Synthesis of methyl acetate from methanol catalyzed by [(η^5-C$_5$H$_5$)(phosphine)$_2$RuX] and [(η^5-C$_5$H$_5$)(phosphine)$_2$Ru(SnX$_3$)] (X=F, Cl, Br): ligand effect

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Abstract

Monometallic Ru and heterobimetallic complexes containing Ru–Sn bonds, [(η^5-C$_5$H$_5$) P$_2$RuX] and [(η^5-C$_5$H$_5$)P$_2$Ru-(SnX$_3$)], where P=PPh$_3$, PPh$_2$Me, P$_2$=1,2-bis(diphenilphosphine) ethane (dppe), and X=F, Cl, Br, were synthesized and characterized. These complexes were tested as catalysts in a single-step methanol conversion to acetic acid (methyl acetate) in the absence of CO. All complexes showed a high selectivity with their catalytic activity being strongly dependent on the nature of the ligands P and X. The effect of the ligand P showed the order of PPh$_3$>PPh$_2$Me≅dppe and the halogen effect: F>Cl≅Br and SnF$_3$>SnCl$_3$≅SnBr$_3$. Heterobimetallic complexes showed ca. doubled activities compared to their monometallic analogues, indicating the importance of the Ru–Sn bond in a catalytic active specie. The order of catalytic activities followed the increase in the positive charge on the ruthenium atom, which was confirmed by ^{31}P and ^{119}Sn NMR spectroscopy and X-ray diffraction techniques. The obtained data support the mechanistic view of acetic acid formation by dehydrogenation of methanol giving formaldehyde via the rate-determining β-hydrogen abstraction in the Ru(II)–OMe intermediate, followed by formaldehyde dimerization into acetic acid. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Acetic acid is a major industrial chemical used in the production of vinyl acetate, pharmaceuticals, cellulose acetate, pesticides, etc., and is made mainly by carbonylation of methanol using an iodide-promoted rhodium catalyst (the Monsanto process) [1,2]. It has been reported [3] that acetic acid (and/or methyl ac-etate due to rapid esterification) can be formed in a single step from methanol alone using heterobimetallic Ru(II)–Sn(II) complexes [Ru(SnCl$_3$)$_5$L]$^{3-}$ (L=PPh$_3$ or MeCN):

$$2CH_3OH \rightarrow CH_3COOH + 2H_2 \qquad (1)$$
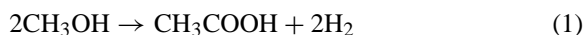
This unique reaction (1) represents a promising alternative route from methanol to acetic acid and has some advantages compared with the Monsanto process because it needs only methanol as a raw material (methanol vs. methanol+CO) and uses the less expen-

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sive metals (Ru+Sn vs. Rh) without a corrosive iodide promoter [4,5].

Comparison of the catalytic activity of a series of Ru(II) complexes [RuCl$_2$\{P(OMe)$_3$\}$_4$], [RuCl(SnCl$_3$) P(OMe)$_3$\}$_4$], and [Ru(SnCl$_3$)$_2$\{P(OMe)$_3$\}$_3$] containing zero, one and two SnCl$_3^-$ ligands revealed their vital importance for the formation of acetic acid from methanol: only the complex with two Ru–Sn bonds showed the activity in this reaction [4]. The RuCl$_3$–SnX$_2$ composite systems (X=F, Cl, Br, I) also catalyze the conversion of methanol into acetic acid, but the reaction does not occur in the absence of SnX$_2$ [6].

The mechanism of this reaction has been studied [4,6–8], but is not yet fully understood. The conversion of methanol was shown not to involve carbonylation because no incorporation of ^{13}C into methyl acetate was observed when the reaction with [Ru(SnCl$_3$)$_5$PPh$_3$]$^{3-}$ as a catalyst was performed under a ^{13}CO atmosphere [7].

The SnCl$_3^-$ ligand due to its high π-acceptor character removes electron density from the central metal atom which enhances its ability to interact with electron-rich organic substrates and prevents its reduction [9]. The strong *trans*-activation effect of the SnCl$_3^-$ group, which is also labile itself, plays an important role in the catalytic activity favoring the ligand-exchange reactions [9,10]. In addition, the SnCl$_3^-$ ligand maintains a Lewis acid character to coordinate to Lewis bases by exchanging with the Cl$^-$ ligand, which may allow an extra interaction with the oxygen functional groups of the substrates coordinated to the adjacent metal atom [5,9]. This unique character of the SnCl$_3^-$ ligand seems to contribute to the activity of the Ru–Sn systems in methanol conversion into acetic acid (methyl acetate) [5]. However, it has been recently reported [8,11] that the [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$RuCl] complex shows the catalytic activity in the formation of methyl acetate from methanol even without the Sn(II) ligand, although the heterobimetallic Ru–Sn complex [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$Ru(SnF$_3$)] is much more active. This behavior seems to be derived from the specific characteristics of the [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$Ru] moiety such as well-defined geometry and configuration stability [8,12].

The aim of the present work was a systematic study of the ligand effect on the catalytic activity in the methanol conversion into methyl acetate of a series of monometallic and heterobimetallic complexes containing the [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$Ru] fragment of general formulae CpP$_2$RuX and CpP$_2$Ru(SnX$_3$) where Cp=η^5-C$_5$H$_5$; P=PPh$_3$, PPh$_2$Me, P$_2$=1,2-bis(diphenylphosphino)ethane (dppe); and X=F, Cl, Br. Heterobimetallic complexes are useful building blocks for the catalyst preparation due to providing a new site where well-thought structural modifications can be made. Substitution of ligands around the ancillary metal allows a stepwise tuning of both the steric crowding and the electronic density around the catalytic center. The substitution of the a Ru–X bond by Ru–SnX$_3$ fragment should result not only in sensible changes in the steric environment around the ruthenium atom, but also in a large increase in the electronic deficiency around this atom, in spite of the increased distance between the ruthenium and halogen atoms.

2. Experimental

All chemicals were purchased from commercial sources and used as received, unless otherwise indicated. Solvents were purified, distilled from the appropriate drying agents and stored under dry N$_2$ over 3 Å molecular sieves. Cyclopentadiene dimer was distilled under dry N$_2$ prior to use. All manipulations were carried out under standard Schlenck or dry-bag techniques under a dry N$_2$ atmosphere.

All solid products were air-stable, but the solutions of the compounds containing the SnF$_3$ moiety bound to Ru slowly hydrolyzed in the presence of moisture to yield SnO$_2$ along with the other products.

Cp(PPh$_3$)$_2$RuCl, Cp(dppe)RuCl and Cp(PPh$_2$Me)$_2$ RuCl, which were the precursor compounds for the remaining syntheses, were prepared and purified according to published methods [13–15].

Cp(PPh$_3$)$_2$RuX compounds (X=F, Br) were prepared according to a slight modification of literature procedures [13,16] by the reaction between Cp(PPh$_3$)$_2$RuCl and an excess of NH$_4$X/KX in a refluxing ethanol/benzene mixture (4/1 v/v). Cp(PPh$_2$Me)$_2$RuX and Cp(dppe)RuX (X=F, Br) were synthesized by analogy with complexes Cp(PPh$_3$)$_2$RuX.

The reaction between the monometallic parent complexes, CpP$_2$RuX (P=PPh$_3$, PPh$_2$Me; P$_2$= dppe)

Table 1
Ru and Ru–Sn complexes used as catalysts for the methanol conversion: empirical formulae, color, melting point (m.p.) and IR data

Complex	Color	Empirical formula	m.p. (°C)	IV (cm^{-1}) (attribution)
1	yellow	$Cp(PPh_3)_2RuF$	117	430 (ν_{Ru-F}), broad
2	orange	$Cp(PPh_3)_2RuCl$	133–135	240 (ν_{Ru-Cl})
3	red-orange	$Cp(PPh_3)_2RuBr$	214	225 (ν_{Ru-Br})
4	light yellow	$Cp(PPh_3)_2Ru(SnF_3)$	199	490 (ν_{Sn-F}), broad
5	bright yellow	$Cp(PPh_3)_2Ru(SnCl_3)$	188	290, 272 (ν_{Sn-Cl})
6	red-orange	$Cp(PPh_3)_2Ru(SnBr_3)$	181	265, 260 (ν_{Sn-Br})
7	yellow	$Cp(PPh_2Me)_2Ru(SnF_3)$	166–168	495 (ν_{Sn-F})
8	red-orange	$Cp(PPh_2Me)_2Ru(SnCl_3)$	196–198	290, 268 (ν_{Sn-Cl})
9	orange	$Cp(PPh_2Me)_2Ru(SnBr_3)$	198–201	258, 270 (ν_{Sn-Br})
10	light yellow	$Cp(dppe)Ru(SnF_3)$	271	493 (ν_{Sn-F}), broad
11	bright yellow	$Cp(dppe)Ru(SnCl_3)$	255	291, 276 (ν_{Sn-Cl})
12	red-orange	$Cp(dppe)Ru(SnBr_3)$	257	256, 263 (ν_{Sn-Br})

with SnX_2 in polar solvents at mild temperatures yielded a homoleptic series of heterometallic complexes in virtually quantitative yield. $CpP_2Ru(SnF_3)$, $CpP_2Ru(SnCl_3)$, and $CpP_2Ru(SnBr_3)$ complexes were prepared by the reaction between CpP_2RuF, CpP_2RuCl, or CpP_2RuBr and SnF_2, $SnCl_2$, or $SnBr_2$, respectively. A typical procedure was as follows: $Cp(PPh_3)_2RuCl$ (0.371 g–5.1×10^{-4} mol) reacted with $SnCl_2$ (0.100 g–5.1×10^{-4} mol) in refluxing ethanol (100 ml) under a flow of dry N_2. After 5 h of reflux, the volume of the solution was reduced to ca. 30 ml under vacuum causing the precipitation of the product. The bulk product was separated by filtration and purified by dissolving in CH_2Cl_2 (4.0 ml) and inducing its precipitation by the addition of chilled *n*-hexane (20 ml). After filtration, the solid was dried in vacuum at 35°C for at least 1 h.

Complexes were characterized by infrared spectroscopy (CsI pellets, a Perkin-Elmer 283B spectrometer); elemental analysis (H, C, F, Cl, Br, Sn); multinuclear (^{1}H, ^{13}C, ^{19}F, ^{31}P and ^{119}Sn) NMR spectroscopy (a Brucker CXP-400 spectrometer). The structures of several complexes were determined by single-crystal X-ray diffraction techniques on a Siemens P4 Smart CCD or an automatic four-circle diffractometer Enraf-Nonius CAD4 using a graphite-monochromated Mo-K$_{\alpha 1}$ (λ=0.71073 Å) radiation and an area detector [17,18]. [1]

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[1] A complete report on the characterization of the complexes will be published elsewhere. The data on some Ru–Sn complexes were published in Refs. [17,18].

The catalytic reactions were carried out in a glass tube-type 5-ml reactor equipped with a 90° angle HI-VAC vacuum valve and manipulated under a dry N_2 atmosphere using a standard Schlenck technique. The solution (1.00 ml) of the catalyst (0.10–1.00×10^{-3} mol l^{-1}) in a methanol/acetonitrile mixture (1/1 v/v) was degassed, frozen by liquid nitrogen and the reactor closed under vacuum. The reactions were monitored by gas chromatography (GC) using a Shimadzu 14B instrument fitted with a Carbowax 20 M capillary column and a flame ionization detector. The product was identified by GC-mass spectroscopy on a Hewlett-Packard MSD 5890/Series II instrument operating at 70 eV.

3. Results and discussion

Reaction (1), which can be seen as a dehydrogenative coupling of methanol, was investigated in the presence of Ru(II) complexes of general formulae CpP_2RuX and $CpP_2Ru(SnX_3)$, where $Cp=\eta^5$-C_5H_5; $P=PPh_3$, PPh_2Me, P_2=dppe; and X=F, Cl, Br. Acetonitrile was employed as a solvent. In Tables 1 and 2, some characterization data for the complexes used as catalysts are summarized. The data of elemental analysis are in agreement with the empirical formula given. All IR spectra of the Sn-containing complexes display the absorption characteristics of Sn–X stretching, which are slightly shifted with respect to those observed for pure SnX_2. After the reaction of the precursors with SnX_2, the disappear-

Table 2
Summary of ^{31}P and ^{119}Sn NMR data and relevant bond lengths and angles for the heterobimetallic complexes Cp(phosphine)$_2$Ru(SnX$_3$)

Complex	Phosphine	SnX$_3$	^{31}P, δ	^{119}Sn, δ	Ru–Sn (Å)	Ru–P (Å)	Angles X–Sn–Ru (°)
4	PPh$_3$	SnF$_3$	48.01	−357.0	2.538	2.346	117.79
						2.331	121.59
							128.62
5	PPh$_3$	SnCl$_3$	45.44	−67.7	2.572	2.349	114.02
						2.348	122.69
							108.90
6	PPh$_3$	SnBr$_3$	45.77	−139.2	2.585	2.349	114.02
						2.348	126.72
							122.85
7	PPh$_2$Me	SnF$_3$	34.12	−339.1			
8	PPh$_2$Me	SnCl$_3$	30.41	−30.4			
9	PPh$_2$Me	SnBr$_3$	30.23	−115.7			
10	1/2dppe	SnF$_3$	79.70	−344.8			
11	1/2dppe	SnCl$_3$	77.80	−22.3			
12	1/2dppe	SnBr$_3$	77.00	−110.8			

ance of the absorptions due to $\nu_{Ru–Cl}$ at 240 cm^{-1}, $\nu_{Ru–Br}$ at 225cm^{-1}, and $\nu_{Ru–F}$ at 430 cm^{-1}, which were replaced by absorptions due to $\nu_{Sn–Cl}$ at ca. 290 and 270cm^{-1}, $\nu_{Sn–Br}$ at ca. 260 and 265 cm^{-1}, and $\nu_{Sn–F}$ at ca. 490 cm^{-1}, respectively, was observed for all pertinent cases (complexes **4–12**). The NMR and X-ray diffraction data confirmed the proposed structures [17,18]. The ^{31}P and ^{119}Sn NMR data and relevant bond lengths and angles for the heterobimetallic Ru–Sn complexes **4–12** are shown in Table 2.

All the complexes studied show the catalytic activity in reaction (1). The only product observed is acetic acid detected as methyl acetate due to rapid esterification with methanol. Neither formaldehyde, which is supposed to be the intermediate in methanol conversion to acetic acid [5], nor methyl formate (possible product of formaldehyde dimerization), is detected in all the cases. It should be mentioned

that we also observed no reaction between methyl formate and Cp(PPh$_3$)$_2$Ru(SnF$_3$). Thus, differently from the complexes [RuCl(SnCl$_3$){P(OMe)$_3$}$_4$] and [Ru(SnCl$_3$)$_2${P(OMe)$_3$}$_3$] [4], Cp(PPh$_3$)$_2$Ru(SnF$_3$) promotes no isomerization of methyl formate into acetic acid. The similar results were obtained earlier [8].

The nature of the phosphorous-containing ligand and the halogen as well as the presence of the Ru–Sn bond exerts a strong influence on the catalytic activity of complexes **1–12** (Tables 3–6). The representative kinetic curves are shown in Fig. 1. Turnover number (TON) is calculated as a ratio between the amounts (mol) of methyl acetate formed and the charged catalyst. After the short period (approximately 2 h) of the relatively fast reaction, the rate of the methyl acetate formation remains virtually unchanged for at least 30 h. The rates given in Tables 3–6 correspond to these

Table 3
Methanol conversion into methyl acetate catalyzed by Cp(PPh$_3$)$_2$RuX and Cp(PPh$_3$)$_2$Ru(SnX$_3$)
Reaction conditions: methanol/acetonitrile=1/1 (v/v), 140°C.

[Catalyst] (10^{-3} mol l^{-1})	Rate of methyl acetate formation (10^{-4} mol l^{-1} h^{-1})					
	X=F		X=Cl		X=Br	
	SnF$_3$	F	SnCl$_3$	Cl	SnBr$_3$	Br
1.00	6.7	3.5	4.4	1.8	4.4	1.8
0.50	3.6	3.2	2.5	1.8	2.0	1.6
0.25	2.3	1.0	1.2	0.8	1.2	0.8

Table 4
Methanol conversion into methyl acetate catalyzed by $CpP_2Ru(SnF_3)$
Reaction conditions: methanol/acetonitrile=1/1 (v/v), 140°C.

[Catalyst] $(10^{-3}$ mol $l^{-1})$	Rate of methyl acetate formation $(10^{-4}$ mol l^{-1} $h^{-1})$		
	P=PPh₃	P=PPh₂Me	P₂=dppe
1.00	6.7	2.2	2.4
0.50	3.6	1.6	2.3
0.25	2.3	1.5	2.0
0.10	1.7	0.8	1.3

Table 6
Methanol conversion into methyl acetate catalyzed by $CpP_2Ru(SnBr_3)$
Reaction conditions: methanol/acetonitrile=1/1 (v/v), 140°C.

[Catalyst] $(10^{-3}$ mol $l^{-1})$	Rate of methyl acetate formation $(10^{-4}$ mol l^{-1} $h^{-1})$		
	P=PPh₃	P=PPh₂Me	P₂=dppe
1.00	4.4	1.4	1.1
0.50	2.0	1.1	1.0
0.25	1.2	1.0	0.5
0.10	0.6	0.5	0.6

stationary reaction periods and are the averaged values for at least three runs.

As can be seen from Table 3, the reactions with the heterobimetallic Ru–Sn complexes are considerably faster (up to 250%) compared to those with their monometallic analogues (CpP_2RuX vs. $CpP_2Ru(SnX)_3$) indicating the importance of the Ru–Sn bond in a catalytic active specie. However, the monometallic complexes **1–3** also promote the conversion of methanol into methyl acetate, differently to what has been observed with $[RuCl_2\{P(OMe)_3\}_3]$ [4] and $RuCl_3$ [6], which were inactive in this reaction in the absence of the $SnCl_3^-$ ligand or SnX_2, respectively.

For both monometallic and heterobimetallic systems, the nature of the halogen is the crucial factor in determining of the reaction rate but not the reaction selectivity. The halogen effect shows the order of F>Cl≅Br for complexes **1–3** and SnF_3>$SnCl_3$≅$SnBr_3$ for complexes **4–12** (Tables 3–6, Fig. 1), which is completely consistent with the electronegativity order of halogens. There has been no observed significant difference in activities of the complexes containing

Table 5
Methanol conversion into methyl acetate catalyzed by $CpP_2Ru(SnCl_3)$
Reaction conditions: methanol/acetonitrile=1/1 (v/v), 140°C.

[Catalyst] $(10^{-3}$ mol $l^{-1})$	Rate of methyl acetate formation $(10^{-4}$ mol l^{-1} $h^{-1})$		
	P=PPh₃	P=PPh₂Me	P₂=dppe
1.00	4.4	1.4	1.2
0.50	2.5	1.1	1.0
0.25	1.2	0.7	0.6
0.10	0.6	0.5	0.6

chloro and bromo atoms (CpP_2RuCl vs. CpP_2RuBr and $CpP_2Ru(SnCl_3)$ vs. $CpP_2Ru(SnBr_3)$), while the complexes with fluor (CpP_2RuF and $CpP_2Ru(SnF_3)$) react approximately twice as fast as their chloro and bromo analogues.

The inductive effects of the SnX_3^- group on Ru in these complexes can be assessed through its influence on the other ligands. ^{31}P and ^{119}Sn NMR spectroscopies are useful to establish the magnitude of these effects. ^{31}P NMR results for the heterobimetallic complexes $CpP_2Ru(SnX_3)$ (Table 2) show that there is a direct correlation between the de-shielding of the Ru-ligated moieties and the electronegativity of the substituents in the SnX_3 fragment. As expected, the greater the electronegativity, the higher the magnitude of de-shielding. More remarkable though, are the ^{119}Sn NMR chemical shifts observed for these com-
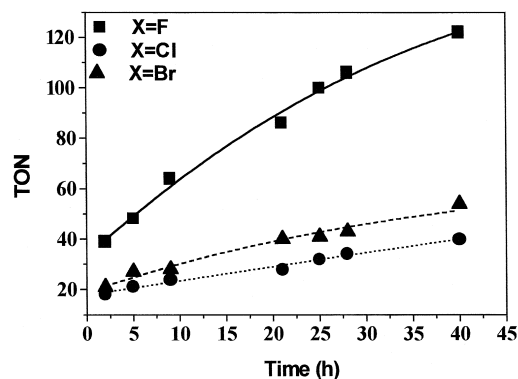

Fig. 1. Time course for the methyl acetate formation from methanol with $Cp(PPh_3)_2Ru(SnX_3)$ catalysts (■: X=F, ●: X=Cl, ▲: X=Br) at 140°C and [catalyst]=10^{-4} mol l^{-1}. TON is calculated as a ratio between the amounts (mol) of methyl acetate formed and the charged catalyst.

plexes (Table 2). While for $SnCl_3$ and $SnBr_3$ derivatives, the de-shielding of the Sn nucleus follows the increase in the electronegativity of the halogen atoms, SnF_3 derivatives show a very abnormal value for the ^{119}Sn resonance. In these cases, Sn is being considerably shielded, implying that at some extent, electronic density is being donated to it.

It seems reasonable to suggest that in the $CpP_2Ru(SnF_3)$ complexes π back-donation from Ru to Sn is accomplished in order to equilibrate the inductive effect of the three fluoride atoms, thus inducing a higher positive charge on Ru. In order to further investigate this phenomena, we solved the structures of complexes $Cp(PPh_3)_2Ru(SnF_3)$ (**4**), $Cp(PPh_3)_2Ru(SnCl_3)$ (**5**), and $Cp(PPh_3)_2Ru(SnBr_3)$ (**6**) [17,18]. The relevant bond lengths and angles are given in Table 2. These results show considerable shortening the Ru–Sn bond length in the order of **6**>**5**>**4**. Also noticeable is smaller, but significative shortening the Ru–P distances in the same order. These findings support the proposed hypothesis that $\pi_{Ru \rightarrow Sn}$ back-bonding takes place, thus providing a charge relief mechanism for Sn and generating an extra positive charge over Ru. In fact, for these derivatives, the "actual" oxidation state of Ru should be regarded as between +2 and +3 and the order of the Ru–Sn bond as between 1 and 2. Also of relevance are the X–Sn–Ru angles, which strongly indicate that fluorides are being pushed away from Ru, further than the other halides. This is also consistent with electronic donation from Ru to Sn.

This is reflected by the order of catalytic activity of these complexes in methanol conversion into acetic acid (methyl acetate), with SnF_3 derivatives being far more efficient than their chloro and bromo analogues in full agreement with the electron-withdrawing ability of the SnX_3^- ligands. Thus, the increased positive charge on Ru in the order of $SnBr_3 < SnCl_3 < SnF_3$ facilitates the catalytic reaction. Furthermore, we also suggest that a steric component may play a role in the catalytic efficiency of these complexes. In the structures of $SnCl_3$ and $SnBr_3$ derivatives, the halides take up a considerable space, hindering the ruthenium atom. This steric hindrance is a much lesser problem for SnF_3 derivatives, facilitating the interaction with the substrate.

The nature of the phosphorous-containing ligand P also exerts a strong effect on the catalytic activity of the $CpP_2Ru(SnX_3)$ complexes (Tables 4–6). When PPh_3 is substituted by more basic ligands, PPh_2Me and dppe, the reaction rate decreases significantly for all complexes studied (Table 4 for X=F, Table 5 for X=Cl, Table 6 for X=Br). The effect of the ligand P shows the order of $PPh_3 > PPh_2Me \cong dppe$ for a given X. Electronic influence of the phosphine on Ru may also be offered as a reasonable explanation for this activity order. The strength of the ligand decreases in the order of $dppe \cong PPh_2Me > PPh_3$, with triphenylphosphine being a poorer ligand conducing higher charges over Ru and also more labile in the ligand exchange reactions. So, the results obtained clearly show that the dehydrogenative coupling of methanol to acetic acid (methyl acetate) catalyzed by Ru(II)–Sn(II) complexes is facilitated by the presence of less electron-donating ligands, as it was found for the related reaction of the methanol dehydrogenation giving formaldehyde with a Ru(II)–phosphine complex catalyst [19].

We studied the effect of the catalyst concentration on the reaction rate for all complexes **1**–**12**. The results of this kinetic study are shown in Fig. 2 for the $CpP_2Ru(SnF_3)$ serie; in Fig. 3 for the $CpP_2Ru(SnCl_3)$ serie; in Fig. 4 for the $CpP_2Ru(SnBr_3)$ serie; and in Fig. 5 for the monometallic $Cp(PPh_3)_2RuX$ serie. For Sn containing series the good straight lines were obtained. From their slopes the values for the reaction orders were calculated and summarized in Table 7. For all Ru–Sn complexes the reaction rate (v) depends on the charged-catalyst amounts in the order lower than 1: $v \alpha$ [complex]^n, where $n < 1$. For the monometallic

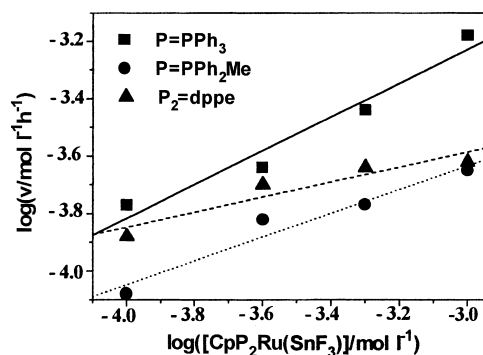Fig. 2. Effect of the concentration of $CpP_2Ru(SnF_3)$ catalysts on the rate of the methyl acetate formation from methanol at 140°C (■: P=PPh₃; ●: P=PPh₂Me; ▲: P₂=dppe).
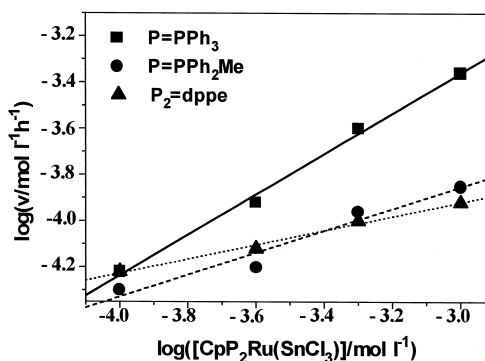
Fig. 3. Effect of the concentration of $CpP_2Ru(SnCl_3)$ catalysts on the rate of the methyl acetate formation from methanol at 140°C (■: $P=PPh_3$; ●: $P=PPh_2Me$; ▲: $P_2=dppe$).

Fig. 5. Effect of the concentration of $Cp(PPh_3)_2RuX$ catalysts on the rate of the methyl acetate formation from methanol at 140°C (■: $X=F$, ●: $X=Cl$; ▲: $X=Br$).

catalysts (Fig. 5), the rate dependence on the catalyst concentration shows the saturation in the region of higher concentrations. The obtained kinetic data can be explained by possible self-association of the complexes in the solutions, such as oligomerization through shared halide ligands between two or more molecules. Sharing the halides in both CpP_2RuX and $CpP_2Ru(SnX_3)$ complexes should decrease the electron-withdrawing effect of X and SnX_3 moieties on Ru which should result in reducing the catalytic activity of dimers/oligomers compared to monomers in methanol conversion. The initial relatively high reaction rates mentioned above could be explained by the higher than equilibrium concentrations of the monomeric complexes, which should be more active, at the beginning of the reaction.
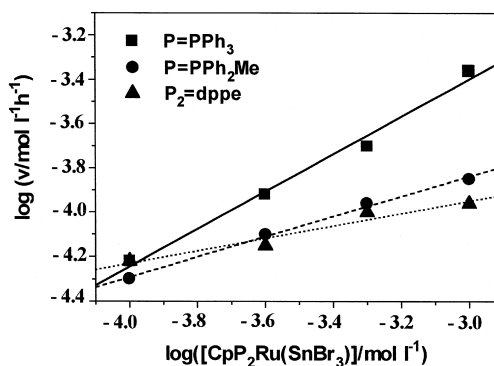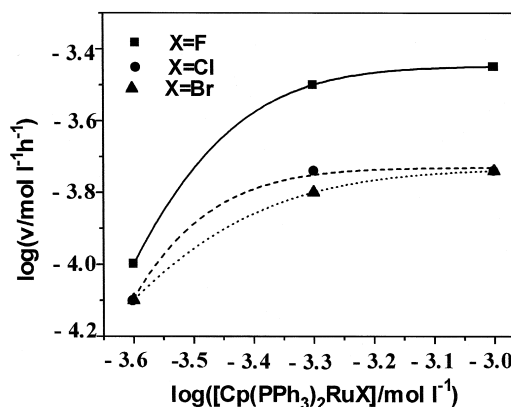
In the case of the complexes with dppe, the spectral (^{31}P NMR in the solution) and X-ray (in the solid state) data obtained [17,18] show that one or two diphosphine molecules can bridge two Ru centers. In fact, all complexes with dppe show the lowest values of the reaction order with respect to the catalyst concentration (Table 7). In addition, the X-ray diffraction data obtained [17,18] confirm self-association of the complexes containing the SnF_3 moiety in the solid state through the intermolecular hydrogen bond involving one of the hydrogen atoms of the cyclopentadienyl ring and one of the fluor atoms of the adjacent molecule. This is a moderate interaction (the F–H bond length=2.43 Å; the Sn–F–H angle=137°) able to bring several molecules in close proximity to each other forming an infinite chain, thus hindering interaction with the substrate. Although such weak

Fig. 4. Effect of the concentration of $CpP_2Ru(SnBr_3)$ catalysts on the rate of the methyl acetate formation from methanol at 140°C (■: $P=PPh_3$; ●: $P=PPh_2Me$; ▲: $P_2=$ dppe).

Table 7
Catalyst concentration effect on the rate (v) of methyl acetate formation from methanol catalyzed by $CpP_2Ru(SnX_3)$: $v\alpha$ $[CpP_2Ru(SnX_3)]^n$

Complex	n		
	$P=PPh_3$	$P=PPh_2Me$	$P_2=dppe$
$CpP_2Ru(SnF_3)$	0.6	0.4	0.3
$CpP_2Ru(SnCl_3)$	0.9	0.5	0.3
$CpP_2Ru(SnBr_3)$	0.8	0.5	0.3

and moderate, long-range interactions detected in the solid state rarely are maintained in solution, the loss of catalytic activity above a threshold concentration supports this as a likely mechanism for catalyst saturation. Thus, the aggregation of the active species by the formation of less active bridging complexes in highly concentrated solutions, which has been confirmed for some complexes by spectroscopy methods, may explain lower than first-order rate dependence on catalyst concentration observed for the Ru–Sn complexes and the tendency of saturation for the Ru complexes.

So, the ligand effect plays a key role in the activity of the Ru(II) complexes containing the $[(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru]$ fragment in methanol conversion. The greater the electron-withdrawing ability of the halide or SnX_3 moieties, the higher the catalytic activity of the complex. Substitution of PPh_3 by more basic phosphines decelerates the reaction. The $Cp(PPh_3)_2Ru(SnF_3)$ complex has been found as the most active catalyst for methanol dehydrogenative coupling into acetic acid (methyl acetate). The strong electron-withdrawing effect of the SnF_3 fragment explains the higher catalytic activity. This fragment causes the development of a higher partial positive charge on the Ru center, increasing its ability to interact with electron-rich organic substrates.

The obtained data support the mechanistic view of acetic acid formation from methanol in the presence of Ru complexes [5]. It was shown [8] that extra addition of chloride ions considerably slowed the methyl acetate formation catalyzed by $Cp(PPh_3)_2RuCl$, while in the case of $Cp(PPh_3)_2Ru(SnF_3)$, the same effect was observed with extra addition of PPh_3. This fact was interpreted in terms of the presence of pre-equilibrium to form the catalyst–reactant complex through the substitution of the chloride ligand in the Ru complex and the PPh_3 ligand in the Ru–Sn complex. The strong halogen effect on the activity of the bimetallic complexes **4–12** observed in the present work supports the exclusion of the SnX_3^- ligand dissociation as a kinetically important step. Monometallic systems (complexes **1–3**) also showed the activity highly dependent on the halogen nature especially for the fluor containing complex **1**. The activities followed the trend **1** (X=F)>**2** (X=Cl)≅**3** (X=Br), which indicates that PPh_3, rather than fluoride, seems to act as a leaving group in the catalytic cycle. Such a difference between chloro/bromo and fluoro analogues could be attributed

to the expected greater strength of the Ru–F bond compared to the Ru–Cl bond. The high electronegativity of the fluoride ligand promotes the increased positive charge on the ruthenium atom and contributes to the higher activity of the complex **1** (approximately doubled compared to those of **2** and **3**)

The reaction can be seen as the dehydrogenation of methanol giving formaldehyde followed by its dimerization into acetic acid. The latter reacts with the excess methanol resulting in the detected product, methyl acetate. The formaldehyde formation was suggested as a rate-determining step [7] and the data on the ligand effect on the catalytic activity of the CpP_2RuX and $CpP_2Ru(SnX_3)$ complexes, obtained in the present study, strongly support this suggestion. The reaction seems to proceed via the rate-determining β-hydrogen abstraction in the Ru(II)–OMe intermediate followed by protonation of the resulting Ru(II) species giving dihydrogen [19]. This view is fully consistent with the tendencies observed in this work. The catalysts containing the less basic phosphine and the more electron-withdrawing X/SnX_3 moiety show the higher activity due to facilitation of the electrophilic interaction of Ru with β-hydrogen.

Heterobimetallic Ru–Sn complexes showed ca. doubled activity compared to their monometallic analogues (CpP_2RuX vs. $CpP_2Ru(SnX)_3$). This accelerating effect can be understood in terms of the specific characteristics of the SnX_3^- ligand discussed in the Section 1. In addition to the strong *trans*-activation effect and π-acceptor character, the SnX_3^- ligand can behave as a Lewis acid via dissociation of X, which may allow an extra interaction with the oxygenates coordinated to the ruthenium atom favoring the formaldehyde and then, acetic acid formation [8,9].

$$\text{(2)}$$
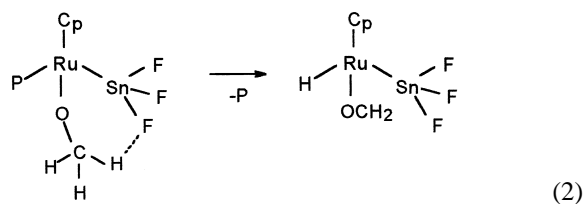
The highest activity of the fluoro derivatives compared to their chloro and bromo analogues could be related not only to the increased positive charge on the ruthenium atom due to elevated electronegativity of the SnF_3 fragment and steric factor mentioned

above, but also to the possibility of the intramolecular hydrogen bond formation, which should facilitate the heterolysis of the C–H bond in the rate-determining β-hydrogen (reaction 2). Such interaction seems sterically reasonable, since it should result in the formation of a six- or five-membered ring in the case of heterobimetallic or monometallic complexes, respectively. The possible mechanism for the further dimerization of the formaldehyde into acetic acid was proposed in Ref. [5]. It includes the formation from formaldehyde of the Ru methyl-formato complex followed by its isomerization via hydrogen abstraction into the hydrido-acetato complex that may give acetic acid by reductive elimination. We believe that the increased positive charge on the ruthenium atom due to the high electronegativity of the F/SnF_3 fragment can also contribute to the higher activity of the fluor-containing complexes in both the hydrogen abstraction and the reductive elimination steps.

Acknowledgements

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