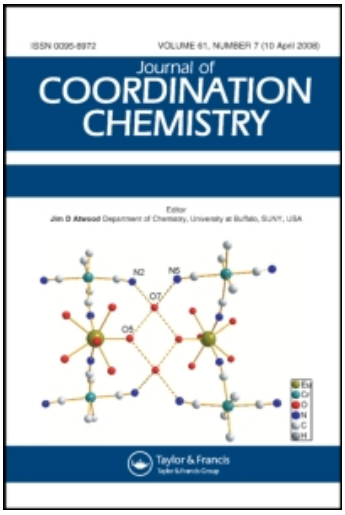

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CATALYSIS OF METHYL ACETATE FORMATION FROM METHANOL ALONE BY $(\eta^5\text{-}C_5H_5)(PPh_3)_2RuX$ (X = Cl, $SnCl_3$, SnF_3): HIGH ACTIVITY FOR THE SnF_3 COMPLEX

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INTRODUCTION

We have recently shown[1,2] that the Ru(II)-Sn(II) bimetallic complex can catalyze the unprecedented one-step formation of acetic acid (or methyl acetate) with methanol used as the sole source. It was suggested that the reaction consists of sequential processes of methanol → formaldehyde (methylal) → methyl formate → acetic acid (methyl acetate). While the Ru(II) complexes capable of catalyzing the dehydrogenation of methanol into methyl formate are known,[3–5] this catalyst system is unique because of its extra ability to isomerize methyl formate to acetic acid without a CO atmosphere (usually high pressure) or an iodide promoter (often corrosive to reaction apparatus).[6] In this communication, we examine the cyclopentadienyl bis(triphenylphosphine) ruthenium(II) auxilliary in view of its well-defined geometry and configurational stability,[7] and demonstrate that combination with the SnF_3^- ligand[8] gives quite high catalytic ability compared to the conventional[9] $SnCl_3^-$ ligand.

EXPERIMENTAL

All procedures were performed under an argon atmosphere using conventional Schlenk techniques. All reagents and solvents were of reagent grade. When used as

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Dedicated to Professor Theodore L. Brown in recognition of his outstanding contributions to coordination chemistry.

a reactant, methanol was dried over CaH_2 and Na, and distilled before use. $(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCl$ and $(\eta^5\text{-}C_5H_5)(PPh_3)_2RuSnCl_3$ were obtained according to the literature methods.[10,11] ^{31}P NMR spectra were recorded on a Jeol JNM-FX60Q spectrometer (24.2 MHz) at 25°C for saturated CH_2Cl_2 solutions, using 85% H_3PO_4 as a standard. Elemental analyses were carried out on a Yanaco MT-3 element analyzer.

Synthesis of $(\eta^5\text{-}C_5H_5)(PPh_3)_2RuSnF_3$

$(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCl$ (0.50 g, 0.69 mmol), SnF_2 (0.26 g, 1.66 mmol) and NH_4F (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 CH_2Cl_2-CH_3OH. ^{31}P NMR: $\delta(P)$ = 46.4 ppm, $J(^{119}Sn\text{-}^{31}P)$ = 504 Hz, $J(^{117}Sn\text{-}^{31}P)$ = 481 Hz. *Anal.* Calcd. for $C_{41}H_{35}P_2F_3SnRu$: C, 56.84; H, 4.07. Found: C, 56.80; H, 4.23.

Catalytic reaction

The reaction solutions were prepared by dissolving 4.0 μmol of Ru(II) complex and methanol (10 ml) in acetonitrile (10 ml). The reactions were carried out at 120 °C with 1.0 ml of the reaction solution in a Pyrex glass ampule (7.0 ml volume), which was sealed under vacuum. Products were identified with GC-MS (Jeol JMS-AX500, DB-1 column) and analyzed quantitatively by GC (PEG-6000 and TCEP columns).

RESULTS AND DISCUSSION

Figure 1 shows a representative plot of catalytic yield of methyl acetate as a function of time with three kinds of homogeneous catalysts, $(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCl$ (**1**), $(\eta^5\text{-}C_5H_5)(PPh_3)_2RuSnCl_3$(**2**) and $(\eta^5\text{-}C_5H_5)(PPh_3)_2RuSnF_3$(**3**). Turnover numbers are calculated from the formed amount (mole) of methyl acetate divided by the amount (mole) of catalyst. Acetic acid was detected as methyl acetate throughout the reaction due to esterification with methanol existing in excess as a reactant. No other product such as formaldehyde, methylal or methyl formate was detected in any case.

It is obvious in Fig. 1 that the catalyst containing SnF_3^- ligand (**3**) is most effective, and that the Ru(II) complex which lacks a Sn(II) ligand (**1**) has very little catalytic activity. While the catalyst containing $SnCl_3^-$ ligand (**2**) is relatively ineffective, quite high selectivity of the catalysts **2** and **3** toward methyl acetate formation seems to be noted.[2]

It was suggested[6] that methyl formate would be activated by the Ru(II)-Sn(II) bimetallic site through the four-center interaction of soft Ru(II) and hard Sn(II) with soft C=0 group and hard OCH_3 group of methyl formate, respectively. Since fluorine is more electronegative than chlorine, rearrangement of a CH_3 group from the oxygen atom to the carbon atom[12] to realize the isomerization to acetic acid may be facilitated by the SnF_3^- ligand. The strategy of activating oxygenates by

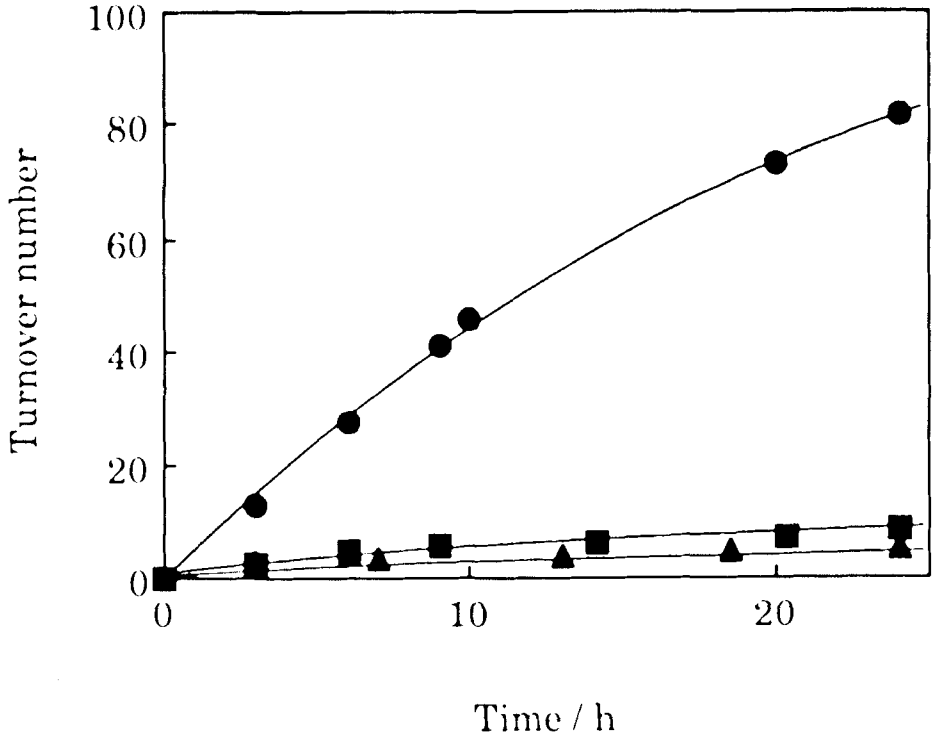

Figure 1 Time-course for the formation of methyl acetate from methanol with (η^5-C_5H_5)$(PPh_3)_2$RuX catalysts (X = Cl (▲), $SnCl_3$ (■), SnF_3 (●)) at 120°C and [catalyst] = 0.20 mM. The solvent used is acetonitrile (methanol/acetonitrile = 1/1 (v/v)).

means of binuclear center with transition and non-transition metals (such as Ru(II)-Sn(II)) may be useful to extend the applicability of catalysis.

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