_2(N\text{–}N)]$ (N–N = bidentate, nitrogen donor) [1,22]. We have tested the catalytic activity of these complexes in the hydrogenation under pressure of some ketones, alkenes, alkynes and unsaturated ketones which are soluble in solvents containing water. The influences of solvent, temperature and reaction time were examined. Reaction rates were also determined.

☆ For II see [1].

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SSDI 0022-328X(95)05517-7

Table 1
Acetone hydrogenation in the presence of $[Ru_2(CO)_4(CH_3COO)(bipy)_2](CH_3COO)$: influence of solvent

Solvent	Conversion (%)	Turn-over frequency [a] (h^{-1})
Water	83.6	133.4
THF	4.8	7.7
Methanol	55.5	88.5
Methanol–water (2:1) [b]	89.1	142.1

Substrate, 74.9 mmol; catalyst, 19.56 μmol Ru; solvent, 8 ml; $T = 100°C$, $p(H_2) = 100$ atm at room temperature; reaction time, 24 h.
[a] The turn-over frequency is the number of moles of substrate converted per number of moles of Ru per hour.
[b] Solvent, 12 ml.

2.1. Hydrogenation of ketones

Acetone was chosen as the representative substrate to test the activity of $[Ru_2(CO)_4(CH_3COO)(bipy)_2](CH_3COO)$ (**1**) and $[Ru_2(CO)_4(CH_3COO)(phen)_2](CH_3COO)$ (**2**) as hydrogenation catalysts. Standard reaction conditions were 100°C, dihydrogen at 100 atm and a 24 h reaction time (Tables 1–4).

2.1.1. Influence of the solvent

Water, tetrahydrofuran (THF) and methanol were used (Table 1). The conversion is greater in polar media, particularly in the water–methanol mixture when

Table 2
Acetone hydrogenation in the presence of $[Ru_2(CO)_4(CH_3COO)(N\text{-}N)_2](CH_3COO)$: influence of reaction time

Time (h)	$[Ru_2(CO)_4(CH_3COO)(bipy)_2](CH_3COO)$ [a]		$[Ru_2(CO)_4(CH_3COO)(phen)_2](CH_3COO)$ [b]	
	Conversion (%)	Turn-over frequency (h^{-1})	Conversion (%)	Turn-over frequency (h^{-1})
3	19.5	248.8	24.4	324.3
6	31.7	202.3	36.1	239.9
12	51.5	164.3	57.2	190.0
24	83.6	133.4	87.4	145.2

Substrate, 74.9 mmol; solvent, (water) 8 ml; $p(H_2) = 100$ atm at room temperature; $T = 100°C$.
[a] Catalyst, 19.56 μmol Ru.
[b] Catalyst, 18.74 μmol Ru.

Table 3
Acetone hydrogenation in the presence of $[Ru_2(CO)_4(CH_3COO)(N\text{-}N)_2](CH_3COO)$: influence of hydrogen pressure

$p(H_2)$ (atm)	T (°C)	$[Ru_2(CO)_4(CH_3COO)(bipy)_2](CH_3COO)$ [a]		$[Ru_2(CO)_4(CH_3COO)(phen)_2](CH_3COO)$ [b]	
		Conversion (%)	Turn-over frequency (h^{-1})	Conversion (%)	Turn-over frequency (h^{-1})
1	100	2.3	3.7	ND [c]	ND
5	60	3.6	5.7	4.0	6.6
30	60	13.4	21.4	16.9	28.1
100	60	21.4	34.1	24.5	40.7

Substrate, 74.9 mmol; solvent, (water) 8 ml; reaction time, 24 h.
[a] Catalyst, 19.56 μmol Ru.
[b] Catalyst, 18.74 μmol Ru.
[c] ND, not determined.

Table 4
Acetone hydrogenation in the presence of $[Ru_2(CO)_4(CH_3COO)(N\text{-}N)_2](CH_3COO)$: influence of reaction temperature

T (°C)	$[Ru_2(CO)_4(CH_3COO)(bipy)_2](CH_3COO)$ [a]		$[Ru_2(CO)_4(CH_3COO)(phen)_2](CH_3COO)$ [b]	
	Conversion (%)	Turn-over frequency (h^{-1})	Conversion (%)	Turn-over frequency (h^{-1})
40	14.2	22.6	9.8	16.2
60	21.4	34.1	24.5	40.7
80	48.5	77.3	53.5	88.8
100	83.6	133.4	87.4	145.2
140	100	159.5		

Substrate, 74.9 mmol; solvent (water) 8 ml; $p(H_2) = 100$ atm at room temperature; reaction time, 24 h.
[a] Catalyst, 19.56 μmol Ru.
[b] Catalyst, 18.74 μmol Ru.

Table 5
Ketone hydrogenation in the presence of $[Ru_2(CO)_4(CH_3COO)(bipy)_2](CH_3COO)$: influence of the ketone structure

Substrate	Solvent: water [a]		Solvent, water–methanol (1 : 2) [b]	
	Conversion (%)	Turn-over frequency (h^{-1})	Conversion (%)	Turn-over frequency (h^{-1})
Acetone	83.6	149.0	89.1	158.8
Butan-2-one	66.7	118.9	57.1	101.8
Pentan-2-one	5.6	10.0	14.9	26.6
4-Methylpentan-2-one	0.0	0.0	66.8	119.1
3,3-Dimethylbutan-2-one	0.0	0.0	21.5	38.3
Cyclohexanone	ND	–	55.4	98.7
Acetophenone	ND	–	9.6	17.1
Acetophenone	ND	–	5.5 [c]	9.8

Substrate, 74.9 mmol; catalyst, 19.56 μmol Ru; $T = 100°C$; $p(H_2) = 100$ atm at room temperature; reaction time, 24 h.
[a] Water, 8 ml.
[b] Water, 4 ml, methanol, 8 ml.
[c] Water, 8 ml; ethanol, 16 ml.

2 is used as catalytic precursor, whereas a less polar solvent such as THF gives poorer conversions.

2.1.2. Reaction rate

The conversions obtained at a given reaction time show that with both **1** and **2**, the hydrogenation rate is first order with respect to the concentration of the substrate (Table 2). The specific rate at 100°C is 1.7×10^{-5} s^{-1} for **1** and 2.0×10^{-5} s^{-1} for **2**.

2.1.3. Influence of dihydrogen pressure

The hydrogenation of acetone in the presence of **1** already occurs at atmospheric pressure and 100°C. However, the reaction rate is very low (2.3% conversion in 24 h). The temperature of 60°C was chosen for a series of tests between 5 and 100 atm because at 100 atm and 100°C the conversion would have been too great. The reaction is first order with respect to dihydrogen pressure (Table 3) with a specific rate at 60°C in the pressure range 5–30 atm of 5.8×10^{-8} s^{-1} atm^{-1} for **1**. Compound **2** has a behaviour analogous to that of **1** with a specific rate under the same conditions of 7.4×10^{-8} s^{-1} atm^{-1}.

2.1.4. Influence of temperature

As expected, the rate of the reaction increases with increasing temperature. Hydrogenation already occurs at 40°C, but with a conversion of only 14.2% after 24 h. At 100°C the conversion is 83.6% and 100% conversion is reached in 24 h at 140°C (Table 4). No decomposition of the catalyst occurs. Catalysts **1** and **2** have almost the same activities.

Table 6
Hydrogenation of acetone to propan-2-ol in the presence of ruthenium carbonyl carboxylates with nitrogen-containing ligands: influence of the methyl substituents on the nitrogen-containing ligands

Catalytic precursor	Conversion (%)	Turn-over frequency (h^{-1})
$[Ru_2(CO)_4(CH_3COO)(bipy)_2](CH_3COO)$	29.2	208.2
$[Ru_2(CO)_4(CH_3COO)(4,4'\text{-dmbipy})_2](CH_3COO)$	31.4	223.9
$[Ru_2(CO)_4(CH_3COO)(phen)_2](CH_3COO)$	22.9	163.3
$[Ru_2(CO)_4(CH_3COO)(4,7\text{-dmphen})_2](CH_3COO)$	39.0	278.0
$[Ru_2(CO)_4(CH_3COO)(5,6\text{-dmphen})_2](CH_3COO)$	29.4	209.6
$[Ru_2(CO)_4(CH_3COO)(bipy)_2][BPh_4]$	6.4	45.6
$[Ru_2(CO)_4(CH_3COO)(4,4'\text{-dmbipy})_2][BPh_4]$	20.7	147.6
$[Ru_2(CO)_4(CH_3COO)(phen)_2][BPh_4]$	2.2	15.7
$[Ru_2(CO)_4(CH_3COO)(4,7\text{-dmphen})_2][BPh_4]$	3.2	22.8
$[Ru_2(CO)_4(CH_3COO)(5,6\text{-dmphen})_2][BPh_4]$	1.9	13.5
$[Ru(CO)_2(CH_3COO)_2(bipy)]$	7.2	51.3
$[Ru(CO)_2(CH_3COO)_2(4,4'\text{-dmbipy})]$	16.0	114.1
$[Ru(CO)_2(CH_3COO)_2(phen)]$	15.6	111.2
$[Ru(CO)_2(CH_3COO)_2(2,9\text{-dmphen})]$	4.1	29.2
$[Ru(CO)_2(CH_3COO)_2(4,7\text{-dmphen})]$	13.2	94.1
$[Ru(CO)_2(CH_3COO)_2(5,6\text{-dmphen})]$	26.9	191.8

Substrate, 74.9 mmol; catalyst, 17.51 μmol Ru; $T = 100°C$; solvent, water (4 ml) and methanol (8 ml); $p(H_2) = 100$ atm at room temperature; reaction time, 6 h.

Table 7
Hydrogenation of acetone to propan-2-ol in the presence of ruthenium(II) carbonyl carboxylate complexes with nitrogen-containing ligands and sodium carbonate

Catalytic precursor	Conversion (%)	Turn-over frequency (h^{-1})
$[Ru(CO)_2(CH_3COO)_2(bipy)$	13.5	99.5
$[Ru(CO)_2(CH_3COO)_2(4,4'\text{-dmbipy})]$	9.3	66.3
$[Ru(CO)_2(CH_3COO)_2(phen)]$	100	712.9
$[Ru(CO)_2(CH_3COO)_2(2,9\text{-dmphen})]$	16.3	116.2
$[Ru(CO)_2(CH_3COO)_2(4,7\text{-dmphen})]$	18.0	128.3
$[Ru(CO)_2(CH_3COO)_2(5,6\text{-dmphen})]$	12.8	91.3

Substrate, 74.90 mmol; catalyst, 17.51 μmol; Na_2CO_3, 0.95 mmol; solvent, water (4 ml) and methanol (8 ml); $p(H_2) = 100$ atm at room temperature; $T = 100°C$; reaction time, 6 h.

The activation parameters in the range 40–100°C were $\Delta H^* = -9.2$ kcal mol^{-1} and $\Delta S^* = -56.0$ entropy units for **1**, and $\Delta H^* = -10.3$ kcal mol^{-1} and a $\Delta S^* = -56.7$ entropy units for **2**. The similarity of the data obtained with the two catalytic precursors suggest analogous pathways for the two systems. The negative values of ΔS^* indicate that in the rate-determining step an associative mechanism is involved (probably the coordination of the ketone to a pre-formed hydridic species).

No hydrogenation products of the nitrogen-containing ligands was detected in solution (by gas–liquid chromatography analysis) or in the ruthenium compounds (by ^1H NMR spectroscopy) recovered at the end of the experiments carried out at the highest temperature (140°C).

2.1.5. Hydrogenation of different ketones

The hydrogenation of different ketones was carried out in water or in water–methanol (1:2) (Table 5). With methyl alkyl ketones the conversion decreases as the length of the alkyl chain increases, or, if the alkyl chain is substituted, particularly by a phenyl group. 4-Methylpentan-2-one seems to be an exception to this.

2.1.6. Influence of the counter-ion and of the nitrogen-containing ligand

The hydrogenation of acetone was investigated using catalytic precursors of the type $[Ru_2(CO)_4(CH_3COO)(N{-}N)_2](X)$ where $X = CH_3COO$ or BPh_4 and N–N = 2,2′-bipyridine (bipy), 4,4′-dimethyl-2,2′-bipyridine (4,4′-dmbipy), 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (4,7-dmphen), 5,6-dimethyl-1,10-phenanthroline (5,6-dmphen) or 2,9-dimethyl-1,10-phenanthroline (2,9-dmphen) (Table 6).

The acetate salts show higher activities than the tetraphenylborate salts do. Among the acetates those with dimethyl-substituted ligands (4,4′-dmbip, 4,7-dmphen and 5,6-dmphen) seem to have higher activities. This increase is greater for complexes containing phenantrolines than in those with bipyridines.

Among the salts containing $[BPh_4]^-$, greater activity is shown by those containing bipyridines, the best performance having demonstrated by $[Ru_2(CO)_4(CH_3COO)(4,4'\text{-dmbip})_2](BPh_4)$ with a turn- over frequency of 147.6 h^{-1}.

The activity of the mononuclear complexes is intermediate between those of the dinuclear salts containing acetate and tetraphenylborate. Greater activity of the binuclear complexes in the hydrogenation of ketones [23,24], olefins [23,24] and carboxylic acids [25] is also shown by the phosphine derivatives.

2.1.7. Influence of sodium carbonate

Phosphine-substituted ruthenium carbonyl acetate complexes react with sodium carbonate under dihydrogen, forming the corresponding hydride [6], which could be the active intermediate in the hydrogenation of unsaturated substrates by this system. We wanted to determine whether the mononuclear ruthenium carbonyl acetate complexes containing nitrogen ligands behaved analogously (Table 7).

Hydrogenation of acetone was therefore performed under the conditions as for Table 6 but with an excess of sodium carbonate. A slight increase in the activity of the system was noted. The best result was achieved using $[Ru(CO)_2(CH_3COO)_2(phen)]$ which showed a conversion which had increased from 15% to 100%.

2.2. Olefin hydrogenation

Hex-1-ene was used as substrate, and water–THF (1:2) as solvent, in order to obtain a homogeneous system.

The results (Table 8) show that all complexes tested act as catalysts in the hydrogenation of this olefin. Isomerization of the olefin also takes place and the starting terminal olefin has almost disappeared at the end of the experiment. In general dinuclear complexes are better catalysts than the mononuclear complexes, although not in every case.

Methyl substituents on the nitrogen-containing ligands increase the catalytic activity of the complexes examined. Among the dinuclear complexes, the anion also affects the catalytic activity.

When sodium carbonate is added to the system there is a general improvement in the catalytic activity of mononuclear complexes at 100°C. The extent of the hydrogenation of an alkene to the corresponding alkane varies from 88.4% to 96.7% (Table 9).

2.3. Hydrogenation of unsaturated ketones

The hydrogenation of these bifunctional products was tested in order to compare the rates of hydrogena-

Table 8
Hydrogenation of hex-1-ene to hexane in the presence of ruthenium carbonyl carboxylate complexes with nitrogen-containing ligands

Catalytic precursor	Reaction products						
	Hexane		*cis*-Hex-2-ene Conversion (%)	*trans*-Hex-2-ene Conversion (%)	*cis*-Hex-3-ene Conversion (%)	*trans*-Hex-3-ene Conversion (%)	Hex-1-ene (%)
	Conversion (%)	Turn-over frequency (h^{-1})					
$[Ru_2(CO)_4(CH_3COO)(bipy)_2](CH_3COO)$	51.7	86.2	12.4	26.9	0.5	4.8	3.7
$[Ru_2(CO)_4(CH_3COO)(4,4'\text{-dmbipy})_2](CH_3COO)$	33.1	55.2	16.2	37.6	0.5	8.1	4.5
$[Ru_2(CO)_4(CH_3COO)(phen)_2](CH_3COO)$	74.4	124.0	4.6	13.7	0.3	5.1	1.9
$[Ru_2(CO)_4(CH_3COO)(4,7\text{-dmphen})_2](CH_3COO)$	79.2	132.0	4.4	11.4	0.4	2.8	1.8
$[Ru_2(CO)_4(CH_3COO)(5,6\text{-dmphen})_2](CH_3COO)$	89.3	148.8	1.9	5.8	–	2.3	0.7
$[Ru_2(CO)_4(CH_3COO)(bipy)_2][BPh_4]$	31.5	52.5	17.3	38.7	0.5	7.0	5.0
$[Ru_2(CO)_4(CH_3COO)(4,4'\text{-dmbipy})_2][BPh_4]$	52.7	87.8	8.8	26.2	0.5	8.7	3.1
$[Ru_2(CO)_4(CH_3COO)(phen)_2][BPh_4]$	87.7	146.2	2.4	6.7	0.1	2.4	0.7
$[Ru_2(CO)_4(CH_3COO)(4,7\text{-dmphen})_2][BPh_4]$	75.6	126.0	4.2	13.2	0.4	4.9	1.7
$[Ru_2(CO)_4(CH_3COO)(5,6\text{-dmphen})_2][BPh_4]$	82.1	136.8	3.3	9.9	0.1	3.6	1.0
$[Ru(CO)_2(CH_3COO)_2(bipy)]$	39.5	65.8	13.0	36.9	0.4	6.5	3.7
$[Ru(CO)_2(CH_3COO)_2(4,4'\text{-dmbipy})]$	45.5	75.8	12.9	32.5	0.5	4.6	4.0
$[Ru(CO)_2(CH_3COO)_2(phen)]$	50.0	83.3	9.2	27.4	0.3	10.0	3.1
$[Ru(CO)_2(CH_3COO)_2(2,9\text{-dmphen})]$	62.7	104.5	7.9	21.0	0.4	5.3	2.7
$[Ru(CO)_2(CH_3COO)_2(4,7\text{-dmphen})]$	93.2	155.3	1.4	3.7	0.4	0.9	0.4
$[Ru(CO)_2(CH_3COO)_2(5,6\text{-dmphen})]$	61.2	102.0	7.1	21.3	0.3	7.6	2.5

Substrate, 17.51 mmol; catalyst, 17.51 μmol Ru; solvent: water (5 ml) and THF (10 ml); $p(H_2) = 100$ atm at room temperature; $T = 100°C$; reaction time, 6 h.

Table 9
Hydrogenation of hex-1-ene to hexane in the presence of ruthenium(II) carbonyl carboxylate complexes with nitrogen-containing ligands and sodium carbonate

Catalytic precursor	Reaction products						
	Hexane		*cis*-Hex-2-ene Conversion (%)	*trans*-Hex-2-ene Conversion (%)	*cis*-Hex-3-ene Conversion (%)	*trans*-Hex-3-ene Conversion (%)	Hex-1-ene (%)
	Conversion (%)	Turn-over frequency (h^{-1})					
$[Ru(CO)_2(CH_3COO)_2(bipy)]$	91.6	152.7	1.1	3.5	1.8	1.3	0.7
$[Ru(CO)_2(CH_3COO)_2(4,4'\text{-dmbipy})]$	88.4	147.3	2.1	6.2	0.4	2.3	0.6
$[Ru(CO)_2(CH_3COO)_2(phen)]$	95.7	159.5	0.7	2.4	0.1	0.8	0.3
$[Ru(CO)_2(CH_3COO)_2(2,9\text{-dmphen})]$	94.5	157.5	0.9	2.8	0.3	1.0	0.5
$[Ru(CO)_2(CH_3COO)_2(4,7\text{-dmphen})]$	94.7	157.8	0.9	2.7	0.1	1.1	0.5
$[Ru(CO)_2(CH_3COO)_2(5,6\text{-dmphen})]$	96.7	161.2	0.8	1.5	0.1	0.6	0.3

Substrate, 17.51 mmol; catalyst, 17.51 μmol Ru; Na_2CO_3, 0.95 mmol; solvent, water (5 ml) and THF (10 ml); $p(H_2) = 100$ atm at room temperature; $T = 100°C$; reaction time, 6 h.

Table 10
Hydrogenation of *trans*-4-phenylbut-3-en-2-one to *trans*-4-phenylbutan-2-one in the presence of ruthenium(I) carbonyl carboxylate complexes with nitrogen-containing ligands [a]

Catalytic precursor	Conversion (%)	Turn-over frequency (h^{-1})
$[Ru_2(CO)_4(CH_3COO)(bipy)_2](CH_3COO)$	9.3	15.5
$[Ru_2(CO)_4(CH_3COO)(4,4'\text{-dmbipy})_2](CH_3COO)$	9.5	15.8
$[Ru_2(CO)_4(CH_3COO)(phen)_2](CH_3COO)$	7.6	12.7
$[Ru_2(CO)_4(CH_3COO)(4,7\text{-dmphen})_2](CH_3COO)$	11.4	19.0
$[Ru_2(CO)_4(CH_3COO)(5,6\text{-dmphen})_2](CH_3COO)$	12.9	21.5
$[Ru_2(CO)_4(CH_3COO)(bipy)_2][BPh_4]$	20.2	33.7
$[Ru_2(CO)_4(CH_3COO)(4,4'\text{-dmbipy})_2][BPh_4]$	17.2	28.7
$[Ru_2(CO)_4(CH_3COO)(phen)_2][BPh_4]$	13.5	22.5
$[Ru_2(CO)_4(CH_3COO)(4,7\text{-dmphen})_2][BPh_4]$	14.9	24.8
$[Ru_2(CO)_4(CH_3COO)(5,6\text{-dmphen})_2][BPh_4]$	10.3	17.2

Substrate, 17.51 mmol; catalyst, 17.51 μmol Ru; solvent, water (12 ml) and methanol (24 ml); $p(H_2) = 100$ atm at room temperature; $T = 100$°C; reaction time, 6 h.
[a] Selectivity, 100%.

tion of the two unsaturated groups. *trans*-4-Phenylbut-3-en-2-one and cyclohex-2-en-1-one were chosen as substrates (Tables 10–12). The dinuclear complexes promote the hydrogenation of the C=C bond with nearly 100% selectivity, while with mononuclear complexes the selectivity was slightly lower.

The higher activity in the hydrogenation of the C=C double bond compared with that of the C=O group of this catalytic system might have been predicted on the basis of the results reported in Tables 6 and 8, although not to such a degree. However, the conjugation of the C=C bond with the C=O group and the aromatic ring reduces the degree of hydrogenation in some cases (see Tables 8 and 10) but does not suppress it entirely. The carbonyl group may still be hydrogenated if it is in a molecule having a little steric hindrance and conjugation (Table 12).

The dinuclear complexes $[Ru_2(CO)_4(CH_3COO)(L\text{–}L)_2](BPh_4)$ have higher catalytic activities than the corresponding acetates, the converse of what was observed in the hydrogenation of hex-1-ene. Complexes containing bipyridines and $[BPh_4]^-$ have higher catalytic activities than those with phenanthrolines.

Cyclohex-2-en-1-one has also been hydrogenated using **1** as catalyst (Table 12). The reaction products are the saturated ketone and the saturated alcohol. In water

Table 11
Hydrogenation of *trans*-4-phenylbut-3-en-2-one in the presence of ruthenium(II) carbonyl carboxylate complexes with nitrogen-containing ligands

Catalytic precursor	Conversion (%)	Reaction products composition (%)	
		4-phenylbutan-2-one	4-phenylbutan-2-olo
$[Ru(CO)_2(CH_3COO)_2(bipy)]$	16.4	16.4	–
$[Ru(CO)_2(CH_3COO)_2(4,4'\text{-dmbipy})]$	19.6	18.7	0.9
$[Ru(CO)_2(CH_3COO)_2(phen)]$	8.4	8.4	–
$[Ru(CO)_2(CH_3COO)_2(2,9\text{-dmphen})]$	55.1	52.1	3.4
$[Ru(CO)_2(CH_3COO)_2(4,7\text{-dmphen})]$	6.8	6.8	–
$[Ru(CO)_2(CH_3COO)_2(5,6\text{-dmphen})]$	6.8	6.8	–

Substrate, 17.51 mmol; catalyst, 17.51 μmol Ru; solvent, water (12 ml) and methanol (24 ml); $p(H_2) = 100$ atm at room temperature; $T = 100$°C; reaction time, 6 h.

Table 12
Hydrogenation of cyclohex-2-en-1-one in the presence of $[Ru_2(CO)_4(CH_3COO)(bipy)_2](CH_3COO)$

Solvent	T (°C)	Conversion (%)	Reaction products composition (%)		
			Cyclohexanone	Cyclohexanol	Cyclohex-2-en-1-one
Water-THF [a]	40	13.0	12.0	1.0	87.0
Water	40	68.3	61.3	7.0	31.7
Water	100	100	55.6	44.4	0.0

Substrate, 74.9 mmol; catalyst, 19.56 μmol Ru; $T = 100$°C; water, 8.2 ml; $p(H_2) = 100$ atm at room temperature; reaction time, 24 h.
[a] THF, 12 ml.

Table 13
Hydrogenation of phenylethyne in the presence of ruthenium carbonyl carboxylate complexes with nitrogen-containing ligands

Catalytic precursor	Conversion %	Reaction products composition (%)	
		$PhCH=CH_2$	$PhCH_2-CH_3$
$[Ru_2(CO)_4(CH_3COO)(bipy)_2](CH_3COO)$	20.9	18.1	2.8
$[Ru_2(CO)_4(CH_3COO)(4,4'\text{-dmbipy})_2](CH_3COO)$	8.5	7.1	1.4
$[Ru_2(CO)_4(CH_3COO)(phen)_2](CH_3COO)$	16.8	10.7	6.1
$[Ru_2(CO)_4(CH_3COO)(4,7\text{-dmphen})_2](CH_3COO)$	6.0	4.8	1.2
$[Ru_2(CO)_4(CH_3COO)(5,6\text{-dmphen})_2](CH_3COO)$	11.6	6.1	5.5
$[Ru_2(CO)_4(CH_3COO)(bipy)_2][BPh_4]$	5.9	4.8	1.1
$[Ru_2(CO)_4(CH_3COO)(4,4'\text{-dmbipy})_2][BPh_4]$	15.9	9.2	6.7
$[Ru_2(CO)_4(CH_3COO)(phen)_2][BPh_4]$	5.4	4.3	1.1
$[Ru_2(CO)_4(CH_3COO)(4,7\text{-dmphen})_2][BPh_4]$	13.4	7.6	5.8
$[Ru(CO)_2(CH_3COO)_2(bipy)]$	11.7	5.4	6.3
$[Ru(CO)_2(CH_3COO)_2(4,4\text{-dmbipy})]$	12.1	5.6	6.5
$[Ru(CO)_2(CH_3COO)_2(phen)]$	5.3	4.1	1.2
$[Ru(CO)_2(CH_3COO)_2(2,9\text{-dmphen})]$	12.7	10.3	2.4
$[Ru(CO)_2(CH_3COO)_2(4,7\text{-dmphen})]$	8.3	6.6	1.7
$[Ru(CO)_2(CH_3COO)_2(5,6\text{-dmphen})]$	11.7	6.1	5.6

Substrate, 17.51 mmol; catalyst, 17.51 μmol Ru; solvent, water (5 ml) and THF (10 ml); $p(H_2) = 100$ atm at room temperature; $T = 100°C$; reaction time, 6 h.

at 40°C and at a conversion of 68.3%, selectivity towards the saturated ketone is 89.7%. At 100°C a greater proportion of alcohol is obtained.

2.4. Hydrogenation of alkynes

Phenylacetylene was chosen as substrate, and in all cases both styrene and ethylbenzene (Table 13) were obtained. The activity of the system in the hydrogenation of the C≡C triple bond is fairly low compared with that shown with an olefin. The ratio of olefin to paraffin formed is not indicative of any special behaviour. It is in fair agreement with what was found in the hydrogenation of hex-1-ene. Perhaps the paraffin is formed by hydrogenation of the olefin released from the previous hydrogenation of the alkyne.

The low selectivity in the hydrogenation of the triple bond to a double bond shows that the double bond is hydrogenated more easily than the triple bond. The behaviour of the dinuclear salts containing acetate or tetraphenylborate are analogous to those in the hydrogenation of the double bond; and there are no significant differences between the complexes tested.

The activity of the catalytic system is slightly reduced by the addition of sodium carbonate, (Table 14). Only in the case of the 5,6-dmphen derivatives was an increase observed, the conversion changing from 11.7% to 76.2%.

3. Conclusions

Ruthenium carbonyl carboxylate complexes with nitrogen-containing ligands catalyse the hydrogenation of C=C, C=O and C≡C bonds in the presence of water and/or polar solvents.

The catalytic activities of the mononuclear complexes are improved by the presence of a base in solution. This suggests that the activation of the catalytic system is due to the formation of a ruthenium carbonyl hydride species with the loss of a carboxylato ligand. An investigation by ^1H NMR spectroscopy of

Table 14
Hydrogenation of phenylethyne in the presence of ruthenium(II) carbonyl carboxylate complexes with nitrogen-containing ligands and sodium carbonate

Catalytic precursor	Conversion %	Reaction products composition (%)	
		$PhCH=CH_2$	$PhCH_2-CH_3$
$[Ru(CO)_2(CH_3COO)_2(bipy)]$	7.8	3.6	4.2
$[Ru(CO)_2(CH_3COO)_2(4,4'\text{-dmbipy})]$	3.2	2.3	0.9
$[Ru(CO)_2(CH_3COO)_2(phen)]$	2.5	1.8	0.7
$[Ru(CO)_2(CH_3COO)_2(2,9\text{-dmphen})]$	5.7	3.1	2.6
$[Ru(CO)_2(CH_3COO)_2(4,7\text{-dmphen})]$	8.7	4.2	4.5
$[Ru(CO)_2(CH_3COO)_2(5,6\text{-dmphen})]$	76.2	47.7	28.5

Substrate, 17.51 mmol; catalyst, 17.51 μmol Ru; Na_2CO_3, 0.95 mmol; solvent, water (5 ml) and THF (10 ml); $p(H_2) = 100$ atm at room temperature; $T = 100°C$; reaction time, 6 h.

the behaviour of these mononuclear complexes under dihydrogen pressure (100 atm), after heating at 100°C in the presence of sodium carbonate, has shown a resonance at −25 ppm indicative of a hydridic hydrogen bridging two ruthenium atoms. Further work is in progress to isolate the products.

No modifications of the nitrogen-containing ligands occur under conditions in which the phosphine ligands start to decompose (140°C) [6].

4. Experimental details

4.1. Apparatus and analytical methods

IR spectra were recorded with a Perkin–Elmer FT-IR 1760 instrument using KBr or CaF_2 windows for solutions and KBr pellets for solid samples.

Elemental analyses were carried out using a Perkin–Elmer 240C analyser.

^1H NMR spectra were recorded at 299.945 MHz on a Varian VXR 300 or at 199.975 MHz on a Varian Gemini-200 spectrometer, using tetramethylsilane as external reference. ^{13}C NMR spectra were recorded at 75.429 MHz on a Varian VXR 300 instrument. All ^{13}C NMR spectra were proton decoupled, using tetramethylsilane as external reference.

An Analytical Instrument 111 conductivity meter was used with an Orion 99.01.01 cell, having a cell-constant of 1.00 cm^{-1} for conductivity determinations. Gas chromatography (GC) analysis was performed using a Shimadzu GC-14A GC apparatus with packed columns and a Shimadzu C-R4A computer and a Perkin–Elmer 8320 GC instrument with capillary columns. All instruments had flame ionization detectors. The following packed columns (2 m) were used: FFAP (free fatty acid phase), 5% supported on Chromosorb GAW-DMCS; Porapak, 100–120 mesh; PPG (polypropylenglycol), LB-550-X 15% supported on Chromosorb W; CW20M, Carbowax 20M 15% supported on Chromosorb W. A Al_2O_3 PLOT capillary column containing alumina (50 m; internal diameter, 0.32 mm) was used.

4.2. Materials

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

2,2′-bipyridine (Fluka) 4,4′-dimethyl-2,2′-bipyridine (Aldrich), 1,10-phenanthroline (Merck), 2,9-dimethyl-1,10-phenanthroline (Aldrich), 4,7-dimethyl-1,10-phenanthroline (Aldrich), 5,6-dimethyl-1,10-phenanthroline (Aldrich), sodium tetraphenylborate (RPE-ACS C. Erba) and triruthenium dodecacarbonyl (Aldrich) were used as purchased. $[\{Ru_2(CO)_4(MeCOO)_2\}_n]$ [26], $[Ru_2(CO)_4(CH_3COO)(bipy)_2](CH_3COO)$ [22], $[Ru_2(CO)_4(CH_3COO)(4,4'\text{-dmbipy})_2](CH_3COO)$ [22], $[Ru_2(CO)_4(CH_3COO)(phen)_2](CH_3COO)$ [22], $[Ru_2(CO)_4(CH_3COO)(4,7\text{-dmphen})_2](CH_3COO)$ [22], $[Ru_2(CO)_4(CH_3COO)(5,6\text{-dmphen})_2](CH_3COO)$ [22], $[Ru_2(CO)_4(CH_3COO)(bip)_2][BPh_4]$ [22], $[Ru_2(CO)_4(CH_3COO)(4,4'\text{-dmbip})_2]$-$[BPh_4]$ [22], $[Ru_2(CO)_4(CH_3COO)(phen)_2]$-$[BPh_4]$ [22], $[Ru_2(CO)_4(CH_3COO)(4,7\text{-dmphen})_2]$-$[BPh_4]$ [22], $[Ru(CO)_2(CH_3COO)_2(bipy)]$ [1], $[Ru(CO)_2(CH_3COO)_2\text{-}(4,4'\text{-dmbipy})]$ [1], $[Ru(CO)_2\text{-}(CH_3COO)_2(phen)]$ [1], $[Ru(CO)_2(CH_3COO)_2(2,9\text{-dmphen})]$ [1], $[Ru(CO)_2\text{-}(CH_3COO)_2(4,7\text{-dmphen})]$ [1], $[Ru(CO)_2(CH_3COO)_2\text{-}(5,6\text{-dmphen})]$ [1] were synthesized as reported. Methanol (C. Erba product) was purified by the Lund–Bjerrunn method reported by Vogel [27]. THF (RPE C. Erba) (900 ml) was dried by heating under reflux over $LiAlH_4$ (10 g). The product, collected by fractional distillation had a boiling point (b.p.) of 65°C. Acetone (RPE-ACS C. Erba) was purified according to Vogel [28]. Hex-1-ene (Aldrich) was passed through an Al_2O_3 column and distilled under dinitrogen. The purity was 99.99%. *trans*-4-Phenylbut-3-en-2-one (Aldrich) was used as supplied. Phenylethyne (Aldrich) was distilled prior to use under dinitrogen (b.p., 143°C).

4.3. Catalytic hydrogenation experiments

The catalytic precursor, the solvent, the substrate and dihydrogen at the pre-fixed pressure were introduced into an evacuated stainless steel autoclave (150 ml). The autoclave was placed in a thermostatic oil bath set at the desired temperature (± 1°C) and rocked for the pre-fixed time. The amounts of catalytic precursors, solvent and substrates and the hydrogen pressure are reported in Tables 1–14. At the end, the reactor was cooled, the gases vented and the solution analysed by GC. The identity of the products was confirmed by GC–mass spectroscopy (MS) analysis. The GC and GC–MS operating conditions are reported below. The results of these experiments are given in Tables 1–14.

4.4. Gas chromatography analysis of the hydrogenation products

For acetone the Porapak column was kept at 100°C for 10 min, then heated to 150°C at 2°C min^{-1} and kept at this temperature for 10 min.

For *trans*-4-phenylbut-3-en-2-one the FFAP column was kept at 50°C for 2 min, then heated to 200°C at 10°C min^{-1} and kept at this temperature for 20 min.

For butan-2-one and pentan-2-one the Porapak column was kept at 130°C for 5 min, then heated to 180°C at 5°C min^{-1} and kept at this temperature for 10 min.

For 4-methylpentan-2-one and 3,3-dimethylbutan-2-one the CW20M column was kept at 80°C for 40 min, then heated to 160°C at 20°C min^{-1} and kept at this temperature for 10 min.

For acetophenone the CW20M column was kept at 60°C for 5 min, then heated to 160°C at 20°C min^{-1} and kept at this temperature for 10 min.

For cyclohexanone and cyclohex-2-en-1-one the FFAP column was kept at 80°C for 10 min, then heated to 150°C at 10°C min^{-1} and kept at this temperature for 15 min.

For phenylethyne the FFAP column was kept at 80°C for 40 min, then heated to 200°C at 10°C min^{-1} and kept at this temperature for 30 min.

For hex-1-ene the Al_2O_3 PLOT capillary column was heated at 130°C for 25 min, then heated to 200°C at 30°C min^{-1} and kept at this temperature for 54 min. When a THF–water solution was used, the two-phase solution obtained at the end of the experiment was made homogeneous at room temperature by the addition of further THF.

The products of the hydrogenation experiments were identified by GC analysis, through their retention time compared with authentic commercial samples and confirmed by GC–MS determination of the products.

Mass spectra of propan-2-ol, *trans*-4-phenylbut-3-en-2-one, butan-2-ol, pentan-2-ol, 4-methylpentan-2-ol, 3,3-dimethylbutan-2-ol, 1-phenylethanol, cyclohex-2-en-1-ol, cyclohex-2-en-1-one, cyclohexanol, styrene, ethylbenzene and hexane were consistent with those in the literature [29].

For 4-Phenylbutan-2-ol: *m/e* 150 (10 $[M]^+$), 132 (20, $[M-H_2O]^+$), 117 (25, $[132-CH_3]^+$), 105 (5, $[M-C_2H_5O]^+$), 104 (90, $[C_6H_5CH{=}CH_2]^+$), 91 (100, $[C_7H_7]^+$), 78 (10, $[C_6H_6]^+$), 77 (10, $[C_6H_6]^+$), 65 (30, $[C_5H_5]^+$), 51 (8, $[C_4H_3]^+$), 39 (12, $[C_3H_3]^+$).

Quantitative determinations were obtained by GC analysis, assuming the same response factors for substrates and hydrogenated products.

4.5. Investigation of the transformation of the catalytic precursor

$[Ru(CO)_2(CH_3COO)_2(5,6\text{-dmphen})]$ (50 mg, 0.1034 mmol) and Na_2CO_3 (100 mg, 0.95 mmol) were placed in a 25 ml glass vial and THF-d_8 added to ensure complete dissolution of the ruthenium complex. The vial was placed under dinitrogen in a high pressure vessel and dihydrogen (100 atm; 20°C) was introduced. The autoclave was heated and stirred at 100°C for 6 h. The reactor was cooled to room temperature, the gas vented and the solution transferred under dihydrogen to an NMR tube sample.

The ^1H NMR spectrum showed resonances due to residual dihydrogen in the solvent, resonances due to the nitrogen ligand and a resonance at −25 ppm, indicative of hydride bridging metal atoms.

Acknowledgements

This work was supported partially by a grant from Consiglio Nazionale delle Ricerche, Progetto Finalizzato Chimica Fine and Secondaria II and by the MURST. Ministero dell'Universitá e della Ricerca Scientifica e Tecnologica.

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