

# Synthesis of acetic acid from methanol alone by homogeneous metal complex catalyst. Part II<sup>1</sup>. Mechanistic study on methyl acetate formation from methanol alone by $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{RuX}]$ ( $\text{X} = \text{Cl}, \text{SnF}_3$ ) complex catalyst

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## Abstract

Catalytic activity of  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{RuX}]$  ( $\text{X} = \text{Cl}$  (**1**),  $\text{SnF}_3$  (**2**)) was investigated for the highly selective formation of methyl acetate with methanol used as the sole source. Complex **2** was found to be more catalytically active than the single-metallic complex **1**. For both complexes, the initial reaction rate was first order with respect to the catalyst concentration, and a saturation curve was obtained for dependence on the reactant concentration. Extra addition of  $\text{Cl}^-$  ion considerably slowed the reaction with **1** taken as catalyst, and an almost linear relationship was obtained between the reciprocal of initial rate and the concentration of added  $\text{Cl}^-$  ion. This fact indicates the presence of pre-equilibrium to form catalyst–reactant complex through the substitution of  $\text{Cl}^-$  ligand. In the case of **2**, extra addition of  $\text{PPh}_3$  gave a similar effect on the rate, allowing the same type of kinetic analysis. The role of  $\text{Sn(II)}$  ligand is considered in line with the mechanism that satisfies the rate equations derived from these kinetic results.

*Keywords:* Acetic acid; Methanol; Methyl acetate; Ruthenium complex

## 1. Introduction

We have recently shown [1–3] that acetic acid (and/or methyl acetate) can be formed in a one-stage reaction with methanol used as the sole source, when  $\text{Ru(II)}$  complex containing the  $\text{Sn(II)}$  ligand [4] is used as catalyst. Comparison of catalytic activities of a series of  $\text{Ru(II)}$  complexes containing zero, one and two  $\text{Sn(II)}$  ligands ( $[\text{RuCl}_2\{\text{P(OMe)}_3\}_4]$ ,  $[\text{RuCl(SnCl}_3)\{\text{P(OMe)}_3\}_4]$ ,  $[\text{Ru(SnCl}_3)_2\{\text{P(OMe)}_3\}_3]$ )

confirmed its importance in the reaction [3]. However, as reported preliminarily [5], when the cyclopentadienyl bis(triphenylphosphine) ruthenium(II) auxiliary is adopted, the reaction can also be catalyzed by a  $\text{Ru(II)}$  complex without the  $\text{Sn(II)}$  ligand ( $[\text{Cp(PPh}_3)_2\text{RuCl}]$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) (**1**)), although  $[\text{Cp(PPh}_3)_2\text{RuSnF}_3]$  (**2**) is much more active than **1**. This feature seemed to be derived from the unique character of this auxiliary (well-defined geometry and configurational stability) [6], and we present here detailed studies to elucidate the reactivity difference between **1** and **2**.

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<sup>1</sup> For Part I see: ref. [3].

## 2. Results and discussion

A representative time course is shown in Fig. 1 for the formation of methyl acetate with **1** and **2** used as catalyst. Turnover numbers are calculated from the formed amount (mol) of methyl acetate divided by the charged amount (mol) of catalyst. Acetic acid was detected as methyl acetate throughout the reaction due to esterification with methanol existing in excess as a reactant. Any other product such as formaldehyde, methylal or methyl formate was not detected in any of the cases. This feature is in contrast to the case of  $[\text{Ru}(\text{SnCl}_3)_2\{\text{P}(\text{OMe})_3\}_3]$  catalyst [3], with which selectivity to methyl formate is higher than that to methyl acetate in the temperature range of 100–140°C. Furthermore, the catalytic activity itself for methyl acetate formation is much higher for **2** than for  $[\text{Ru}(\text{SnCl}_3)_2\{\text{P}(\text{OMe})_3\}_3]$  (e.g., turnover frequency at 140°C:  $5.8 \text{ h}^{-1}$  and  $1.5 \text{ h}^{-1}$ , respectively).

It is obvious in Fig. 1 that the order of catalytic activity is  $2 > 1$ , and this order was not changed in the temperature range of 120–160°C as shown in the form of Arrhenius plots in Fig. 2. Good straight lines indicate that the same reaction mechanisms are operative in this temperature range, respectively. From their slopes values of 71.9 (**1**) and 40.4 (**2**)  $\text{kJ mol}^{-1}$  were obtained as an apparent activation energy, which are in harmony with the order of catalytic activity described above.

### 2.1. Dependence on the catalyst concentration

With **1** and **2** adopted as catalyst, the catalyst concentration was varied between 0.05–0.20 mM, while the reactant concentration was maintained at 12.5 M. The dependence of the initial rate on the concentration of catalyst is shown in Fig. 3. It is clearly seen from this figure that the rate shows first-order dependence with respect to the catalyst concentration in both cases.

### 2.2. Dependence on the reactant concentration

The reactant concentration was varied between 0.25–12.5 M at the constant catalyst concentration

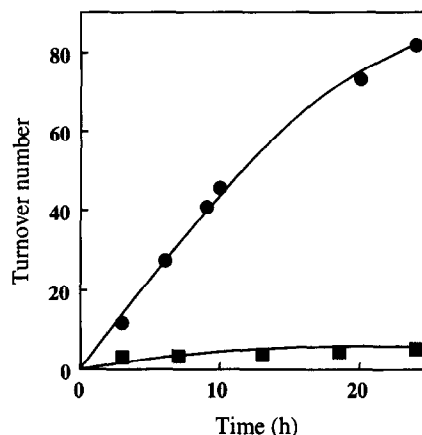


Fig. 1. Time course for the formation of methyl acetate from methanol with  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{RuX}]$  complex catalyst ( $X = \text{Cl}$  (■),  $\text{SnF}_3$  (●)) at 120°C and  $[\text{catalyst}] = 0.20 \text{ mM}$ .

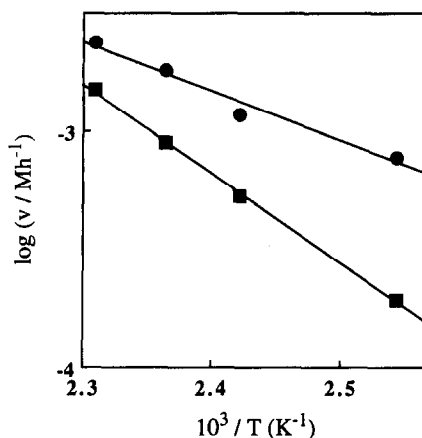


Fig. 2. Temperature dependence of the initial rate for the formation of methyl acetate from methanol with  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{RuX}]$  complex catalyst ( $X = \text{Cl}$  (■),  $\text{SnF}_3$  (●)) at  $[\text{catalyst}] = 0.20 \text{ mM}$ .

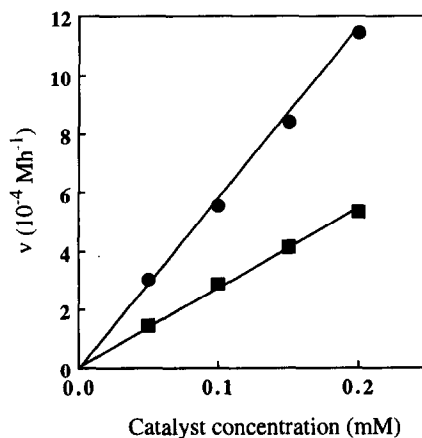


Fig. 3. Dependence of the initial rate on the concentration of catalyst with  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{RuX}]$  complex catalyst ( $X = \text{Cl}$  (■),  $\text{SnF}_3$  (●)) at 140°C.

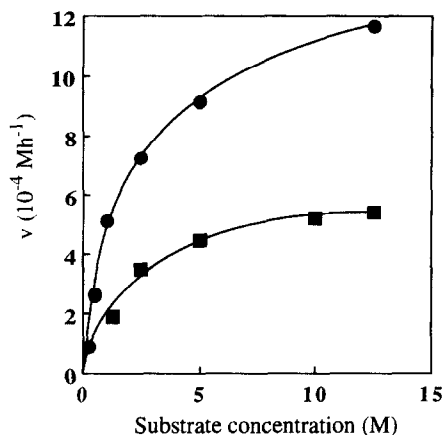


Fig. 4. Dependence of the initial rate on the concentration of reactant with  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{RuX}]$  complex catalyst ( $X = \text{Cl}$  (■),  $\text{SnF}_3$  (●)) at  $140^\circ\text{C}$ .

of 0.20 mM. In each case, the dependence of the initial rate on the concentration of reactant showed saturation in the high-concentration region (Fig. 4).

### 2.3. Rate equations

Dissociation of chloride ligand (solvolysis) of the  $[\text{Cp}(\text{L})_2\text{RuCl}]$  complexes ( $\text{L} =$  phosphorus ligands) is highly and preferentially promoted in polar solvents [6]. While most of the solvolysis reactions with DMSO (dimethyl sulfoxide) reach completion [7], partial solvolysis occurs in acetonitrile to give an equilibrium between starting material and the ionic product [8]. Methanol as donor solvent would more resemble acetonitrile than DMSO, and it is estimated that the solvolysis with acetonitrile reaches equilibrium within a few minutes at  $140^\circ\text{C}$  [8].

Since the solvolysis of chloride ligand with methanol should lead to the formation of catalyst-reactant complex in the overall reaction (as a pre-equilibrium process), the effect of adding free  $\text{Cl}^-$  ion on the initial reaction rate was investigated. It was found that the rate was progressively slowed down (Fig. 5a), and when the reciprocal of the initial rate was plotted as a function of the concentration of added  $\text{Cl}^-$  ion, linear dependence was obtained with a slight deviation in the region of low concentration (Fig. 5b).

It was found that the reaction with **2** used as catalyst was retarded by extra addition of  $\text{PPh}_3$  (Fig. 6a). Linear dependence was also observed between the reciprocal of the initial rate and the concentration of added  $\text{PPh}_3$  with a slight deviation in the region of low concentration (Fig. 6b). It is to be noted that when  $\text{SnF}_2$  or  $(\text{SnF}_2 + \text{NEt}_4\text{F})$  was added for the reaction with **2**, the reaction rate was not decreased but increased slightly (Table 1). This fact may allow us to exclude the dissociation of  $\text{SnF}_3^-$  ligand as a kinetically important step; it has been reported that while solvolysis of chloride ligand occurs easily for  $[\text{Cp}(\text{L})_2\text{RuCl}]$  ( $\text{L} = \text{PPh}_2\text{OMe}$  or  $(\text{L})_2 = 1,2\text{-bis}(\text{diphenylphosphinoethane})$ ) in acetonitrile, the corresponding reaction does not occur for  $[\text{Cp}(\text{L})_2\text{RuSnCl}_3]$

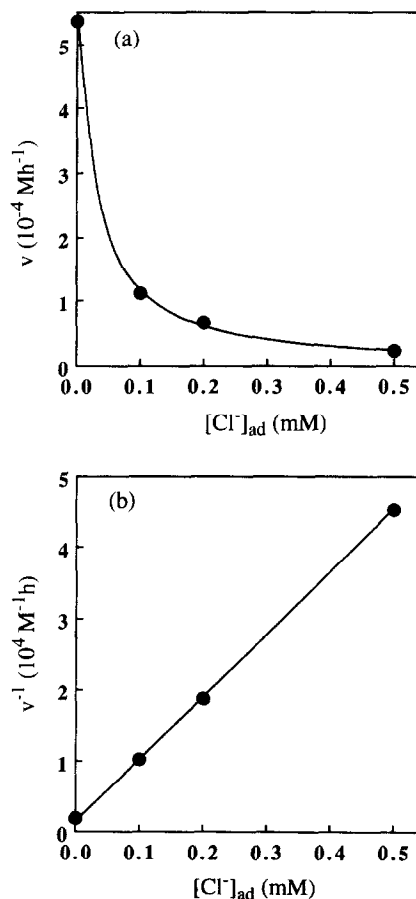


Fig. 5. Effect of the addition of free  $\text{Cl}^-$  (as  $(\text{Et}_4\text{N})\text{Cl}$ ) on the initial rate of the formation of methyl acetate from methanol with  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{RuCl}]$  complex catalyst at  $140^\circ\text{C}$  and  $[\text{catalyst}] = 0.20 \text{ mM}$ .

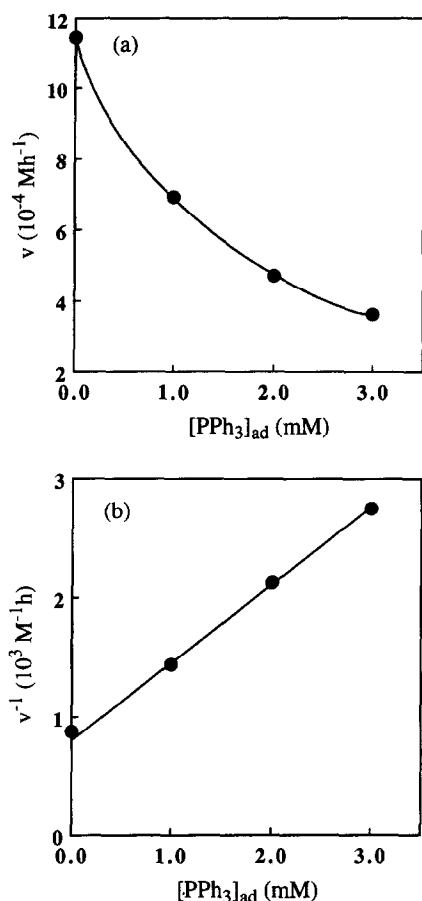


Fig. 6. Effect of the addition of free  $\text{PPh}_3$  on the initial rate of the formation of methyl acetate from methanol with  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{RuSnF}_3]$  complex catalyst at  $140^\circ\text{C}$  and  $[\text{catalyst}] = 0.20 \text{ mM}$ .

[8]. The observed positive effect may be due to the Lewis acidity of the addendum (see below).

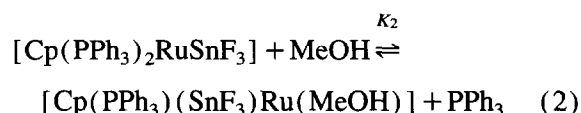
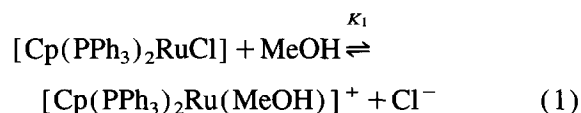
Rate retardation by the extra addition of free ligand (Figs. 5 and 6) indicates the presence of pre-equilibrium ligand dissociation (Eqs. (1) and

Table 1  
Effect of additives on methyl acetate formation with  $[\text{CpRu}(\text{PPh}_3)_2\text{SnF}_3]$  complex catalyst<sup>a</sup>

Additive (mM)		Initial turnover rate ( $\text{h}^{-1}$ )
$\text{SnF}_2$	$\text{NEt}_4\text{F}$	
0	0	5.8
0.5	0	6.5
1.0	3.0	9.0

<sup>a</sup> Reaction temperature  $140^\circ\text{C}$ , catalyst concentration  $0.20 \text{ mM}$ ,  $\text{MeOH}/\text{solvent (MeCN)} = 1/1$  ( $v/v$ ).

(2)) to form the catalyst–reactant complex (C–R). The comparatively high stability of the ionized (solvated) state (Eqn. (1)) [6] may be a reason for some catalytic activity of 1. Although the first step of the reaction is thus commonly considered to be the pre-equilibrium coordination of methanol, the nature of the residual ligands may cause a considerable reactivity difference between 1 and 2.



If C–R's in Eqs. (1) and (2) give the product with first-order rate constant  $k_1$  and  $k_2$ , respectively, each rate can be expressed as follows, where  $[\text{Ru}]_0$  is the concentration of the catalyst as charged (total ruthenium concentration), and  $[\text{R}]$  is the concentration of the reactant methanol.

$$R_1 = \frac{k_1 K_1 [\text{Ru}]_0 [\text{R}]}{K_1 [\text{R}] + [\text{Cl}^-]} \quad (3)$$

$$R_2 = \frac{k_2 K_2 [\text{Ru}]_0 [\text{R}]}{K_2 [\text{R}] + [\text{PPh}_3]} \quad (4)$$

The observed linear correlation between  $R$  and  $[\text{Ru}]_0$  (Fig. 3), and the saturation curve for the  $R$  vs.  $[\text{R}]$  plot (Fig. 4) are both consistent with these equations.

Eqs. (3) and (4) can be rearranged to give Eqs. (5) and (6).

$$\frac{1}{R_1} = \frac{1}{k_1 [\text{Ru}]_0} + \frac{[\text{Cl}^-]}{k_1 K_1 [\text{Ru}]_0 [\text{R}]} \quad (5)$$

$$\frac{1}{R_2} = \frac{1}{k_2 [\text{Ru}]_0} + \frac{[\text{PPh}_3]}{k_2 K_2 [\text{Ru}]_0 [\text{R}]} \quad (6)$$

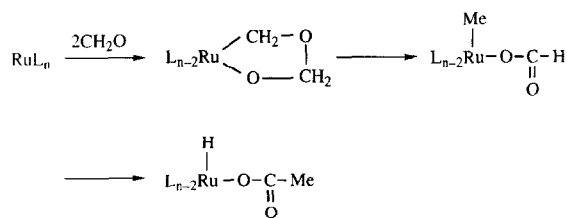
These equations account for the observed linear relationships between  $1/R_1$  and  $[\text{Cl}^-]_{\text{added}}$  (Fig. 5b) and between  $1/R_2$  and  $[\text{PPh}_3]_{\text{added}}$  (Fig. 6b) in the high-concentration region. The upward deviations in the low-concentration region would be due to the inherent contribution of the ligand

dissociation to the total concentration of free ligand, which should become appreciable in this region. The values of  $k_1$  and  $k_2$  obtained from the two intercepts are  $3.6 \text{ h}^{-1}$  and  $6.3 \text{ h}^{-1}$ , respectively. By coupled use of intercepts and slopes,  $K_1$  and  $K_2$  are calculated as  $1.3 \times 10^{-6}$  and  $9.9 \times 10^{-5}$ , respectively. These values clearly indicate that **2** is advantageous over **1** from the viewpoint of both coordination equilibrium of methanol ( $K$ ) and the net reaction ( $k$ ) after equilibrium.

#### 2.4. Mechanistic considerations

The selectivity of the conversion of methanol by use of the present catalysts is quite high, producing methyl acetate exclusively. It is reasonable to consider that the first step of the net reaction is the dehydrogenation of methanol to form formaldehyde [1,9,10]. Since either formaldehyde or its dimerization product (methyl formate) through the Tischenko-type reaction [11] was not detected during the reaction, two situations may be possible. (i) Dehydrogenation of methanol to form formaldehyde is rate-determining, which is consistent with the rate equations. (ii) Formaldehyde exists in a very low but almost steady concentration during the reaction, and thus the rate is first order with respect to both  $[\text{HCHO}]$  and  $[\text{Ru}]_0$  (steady state approximation for  $[\text{HCHO}]$ ). Discrimination between these two situations is, however, somewhat difficult because the rate of dehydrogenation of methanol should be also very slow in the situation (ii).

It is notable that no reaction occurred when methyl formate was reacted with either **1** or **2** taken as catalyst ( $[\text{cat.}] = 0.20 \text{ mM}$ , methyl formate/acetonitrile = 1/1 (v/v),  $140^\circ\text{C}$ , 24 h). It was suggested [3] that the first-order kinetics for the formation of methyl acetate from methanol could be accounted for by the sequential processes of (i) formation of a methyl-formato complex via the metallacyclic intermediate, formed by head-to-tail dimerization of formaldehyde [12,13], (ii) conversion of the methyl-formato complex into a hydrido-acetato complex [14], and finally (iii)



Scheme 1.

reductive elimination of acetic acid from the hydrido-acetato complex (Scheme 1). The lack of reactivity of methyl formate with these catalysts supports the reaction scheme suggested above, because it does not require any formation of free methyl formate which can potentially be isomerized [15] to acetic acid.

Since Sn(II) retains Lewis acidity in the coordinated state [4], it can interact with the oxygen functional group of oxygenates coordinated to Ru(II). It is conceivable that such a kind of extra interaction between the Lewis acid and the Lewis base may facilitate the overall rearrangement of coordinated oxygenates to produce acetic acid. The effect of added  $\text{SnF}_2$  or  $(\text{SnF}_2 + \text{NEt}_4\text{F})$  on the reaction with **2** may suggest the possibility of similar interactions taking place in an intermolecular manner [16].

### 3. Experimental

All procedures were performed under an argon atmosphere using conventional Schlenk techniques. All reagents and solvents were of reagent grade. When used as a reactant, methanol was dried over  $\text{CaH}_2$  and Na, and distilled before use.  $[\text{Cp}(\text{PPh}_3)_2\text{RuCl}]$  was obtained according to the literature method [17].  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a JEOL JNM-FX60Q spectrometer (24.2 MHz) at  $25^\circ\text{C}$  for saturated  $\text{CH}_2\text{Cl}_2$  solution, using 85%  $\text{H}_3\text{PO}_4$  as a standard. Elemental analyses were carried out on a Yanaco MT-3 element analyzer.

#### 3.1. Synthesis of $[\text{Cp}(\text{PPh}_3)_2\text{RuSnF}_3]$

$[\text{Cp}(\text{PPh}_3)_2\text{RuCl}]$  (0.50 g, 0.69 mmol),  $\text{SnF}_2$  (0.26 g, 1.66 mmol) and  $\text{NH}_4\text{F}$  (1.26 g, 34.0

mmol) were dissolved in a mixed solvent of methanol (50 ml) and water (2 ml), and heated under reflux for 30 min. Upon cooling to room temperature, yellow crystals were precipitated, which were filtered, washed with water, methanol and then diethyl ether, and dried under vacuum (0.60 g, 90% yield). The product was purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{OH}$ .  $^{31}\text{P}$  NMR:  $\delta(\text{P}) = 46.4$  ppm,  $J(^{119}\text{Sn}-^{31}\text{P}) = 504$  Hz,  $J(^{117}\text{Sn}-^{31}\text{P}) = 481$  Hz. Analyses found: C 56.80, H 4.23; calcd for  $\text{C}_{41}\text{H}_{35}\text{P}_2\text{F}_3\text{SnRu}$ : C 56.84 and H 4.07%.

### 3.2. Catalytic reaction

The reaction solutions were prepared by dissolving 4.0  $\mu\text{mol}$  of the Ru(II) complex and the substrate in acetonitrile (methanol 10 ml + acetonitrile 10 ml, unless otherwise stated). The reactions were carried out with 1.0 ml of the degassed reaction solution in a Pyrex glass ampule (7.0 ml volume), which was sealed under vacuum with the solution frozen by liquid nitrogen. Products were identified with GC–MS (JEOL JMS-AX500, DB-1 column) and analyzed quantitatively by GC (PEG-6000 and TCEP columns). The initial rates were obtained from the initial linear slopes of the time vs. conversion curves (typically 0–3 h).

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