

# Hydrogenation and hydroformylation of olefins with water-soluble $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$ catalyst

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## Abstract

Water-soluble and air-stable triruthenium carbonyl cluster  $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$  (TPPMS = sodium diphenylphosphinobenzene-*m*-sulphonate) was used as catalyst precursor to hydrogenated acrylic acid in good yield. The cluster also catalyzed the hydroformylation of propylene with syngas in water, the main product is *n*-butyraldehyde; side-products are *iso*-butyraldehyde and a small amount of 1-butyl and isobutyl alcohols. At 120°C and propylene, CO and  $\text{H}_2$  partial pressures of 0.7 MPa, 2.0 MPa and 2.0 MPa, respectively, catalytic turnover of 61.2 mol products/mol cluster h and product *n*:*i* ratio of 15.9 were obtained. For ethylene hydroformylation, the main product is propanal; side-products are 3-pentanone, 1-propanol and 2-methyl-pent-2-en-1-al. The catalyst was characterized before and after the reaction by IR and X-ray photoelectron spectroscopy and the results were discussed as related to the possible catalytic active species. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydrogenation; Hydroformylation; Propylene; Ethylene; Water-soluble cluster catalyst

## 1. Introduction

Ruthenium carbonyl cluster complexes,  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ ,  $[\text{PPN}][\text{HRu}_3(\text{CO})_{11}]^-$  and  $[\text{PPN}][\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$  have been reported to catalyse a variety of CO transformation, including syngas conversion [1], the water gas shift reaction [2] and also alkene hydroformylation [3,4]. The latter reaction has been thought to involve the anion  $[\text{HRu}_3(\text{CO})_{11}]^-$ , rather than

$[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ , which has been observed in some water gas shift systems [5].

In our previous work, FTIR spectra in the C–O stretching region indicated anionic  $[\text{HRu}_3(\text{CO})_{11}]^-$  as the catalytic active component on a ruthenium carbonyl hydroformylation system and a possible cycle mechanism of catalysis by triruthenium cluster has been proposed [6,7].

However, ruthenium anions  $[\text{HRu}_3(\text{CO})_{11}]^-$  and  $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$  are air-sensitive and unstable in water. Thereby, we have been interested in the catalytic properties of water-soluble and air-stable ruthenium cluster  $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$  [8]. In this paper, we would like to report

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the use of  $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$  as a water-soluble catalyst precursor for the hydrogenation of several functional olefins and the hydroformylation of propylene and ethylene.

## 2. Experimental

The water-soluble ligand TPPMS and cluster  $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$  was prepared according to literature methods [8,9]. IR spectra were recorded on a PE-Spectroy 2000 spectrophotometer. XPS spectra were measured on VG Escalab MKII photoelectron spectrometer. All catalytic experiments were carried out in a 160-ml stainless steel autoclave with a glass liner. After introduction of the catalyst components, the autoclave was flushed with  $\text{H}_2$  to remove oxygen, and then pressurized to the desired pressure and  $\text{CO}/\text{H}_2$  ratio. The autoclave was heated to the required temperature and the solution was stirred vigorously during the reaction. At the end of the experiment, the autoclave was cooled, depressurized and organic products were analyzed by conventional GC techniques.

## 3. Results and discussion

### 3.1. Selective hydrogenation of functional olefins by $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$

Some olefins with various functional groups have been reduced by using water-soluble

$\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$ . These are listed in Table 1 which indicates that acrylic acid and phenylethylene have been hydrogenated in good to excellent yields, while 2-methylacrylic acid having an methyl substituent group, only lower rate is observed. Acetophenone was rather difficult to be reduced even at  $100^\circ\text{C}$  and hydrogen pressure of 5.0 MPa.

### 3.2. Hydroformylation of propylene with $\text{CO}/\text{H}_2$ in water catalyzed by $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$

In the attempt of searching for non-rhodium and water-soluble transition metal complexes as catalysts, several catalytic systems were investigated (Table 2). The  $\text{Fe}(\text{CO})_5/\text{TPPMS}$  system showed only negligible activity. When  $\text{Co}_2(\text{CO})_8/\text{TPPMS}$  or  $\text{Ru}_3(\text{CO})_{12}/\text{TPPMS}$  were used, the activity improved slightly but still low. When  $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$  was employed as catalyst at  $120^\circ\text{C}$  and a total gas pressure of 4.7 MPa, high activity (turnover =  $61.2 \text{ h}^{-1}$ ) was observed. Such turnover value is a magnitude higher than the value when  $[\text{Et}_4\text{N}][\text{HRu}_3(\text{CO})_{11}]$  was used as catalyst. The main product was *n*-butyraldehyde; side products were *iso*-butyraldehyde and a small amount of 1-butyl and isobutyl alcohols due to further hydrogenation of the corresponding butanals.

The effect of catalyst concentration variation is shown in Fig. 1. The increase of reaction temperature and partial pressure of the gaseous reagents enhanced the catalytic activity. The effect of temperature was remarkable; a change

Table 1  
Hydrogenation of various functional olefins with  $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3^a$

Substrate	Product	Temperature ( $^\circ\text{C}$ )	Hydrogen pressure (MPa)	Yield (%)	Turnover ( $\text{h}^{-1}$ )
Acrylic acid	Propionic acid	40	3.0	93.6	780
2-Methylacrylic acid	Isobutyric acid	40	3.0	26.4	220
Phenylethylene	Phenylethane	40	3.0	85.4	712
Acetophenone	1-Phenylethanol	100	5.0	7.1	59
Benzaldehyde	Benzylalcohol	100	5.0	38.2	318
2-Hydroxybenzaldehyde	2-Hydroxybenzyl alcohol	100	5.0	45.7	381
Cyclohexanone	Cyclohexanol	100	5.0	28.1	234

<sup>a</sup> $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$ , 0.012 mmol.

Substrate:catalyst = 2500:1 (molar ratio).

MeOH, 35 ml; 3 h.

Table 2  
Hydroformylation of propylene with CO/H<sub>2</sub> catalyzed by Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub><sup>a</sup>

Catalyst	Solvent	Temperature (°C)	Composition of products (%) <sup>b</sup>				Turnover <sup>c</sup>	<i>n</i> : <i>i</i> <sup>d</sup>
			A	B	C	D		
Fe(CO) <sub>5</sub> /(TPPMS)	0.05 M NaOH/H <sub>2</sub> O	80	3.2	45.4	51.4	–	< 1.0	0.8
Co <sub>2</sub> (CO) <sub>8</sub> /(TPPMS)	0.05 M Na <sub>3</sub> PO <sub>4</sub> /H <sub>2</sub> O	100	8.2	75.4	14.9	1.5	24.0	3.3
Ru <sub>3</sub> (CO) <sub>12</sub> /(TPPMS)	H <sub>2</sub> O	100	5.5	57.2	35.2	2.1	17.6	1.5
Ru <sub>3</sub> (CO) <sub>9</sub> (TPPMS) <sub>3</sub>	H <sub>2</sub> O	80	5.5	73.5	19.5	1.5	34.4	3.0
Ru <sub>3</sub> (CO) <sub>9</sub> (TPPMS) <sub>3</sub>	H <sub>2</sub> O	100	2.4	88.1	4.9	4.6	148.8	12.7
Ru <sub>3</sub> (CO) <sub>9</sub> (TPPMS) <sub>3</sub>	H <sub>2</sub> O	120	3.0	89.5	2.9	4.6	489.6	15.9
Ru <sub>3</sub> (CO) <sub>9</sub> (TPPMS) <sub>3</sub>	0.1 M HOAc/0.1 M NaOAc	100	8.6	85.2	5.4	0.8	82.4	6.1
Ru <sub>3</sub> (CO) <sub>9</sub> (TPPMS) <sub>3</sub>	0.05 M Na <sub>3</sub> PO <sub>4</sub> /H <sub>2</sub> O	100	6.8	76.9	15.2	1.1	32.8	3.5

<sup>a</sup>Catalyst, 0.05 mmol; solvent, 25 ml; PC<sub>3</sub>H<sub>6</sub>/PCO/PH<sub>2</sub> = 0.7/2.0/2.0 (MPa); 8 h.

<sup>b</sup>A = isobutyraldehyde, B = 1-butanal, C = isobutyl alcohol, D = 1-butanol.

<sup>c</sup>Turnover = overall products mol/cluster mol.

<sup>d</sup>*n*/*i* = B + D/A + C (molar ratios).

of temperature from 100°C to 120°C would double the turnover value (Fig. 2). In the cases of high activity, high *n*:*i* molar ratios were also observed. Increase of reaction temperature seems to favour the formation of *n*-butyraldehyde. At 120°C, the highest *n*:*i* ratio of 15.9 was obtained.

The pH value of the reaction solution also affects the activity. In our earlier work in which Ru<sub>3</sub>(CO)<sub>12</sub> was used as catalyst to hydroformylate ethylene, basic media were needed to form the catalytic active anion [HRu<sub>3</sub>(CO)<sub>11</sub>]<sup>−</sup> [1,2]. In the present studies, neutral water was found to be the most suitable for propylene hydroformylation.

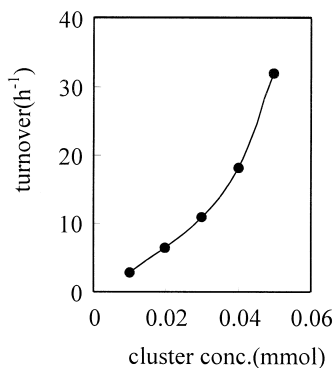


Fig. 1. Dependence of reaction rate upon the concentration of Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub>. Reaction conditions: H<sub>2</sub>O, 25 ml; 100°C; partial pressure: 0.7 MPa propylene/2.0 MPa CO/2.0 MPa H<sub>2</sub>.

### 3.3. Hydroformylation of ethylene with CO/H<sub>2</sub> in water catalyzed by Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub>

The results for the hydroformylation of ethylene with CO/H<sub>2</sub> are shown in Table 3. With Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub> alone, the main product is propanal, side-products are 3-pentanone, 1-propanal and 2-methyl-pent-2-en-1-al. Interestingly, the addition of halide or alkali metal cation promoters increased the catalytic activity and led to the formation of 3-pentanone. In the case of KBr as promoter, the highest yield (52.7%) of 3-pentanone was obtained. The or-

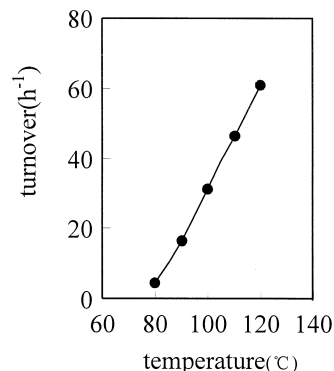


Fig. 2. Dependence of reaction rate on temperature. Reaction conditions: Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub>, 0.05 mmol; H<sub>2</sub>O, 25 ml; others are the same as shown in Fig. 1.

Table 3

Hydroformylation of ethylene with CO/H<sub>2</sub> in water catalyzed by Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub><sup>a</sup>

Halide-additive	Ru <sub>3</sub> (CO) <sub>9</sub> (TPPMS) <sub>3</sub> / halide (molar ratios)	Composition of products (%) <sup>b</sup>				Turnover <sup>c</sup>
		A	B	C	D	
–	–	55.3	37.0	6.2	1.5	113.4
NaI	1:3	55.1	36.0	6.9	2.0	121.5
LiBr · H <sub>2</sub> O	1:3	44.5	44.6	8.4	2.5	137.6
CsCl	1:3	44.8	41.8	11.7	1.7	214.6
KBr	1:3	40.3	44.6	13.8	13.3	255.4
KBr	1:9	48.0	40.8	6.4	4.8	180.8
KBr	1:15	39.9	52.7	5.7	1.7	138.9
Bu <sub>4</sub> NI	1:3	58.7	29.7	3.9	7.7	64.3
Bu <sub>4</sub> NBr	1:3	72.0	15.7	4.3	8.0	61.2
I <sub>2</sub>	1:1	55.5	35.7	4.4	4.4	89.9

<sup>a</sup>Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub>, 0.05 mmol; solvent, H<sub>2</sub>O, 30 ml; PC<sub>2</sub>H<sub>4</sub>/PCO/PH<sub>2</sub> = 3.5/0.75/0.75 (MPa); 100 °C, 2.5 h.<sup>b</sup>A = Propanal, B = 3-Pentanone, C = 1-Propanol, D = 2-Methyl-pent-2-en-1-al.<sup>c</sup>Turnover = products mol/cluster mol.

ganic halide promotes have little effect on the formation of 3-pentanone.

however the addition of I<sub>2</sub> led to the selective formation of 3-pentanone.

### 3.4. Carbonylation of ethylene with CO/H<sub>2</sub> in methanol catalyzed by Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub>

Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub>-halide systems have also been used to catalyzed the carbonylation of ethylene with CO in methanol. The results are giving in Table 4. With Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub> alone, the catalytic activity is very low. The addition of alkali metal halide such as NaI, remarkably enhanced the activity and led to produce a main product of methyl propionate,

### 3.5. Study on catalytic active species

Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub> is violet-red in colour. The colour changed to yellow after the reaction. Such colour change could also be observed if the violet-red solution was treated with CO(2.0 MPa) and H<sub>2</sub> (2.0 MPa) mixture at 100°C for 8 h. After the organic products were removed by distillation, the yellow solution still exhibited good catalytic activity and could be used repeatedly. Similar to Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub>, this yel-

Table 4

Effect of alkali metal halide promoters on carbonylation of ethylene with CO<sup>a</sup>

Additive	Temperature (°C)	Composition of products (%)		Turnover (h <sup>-1</sup> )
		Methyl propionate	3-Pentanone	
–	150	73.5	26.5	5
–	190	90.8	9.2	17
LiBr	150	89.1	10.9	36
NaI	150	99.0	1.0	50
NaI	190	94.7	5.3	315
I <sub>2</sub>	150	40.6	59.4	58
Bu <sub>4</sub> NI	150	98.9	1.1	28

<sup>a</sup>Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub>, 0.05 mmol; PC<sub>2</sub>H<sub>4</sub>/PCO = 2.0:4.0(MPa); CH<sub>3</sub>OH, 30 ml; 5 h.

low complex was soluble in water and methanol but insoluble in dichloromethane and diethyl ether. It is still stable in air as judged by IR spectroscopy (Figs. 3 and 4) and its catalytic performance after exposed to air for several days.

A yellowish-brown solid was obtained by drying the yellow solution. The solid was examined by X-ray photoelectron spectroscopy (Table 5). Comparing with the results of  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$  complexes, the  $\text{Ru } 3d_{5/2}$  peak appeared at around 281.0 eV in binding energy in all the three cases; that is roughly 1 eV higher than that of metallic ruthenium. For  $\text{Ru}_3(\text{CO})_{12}$ , the C 1s and O 1s peaks were at 286.8 eV and 533.3 eV respectively, corresponding to the presence of carbonyl groups.

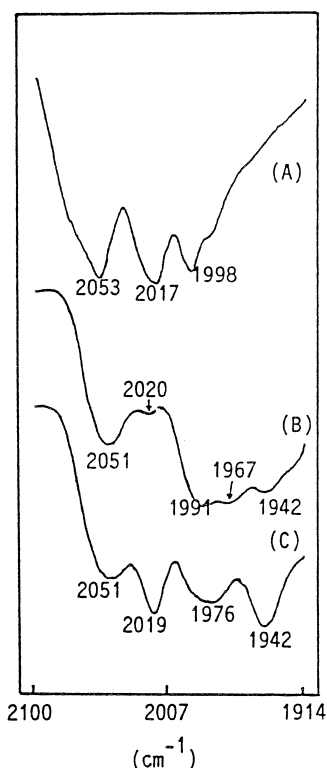


Fig. 3. IR ( $\nu_{\text{CO}}$ ) of sample in KBr disk. (A)  $\text{Ru}_3(\text{CO})_{12}$ ; (B)  $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$  (before reaction); (C)  $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$  (after reaction).

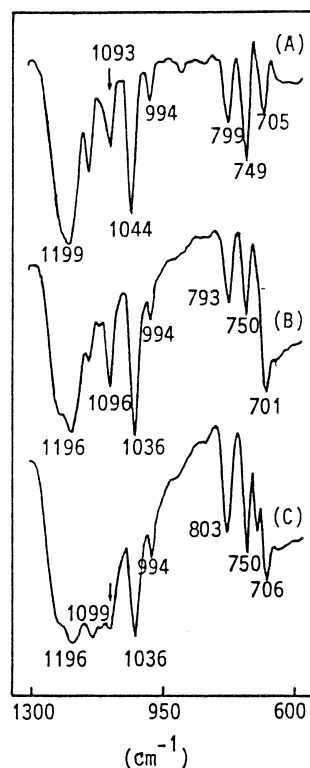


Fig. 4. IR ( $\nu_{\text{SO}}$ ) of sample in KBr disk. (A) free ligand TPPMS; (B) same as Fig. 3(B); (C) same as Fig. 3(C).

When  $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$  was formed, the  $\text{Ru } 3d_{5/2}$  peak was greatly attenuated and the C 1s and O 1s peak shifted to 284.0 eV and 531.0 eV respectively, indicating the ligand TPPMS is very much on the surface with the ruthenium atoms and CO ligands buried underneath. The S 2p, P 2p and Na 1s peak positions were at 167.4 eV, 130.7 eV and 1071.5 eV respectively before and after the reaction, an implication that the ruthenium cluster remained essentially intact through out the reaction. IR studies led to similar conclusion (Figs. 3 and 4). By direct comparisons, one can see that both  $\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3$  and the yellow complex are very similar in IR pattern, especially in the IR band position within the  $\nu_{\text{CO}}$  and  $\nu_{\text{SO}}$  regions. The result clearly indicate the presence of the soluble ligand TPPMS in the yellow complex and the possible analogous structure be-

Table 5  
X-ray photoelectron spectroscopic studies of the complexes

Complexes	Peak positions: in binding energy (eV) <sup>a</sup>						In kinetic energy (eV) NaKL <sub>23</sub> L <sub>23</sub>
	Ru 3d <sub>5/2</sub>	C 1s	O 1s	S 2p	P 2p	Na 1s	
Ru <sub>3</sub> (CO) <sub>12</sub>	281.0	285.8	533.3	–	–	–	–
Ru <sub>3</sub> (CO) <sub>9</sub> (TPPMS) <sub>3</sub>	280.6	284.0	531.0	167.4	130.7	1071.5	990.3
yellow complex	280.7	284.0	531.0	167.4	131.1	1071.6	990.2

<sup>a</sup>Calibrated against the Au4f levels (833.8 eV, 87.45 eV).

tween the two compounds. Whether this yellow ruthenium carbonyl complex represents the actual active species is under further investigation.

#### 4. Conclusion

Water-soluble and air-stable cluster Ru<sub>3</sub>-(CO)<sub>9</sub>(TPPMS)<sub>3</sub> was used as effective catalyst for hydrogenation of acrylic acid and phenylethylene. For hydroformylation of propylene, catalytic turnover of 61.2 h<sup>-1</sup> and product *n*:*i* ratio of 15.9 were obtained and neutral water was the most suitable for the reaction. Ru<sub>3</sub>(CO)<sub>9</sub>(TPPMS)<sub>3</sub> have also been used to catalyze the hydroformylation and carbonylation of ethylene. The addition of halide promoters enhanced the catalytic activity and led to the selective formation of 3-pentanone. According to the results from IR and XPS studies of catalyst before and after reaction, the triruthenium cluster remained essentially intact through out the reaction and represented the possible active species.

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#### References

- [1] B.D. Dombek, J. Am. Chem. Soc. 103 (1981) 6508.
- [2] P.C. Ford, R.G. Rindker, C. Ungermaun, R.M. Laine, V. Landis, S.A. Moya, J. Am. Chem. Soc. 100 (1978) 4595.
- [3] G. Süß-Fink, J. Organomet. Chem. 193 (1980) C20.
- [4] G. Süß-Fink, J. Reiner, J. Mol. Catal. 16 (1982) 231.
- [5] J.C. Bricker, C.C. Nagel, S.G. Shore, J. Am. Chem. Soc. 104 (1982) 1444.
- [6] J.X. Gao, J. Evans, J. Catal. (Chinese) 8 (1987) 384.
- [7] J. Evans, J.X. Gao, H. Leach, A.C. Street, J. Organomet. Chem. 372 (1989) 61.
- [8] B. Fontal, J. Orlewski, C.C. Santini, J.M. Basset, Inorg. Chem. 25 (1986) 4320.
- [9] S. Ahrland, J. Chatt, N.R. Davies, A.A. William, J. Chem. Soc. (1958) 276.