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# Synthesis, characterisation and molecular structure of Ru–Sn(II) containing derivatives

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### Abstract

A series of new ruthenium-based derivatives were obtained by reactions of  $[Ru(\eta-C_5H_5)(PPh_3)_2Cl]$ . They are as follows:  $[Ru(\eta-C_5H_5)(PPh_3)_2SnF_3]$  (1),  $[Ru(\eta-C_5H_5)(PPh_3)_2SnCl_3]$  (2),  $[Ru(\eta-C_5H_5)(PPh_3)_2SnBr_3]$  (3),  $[Ru(\eta-C_5H_5)(dppe)SnF_3]$  (4),  $[Ru(\eta-C_5H_5)(dppe)SnCl_3]$  (5), and  $[Ru(\eta-C_5H_5)(dppe)SnBr_3]$  (6). Compounds 1–6 were studied by IR, NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>119</sup>Sn) and <sup>119</sup>Sn Mössbauer spectroscopies. In addition, 1, 2, 3 and 6 were structurally authenticated by X-ray crystallographic studies. Finally all the derivatives were tested as catalysts in the methanol to acetic acid conversion process, showing promising activities.  $\bigcirc$  2002 Elsevier Science Ltd. All rights reserved.

Keywords: Organometallics; Heterobimetallics; Organoruthenium; Catalysis; Mössbauer; NMR

# 1. Introduction

The fragment  $[Ru(\eta-C_5H_5)(PPh_3)_2Cl]$  still plays an important role in the organo-ruthenium chemistry development. Due to its stability and facile manipulation it is being used as a versatile starting material for other type-compounds. Many works have shown that a wide range of other ligands with different steric and electronic properties can displace not only the Cl ligand also the phosphine groups but in  $[Ru(\eta C_5H_5$ )(PPh<sub>3</sub>)<sub>2</sub>Cl] [1]. The interest in this fragment and related derivatives concerns its ability to act as a catalyst in a variety of reactions such as decarbonylation of both aromatic and aliphatic aldehydes [2], hydroformylation reactions [3] as well as anti-Markovnikov hydration of terminal alkynes [4].

Following the steps of Bruce et al. [5], who first investigated the phosphine displacement in  $[Ru(\eta - C_5H_5)(PPh_3)_2Cl]$ , some of us have shown in a preliminary report an interesting temperature-dependant-chelating versus bridging reversible behaviour observed for

 $[Ru(\eta-C_5H_5)(dppe)Cl] \quad \{dppe = Ph_2PCH_2CH_2PPh_2\}.$ When  $[Ru(\eta-C_5H_5)(PPh_3)_2Cl] \text{ reacts with dppe, apart} from the expected derivative <math display="block">[Ru(\eta-C_5H_5)(dppe)Cl], \text{ we} managed to isolate an unexpected secondary product, a dimeric 10-membered-ring derivative, <math display="block">[\{Ru(\eta-C_5H_5)Cl\}_2(\mu-dppe)_2], \text{ which was obtained in both the boat and chair conformations [6]. Variable temperature NMR experiments revealed that at room temperature this compound exists in both the conformations, whilst at low temperature only the chair conformer is observed.$ 

The field of heterometallic  $\text{SnX}_3^-$  containing derivatives is also of particular interest. In spite of a vast number of reports concerning the insertion of  $\text{SnCl}_2$  into  $L_nM-X$  {X = F, Cl and Br} bond, mainly for M = Ni, Pd and Pt [7], leading to  $L_nM-\text{SnCl}_2X$  derivatives, there is still a lack of information about heterometallic Sn(II) complexes of Fe(II) and Ru(II) [8]. Apart from the work of Consiglio et al. [9], little has been done to investigate aspects relative to structure and reactivity of Ru-SnX<sub>3</sub> species.

Therefore, in view of our interest in this field, herein we describe the synthesis, characterisation and reactivity of  $[Ru(\eta-C_5H_5)(PR_3)_y(SnX_3)]$  {for  $PR_3 = PPh_3$  y = 2 and for  $PR_3 = dppe$  y = 1; X = F, Cl, Br for both phosphines}.

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## 2. Experimental

### 2.1. Material and procedures

Experimental work was carried out under an atmosphere of dry nitrogen. All manipulations were conducted using Schlenk techniques, employing a vacuum/ nitrogen line or using a glove box under an atmosphere of nitrogen. Solvents were distilled from K or Na suspension and kept in Schlenk flasks with K or Na mirror or else dry molecular sieves. NMR spectra were recorded at 100.62 MHz (<sup>13</sup>C) and 148.97 MHz (<sup>119</sup>Sn) using a Bruker DPX-400 spectrometer equipped with an 89 mm wide-bore magnet. <sup>13</sup>C shifts are reported relative to SiMe<sub>4</sub> and <sup>119</sup>Sn shifts relative to SnMe<sub>4</sub>. <sup>119</sup>Sn Mössbauer spectra were collected with samples kept at 77 K using a CaSnO<sub>3</sub> source kept at room temperature. All spectra were fitted by means of Lorentzian line shapes. The infrared spectra were recorded with samples pressed as CsI pellets on a Perkin-Elmer 283B spectrometer in the 4.000-200 cm<sup>-1</sup> range. Carbon, nitrogen and hydrogen analyses were performed on a Perkin-Elmer PE-2400 CHNanalyses using tin sample-tubes. Chlorine and bromine analyses were performed by means of X-ray fluorescence in Rigaku-Geigerflex spectrophotometer with samples pressed as borax plates. Tin analysis was carried out using a Hitachi Z-8200 atomic absorption spectrophotometer (Sn lamp,  $\lambda_{max} = 224.6$  nm, N<sub>2</sub>O/acetylene flame).

# 2.2. X-ray structure determination of 1, 2, 3 and 6

The data were collected using a Siemens P4 diffractometer equipped with a SMART CCD area detector; graphite-monochromated Mo K $\alpha$ . The structures were solved by direct methods with SHELXTL version 5.0 [10] and the refinements were carried out using SHELXTL96 software [11]. Further details are given in Table 1. Tables of atom positions and thermal parameters have been deposited with the CCDC. All non-H atoms were anisotropic. Methyl groups were fixed at idealised geometry but with the torsion angle defining the H atom positions refined and  $U_{iso}(H)$  equal to  $1.5U_{eq}(C)$ . The ORTEP drawing shows the non-H atoms as 50% thermal vibration ellipsoids.

# 2.3. Synthesis of $[Ru(\eta-C_5H_5)(PPh_3)_2N_3]$

To a Schlenk flask containing  $[Ru(\eta-C_5H_5)(PPh_3)_2Cl]$ (0.5 g, 0.69 mmol), under an atmosphere of dry N<sub>2</sub>, dissolved in 100 ml of ethanol, was added at once NaN<sub>3</sub> (0.67 g, 10.33 mmol). The resultant mixture was stirred and refluxed for 6 h. Thus, the solvent was partially removed under vacuum to 40 ml and an orange precipitate was obtained. After filtration the solid was washed with *n*-hexane and re-crystallised in a mixture of dichloromethane and *n*-hexane. Yield 85%. M.p. (dec.) 118–120. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz),  $\delta$  4.2 (s, C<sub>5</sub>H<sub>5</sub>), 6.7–7.4 (m, C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.61 MHz),  $\delta$  81.3 (s, C<sub>5</sub>H<sub>5</sub>), 127.6–131.2 (m, C<sub>6</sub>H<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H} (CDCl<sub>3</sub>, 161,98 MHz),  $\delta$  42.4 (s, PPh<sub>3</sub>). IR (CsI) *v*(N<sub>3</sub>) 2005,  $\delta$ (N<sub>3</sub>) 675 *v*(Ru–N) 390 cm<sup>-1</sup>. Elemental analysis for C<sub>41</sub>H<sub>35</sub>N<sub>3</sub>P<sub>2</sub>Ru, calc. (found): C, 66.18 (67.20); H, 4.65 (4.81); N, 5.77 (5.73)%.

# 2.4. Synthesis of $[Ru(\eta-C_5H_5)(dppe)N_3]$

To a solution of  $[Ru(\eta-C_5H_5)(dppe)Cl]$  (0.25 g, 0.42 mmol) and 50 ml of ethanol in a Schlenk flask, under an atmosphere of dry N2, was added at once NaN3 (0.25 g, 2.5 mmol). After 6 h of stirring and reflux the solvent was partially removed under vacuum to 20 ml and an orange precipitate was obtained. Following filtration, the solid was washed with n-hexane and recrystallised in a mixture of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane. Yield 92%. M.p. (dec.) 245–255. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz),  $\delta$  2.2 (m, CH<sub>2</sub>), 4.5 (s, C<sub>5</sub>H<sub>5</sub>), 7,4–7.8 (m, C<sub>6</sub>H<sub>5</sub>);  ${}^{13}C{}^{1}H{}$ NMR (CDCl<sub>3</sub>, 100.61 MHz), δ 31.0 (m, CH<sub>2</sub>), 81.9 (s,  $C_5H_5$ ), 127.8–135.8 (m,  $C_6H_5$ ); <sup>31</sup>P{<sup>1</sup>H} (CDCl<sub>3</sub>, 161.98 MHz),  $\delta$  81.5 (s, dppe). IR (CsI)  $v(N_3)$  2000,  $\delta(N_3)$  680 v(Ru-N) 393 cm<sup>-1</sup>. Elemental analysis for C<sub>31</sub>H<sub>29</sub>N<sub>3</sub>P<sub>2</sub>Ru, calc. (found): C, 59.62 (61.28); H, 4.10 (4.18); N, 6.59 (6.62)%.

### 2.5. Synthesis of $[Ru(\eta-C_5H_5)(PPh_3)_2SnF_3]$

To a Schlenk flask containing  $[Ru(\eta-C_5H_5) (PPh_3)_2N_3$  (0.47 g, 0.64 mmol), under an atmosphere of dry N<sub>2</sub>, dissolved in 100 ml of ethanol, was added at once  $SnF_2$  (0.20 g, 1.28 mmol). The resultant mixture was stirred and refluxed for 6 h. Thus, a yellow solution was separated by filtration from a colourless solid. Then the yellow solid was washed with *n*-hexane and recrystallised in a mixture of  $CH_2Cl_2$  and *n*-hexane. Yield 70%. M.p. 199–202. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz),  $\delta$ 4.5 (s,  $C_5H_5$ ), 7.1–7.4 (m,  $C_6H_5$ ); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.61 MHz), *δ* 81.3 (s, C<sub>5</sub>H<sub>5</sub>), 128.2-138.5 (m,  $C_6H_5$ ); <sup>31</sup>P{<sup>1</sup>H} (CDCl<sub>3</sub>, 161.98 MHz),  $\delta$  48 (s, PPh<sub>3</sub>) {<sup>2</sup>J<sub>(31P-117Sn)</sub> = 480 Hz, <sup>2</sup>J<sub>(31P-119Sn)</sub> = 500 Hz}, <sup>119</sup>Sn{<sup>1</sup>H} (CDCl<sub>3</sub>, 149.21 MHz),  $\delta$  -357 (qt, SnF<sub>3</sub>)  $\{{}^{1}J_{(19F-119Sn)} = 3714 \text{ Hz}, {}^{2}J_{(31P-119Sn)} = 500 \text{ Hz}\}.$   ${}^{119}Sn$ Mössbauer: isomer shift (IS) 1.53 mm s<sup>-1</sup>, QS 2.17 mm s<sup>-1</sup>. IR (CsI):  $\nu$ (Sn-F) 490 cm<sup>-1</sup>. Elemental analysis for C<sub>41</sub>H<sub>35</sub>F<sub>3</sub>P<sub>2</sub>RuSn, calc. (found): C, 54.22 (54.86); H, 3.44 (3.57); Sn, 13.18 (13.70)%.

## 2.6. Synthesis of $[Ru(\eta-C_5H_5)(PPh_3)_2SnCl_3]$

Was similarly prepared employing  $[Ru(\eta-C_5H_5)-(PPh_3)_2Cl]$  (0.35 g, 0.52 mmol) and SnCl<sub>2</sub> (0.09 g, 0.52

Table 1					
Crystal data	and structure	refinement	for 1,	2, 3 a	nd 6

	$[Ru(\eta-C_5H_5)(PPh_3)_2SnF_3] $ (1)	$[Ru(\eta-C_5H_5)(PPh_3)_2SnCl_3] $ (2)	$[Ru(\eta-C_5H_5)(PPh_3)_2SnBr_3] (3)$	$[Ru(\eta-C_5H_5)(dppe)SnBr_3]$ (6)
Empirical formula	$C_{41}H_{35}F_3P_2RuSn$	C41H35Cl3P2RuSn	C41H35Br3P2RuSn	C31H29Cl3P2SnRu
Formula weight	908.85	1035.11	1668.49	1042.34
Temperature (K)	227(2)	293(2)	293(2)	193(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	Pbca	$P2_1/c$	$P2_1/c$	$P2_1/n$
Unit cell dimensions				
a (Å)	21.1767(3)	11.8421(10)	12.0346(10)	11.63290(10)
b (Å)	20.5368(3)	15.7095(10)	15.6844(10)	15.65340(10)
c (Å)	33.9725(3)	22.6490(10)	22.9077(10)	19.41120(10)
α (°)	90			
β(°)	90	95.615	95.620(10)	99.2030(10)
γ (°)	90			
$V(Å^3)$	1474.7(3)	4193.3(4)	4303.2(4)	3489.17(4)
Ζ	16	4	4	4
$D_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.634	1.640	1.804	1.984
Crystal size (mm)	$0.26 \times 0.26 \times 0.15$	$0.43 \times 0.33 \times 0.16$	$0.43 \times 0.33 \times 0.16$	$0.26 \times 0.25 \times 0.18$
Reflections collected/unique	$18006\ [R_{\rm int} = 0.0949]$	$6397/7439 [R_{int} = 0.0182]$	$8381/7983 [R_{int} = 0.0486]$	$37264/8419 [R_{int} = 0.0460]$
Refinement method	semi-empirical from	full-matrix least-squares	full-matrix least-squares	full-matrix least-squares
	equivalents	on $F^2$	on $F^2$	on $F^2$
Data/restraints/parameters	18 006/0/892	7439/0/478	7983/0/478	8419/0/499
Goodness-of-fit on $F^2$	1.064	1.048	0.986	1.160
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0561, wR_2 = 0.12134$	$R_1 = 0.0322, wR_2 = 0.0882$	$R_1 = 0.0400, wR_2 = 0.0723$	$R_1 = 0.0388, wR_2 = 0.0654$
R indices (all data)	$R_1 = 0.1110, wR_2 = 0.1547$	$R_1 = 0.0564, wR_2 = 0.0969$	$R_1 = 0.1516, wR_2 = 0.0909$	$R_1 = 0.0585, wR_2 = 0.0723$
Largest difference peak and hole (e $Å^{-3}$ )	0.973 and -1.413	0.888  and  -0.844	0.883 and -0.807	1.311 and -0.905
CCDC reference	166690	166691	166692	166693

mmol). Yield 85%. M.p. 188–189. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz),  $\delta$  4.5 (s, C<sub>5</sub>H<sub>5</sub>), 7.0–7.4 (m, C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.61 MHz),  $\delta$  81.3 (s, C<sub>5</sub>H<sub>5</sub>), 128.0–138.6 (m, C<sub>6</sub>H<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H} (CDCl<sub>3</sub>, 161.98 MHz),  $\delta$  45.4 (s, PPh<sub>3</sub>) {<sup>2</sup>J<sub>(31P-119Sn)</sub> = 437 Hz}, <sup>119</sup>Sn{<sup>1</sup>H} (CDCl<sub>3</sub>, 149.21 MHz),  $\delta$  –67.7 (t, SnCl<sub>3</sub>) {<sup>2</sup>J<sub>(119Sn-31P)</sub> = 443 Hz}. <sup>119</sup>Sn Mössbauer: IS 1.98 mm s<sup>-1</sup>, QS 1.93 mm s<sup>-1</sup>. IR (CsI):  $\nu$ (Sn–Cl) 272 and 290 cm<sup>-1</sup>. Elemental analysis for C<sub>41</sub>H<sub>35</sub>Cl<sub>3</sub>P<sub>2</sub>RuSn, calc. (found): C, 53.77 (54.31); H, 3.85 (3.85); Cl, 11.61 (11.20); Sn, 12.96 (13.23)%.

# 2.7. Synthesis of $[Ru(\eta-C_5H_5)(PPh_3)_2SnBr_3]$

Was similarly prepared employing [Ru( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-(PPh<sub>3</sub>)<sub>2</sub>N<sub>3</sub>] (0.26 g, 0.36 mmol) and SnBr<sub>2</sub> (0.20 g, 0,72 mmol). Yield 82%. M.p. 181–182. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz),  $\delta$  4.5 (s, C<sub>5</sub>H<sub>5</sub>), 7.1–7.5 (m, C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.61 MHz),  $\delta$  83.3 (s, C<sub>5</sub>H<sub>5</sub>), 128.0–137.5 (m, C<sub>6</sub>H<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H} (CDCl<sub>3</sub>, 161.98 MHz),  $\delta$  45.80 (s, PPh<sub>3</sub>) {<sup>2</sup>J<sub>(31P-119Sn)</sub> = 409 Hz}, <sup>119</sup>Sn{<sup>1</sup>H} (CDCl<sub>3</sub>, 149.21 MHz),  $\delta$  –139.2 (t, SnBr<sub>3</sub>) {<sup>2</sup>J<sub>(119Sn-31P)</sub> = 417 Hz}. <sup>119</sup>Sn Mössbauer: IS 2.85 mm s<sup>-1</sup>, QS 1.80 mm s<sup>-1</sup>. IR (CsI):  $\nu$ (Sn–Br) 260 and 265 cm<sup>-1</sup>. Elemental analysis for C<sub>41</sub>H<sub>35</sub>Br<sub>3</sub>P<sub>2</sub>RuSn, calc.

(found): C, 46.94 (46.90); H, 3.36 (3.37); Br, 22.85 (22.71); Sn, 11.31 (11.56)%.

# 2.8. Synthesis of $[Ru(\eta-C_5H_5)(dppe)SnF_3]$

Similarly prepared using [Ru( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(dppe)N<sub>3</sub>] (0.39 g, 0.64 mmol) and SnF<sub>2</sub> (0.20 g, 1.27 mmol). Yield 70%. M.p. 271–273. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz),  $\delta$  2.4–2.9 (m, CH<sub>2</sub>), 4.9 (s, C<sub>5</sub>H<sub>5</sub>), 7.0–7.7 (m, C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.61 MHz),  $\delta$  28.1 (s, CH<sub>2</sub>), 81.1 (s, C<sub>5</sub>H<sub>5</sub>), 128.0–133.2 (m, C<sub>6</sub>H<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H} (CDCl<sub>3</sub>, 161.98 MHz),  $\delta$  79.7 (s, PPh<sub>3</sub>) {<sup>2</sup>J<sub>(31P-119Sn)</sub> = 452 Hz}, <sup>119</sup>Sn{<sup>1</sup>H} (CDCl<sub>3</sub>, 149.21 MHz),  $\delta$  –345 (qt, SnCl<sub>3</sub>) {<sup>1</sup>J<sub>(19F-119Sn)</sub> = 3714 Hz, <sup>2</sup>J<sub>(119Sn-31P)</sub> = 443 Hz}. <sup>119</sup>Sn Mössbauer: IS 1.59 mm s<sup>-1</sup>, QS 2.19 mm s<sup>-1</sup>. IR (CsI):  $\nu$ (Sn–F) 493 cm<sup>-1</sup>. Elemental analysis for C<sub>31</sub>H<sub>29</sub>F<sub>3</sub>P<sub>2</sub>RuSn, calc. (found): C, 50.30 (51.15); H, 3.95 (3.65); Sn, 16.03 (15.05)%.

# 2.9. Synthesis of $[Ru(\eta-C_5H_5)(dppe)SnCl_3]$

Prepared similarly reacting [Ru( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(dppe)Cl] (0.35 g, 0.52 mmol) with SnCl<sub>2</sub> (0.09 g, 0,52 mmol). Yield 85%. M.p. 255–257. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz),  $\delta$  2.3–3.0 (m, *CH*<sub>2</sub>), 4.9 (s, C<sub>5</sub>H<sub>5</sub>), 7.0–8.0 (m, C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.61 MHz),  $\delta$  27.7 (s, CH<sub>2</sub>), 80.4 (s,  $C_5H_5$ ), 128.3–133.1 (m,  $C_6H_5$ ); <sup>31</sup>P{<sup>1</sup>H} (CDCl<sub>3</sub>, 161.98 MHz),  $\delta$  77.8 (s, PPh<sub>3</sub>) {<sup>2</sup>J<sub>(<sup>31</sup>P-<sup>119</sup>Sn)</sub> = 389 Hz}, <sup>119</sup>Sn{<sup>1</sup>H} (CDCl<sub>3</sub>, 149.21 MHz),  $\delta$  –22.3 (t, SnCl<sub>3</sub>) {<sup>2</sup>J<sub>(<sup>119</sup>Sn-<sup>31</sup>P)</sub> = 389 Hz}. <sup>119</sup>Sn Mössbauer: IS 1.92 mm s<sup>-1</sup>, QS 1.94 mm s<sup>-1</sup>. IR (CsI):  $\nu$ (Sn–Cl) 276 and 291 cm<sup>-1</sup>. Elemental analysis for C<sub>31</sub>H<sub>29</sub>Cl<sub>3</sub>P<sub>2</sub>RuSn, calc. (found): C, 47.15 (46.39); H, 3.70 (3.65); Cl, 13.46 (13.38); Sn, 15.03 (15.15)%.

# 2.10. Synthesis of $[Ru(\eta-C_5H_5)(dppe)SnBr_3]$

Synthesised in a similar way using [Ru( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(dppe)N<sub>3</sub>] (0.22 g, 0.36 mmol) and SnBr<sub>2</sub> (0.20 g, 0,72 mmol). Yield 82%. M.p. 253–255. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz),  $\delta$  2.2–3.3 (m, CH<sub>2</sub>), 4.9 (s, C<sub>5</sub>H<sub>5</sub>), 7.2–7.8 (m, C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.61 MHz),  $\delta$  28.1 (s, CH<sub>2</sub>), 81.1 (s, C<sub>5</sub>H<sub>5</sub>), 128.4–133.2 (m, C<sub>6</sub>H<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H} (CDCl<sub>3</sub>, 161.98 MHz),  $\delta$  77.4 (s, PPh<sub>3</sub>) {<sup>2</sup>J<sub>(31P-117Sn)</sub> = 355 Hz, <sup>2</sup>J<sub>(31P-119Sn)</sub> = 370 Hz}, <sup>119</sup>Sn{<sup>1</sup>H} (CDCl<sub>3</sub>, 149.21 MHz),  $\delta$  –110.8 (t, SnCl<sub>3</sub>) {<sup>2</sup>J<sub>(119Sn-31P)</sub> = 373 Hz}. <sup>119</sup>Sn Mössbauer: IS 2.05 mm s<sup>-1</sup>, QS 1.80 mm s<sup>-1</sup>. IR (CsI):  $\nu$ (Sn–Cl) 256 and 263 cm<sup>-1</sup>. Elemental analysis for C<sub>31</sub>H<sub>29</sub>Cl<sub>3</sub>P<sub>2</sub>RuSn, calc. (found): C, 40.30 (41.10); H, 3.17 (3.05); Br, 26.00 (25.02); Sn, 12.86 (12.85)%.

# 3. Results and discussion

The starting material  $[Ru(\eta-C_5H_5)(PPh_3)_2Cl]$  was prepared as follows (Eq. (1)):

The authentication was carried out by experiments of multinuclear NMR, which showed the expected resonances for <sup>1</sup>H at  $\delta$  4.1 (C<sub>5</sub>H<sub>5</sub>) and 6.7–7.5 (C<sub>6</sub>H<sub>5</sub>); for <sup>13</sup>C{<sup>1</sup>H} at  $\delta$  81 (C<sub>5</sub>H<sub>5</sub>) and 127–139 (C<sub>6</sub>H<sub>5</sub>); and <sup>31</sup>P{<sup>1</sup>H} at  $\delta$  39.6. Its identity was confirmed by infrared spectroscopic studies as well as by melting point and carbon and hydrogen elemental analysis.

The insertion of  $SnX_2$  into the Ru-X bond was conducted by reacting  $[Ru(\eta-C_5H_5)(PPh_3)_2Cl]$  or  $[Ru(\eta-C_5H_5)(dppe)Cl]$  with  $NaN_3$  and following equimolar addition of  $SnX_2$  (Scheme 1).

In all experiments the starting materials were refluxed with  $SnX_2$  {X = F, Cl, Br} in EtOH for 6 h. After removing part of the solvent a precipitate was isolated and filtrated.

# 3.1. Reactions of $[Ru(\eta-C_5H_5)(PPh_3)_2N_3]$ with $SnX_2$ (X = F, Cl and Br)

The reaction of  $[Ru(\eta-C_5H_5)(PPh_3)_2Cl]$  with NaN<sub>3</sub> yielded  $[Ru(\eta-C_5H_5)(PPh_3)_2N_3]$  which was treated with



Scheme 1. Reactions of  $[Ru(\eta-C_5H_5)(PPh_3)_2X]$  where X = F, Cl and Br. \* The exchanging reaction of PPh<sub>3</sub> by dppe also yielded the boat and chair conformer of  $[{Ru(\eta-C_5H_5)Cl}_2(\mu-dppe)_2]$ . However, for the insertion of SnCl<sub>2</sub> or the reaction with NaN<sub>3</sub> only the major product  $[Ru(\eta-C_5H_5)(dppe)Cl]$  was employed [12,13].

equimolar amounts of SnX<sub>2</sub>. [Ru( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>SnF<sub>3</sub>] (1), [Ru( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>SnCl<sub>3</sub>] (2) and [Ru( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>SnBr<sub>3</sub>] (3) were isolated as mixture-free derivatives. They were obtained as air- and moisture-stable orange crystalline solids, readily soluble in polar organic solvents. After recrystallisation from a mixture of CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane compounds 1, 2 and 3 showed acceptable melting points at 199–202, 188–189 and 181–182 °C, respectively, as well as satisfactory elemental analysis.

All three compounds were studied by X-ray crystallography (Table 1). Apart from the Ru–Sn and Sn–X distances, the other structural results revealed similar angles and bond lengths for all three compounds. The X-ray study of 1 showed the presence of two unique molecules in the unit cell, not related one to another by symmetry but linked by an intermolecular  $F \cdots H$  bond, 2.43 Å at the Cp ring. Such interactions are observed only in the solid state since no splitting of the hydrogen atoms or coupling with the fluorine was observed in the solution-state <sup>1</sup>H NMR spectrum (Figs. 1 and 2).

The RuCp(PPh<sub>3</sub>)<sub>2</sub> fragment remains almost unchanged when the Cl is replaced by the SnX<sub>3</sub><sup>-</sup> anion. The geometry at the Sn(II) centre is pyramidal trigonal with the Sn-X bond of 1.956 Å (av.), X = F, 2.394 Å (av.), X = Cl and 2.549 Å (av.) X = Br. The Ru-Sn distance, 2.5375 (av.) Å in the fluorine compound is a bit shorter than in the other two derivatives, implying a stronger interaction of the Ru fragment with the Sn moiety. The Sn-Cl bond in **2** is comparable with other known results and lies in the range of bond lengths which should be expected for such complexes [8,9]. All the molecules present a quasi-symmetry plane through Sn, Ru and the centroid of the Cp ring (Table 2).



Fig. 1. The molecular structure of 1 and atom numbering scheme. For clarity the hydrogen atoms have been omitted in (A) and in (B) also the phenyl groups.



Fig. 2. The molecular structure of 2, X = Cl, and 3, X = Br, and atom numbering scheme. Hydrogen atoms have been omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for 1, 2, 3 and 6

1				2		3		6	
Bond lengths									
Ru(1)-Sn(1)	2.5392(5)	Ru(1) - P(1)	2.3499(14)	Ru-Sn	2.5720(4)	Ru-Sn	2.5854(7)	Ru-Sn	2.5649(4)
Ru(1) - P(2)	2.3306(14)	Sn(1)-F(1)	1.949(4)	Ru-P(2)	2.3475(10)	Ru-P(2)	2.3533(17)	Ru-P(2)	2.2907(10)
Sn(1) - F(2)	1.954(4)	Sn(1)-F(4)	1.965(4)	Sn-Cl(2)	2.3790(12)	Sn-Br(2)	2.5600(9)	Sn-Br(2)	2.5639(5)
Ru(1)-M	2.229(5)	Ru(2) - P(3)	2.3226(14)	Ru-M	2.210(9)	Ru-M	2.2136(6)	Ru-M	2.2238(4)
Ru(2)-Sn(2)	2.5357(6)	Sn(2)-F(4)	1.952(4)	Ru-P(1)	2.3461(10)	Ru-P(1)	2.3504(17)	Ru-P(1)	2.2871(10)
Ru(2) - P(4)	2.3243(14)	Sn(2) - F(6)	1.961(4)	Sn-Cl(1)	2.4019(12)	Sn-Br(1)	2.5579(9)	Sn-Br(1)	2.5478(5)
Sn(2) - F(5)	1.956(4)	Ru(2)-M	2.2254(6)	Sn-Cl(3)	2.4012(12)	Sn-Br(3)	2.5298(8)	Sn-Br(3)	2.5408(5)
Bond angles									
P(1)-Ru(1)-Sn(1)	96.28(4)	P(2)-Ru(1)-Sn(1)	94.79(4)	P(1)-Ru-Sn	93.75(3)	P(1)-Ru-Sn	94.26(3)	P(1)-Ru-Sn	89.48(3)
F(1)-Sn(1)-F(2)	93.88(17)	F(1)-Sn(1)-F(3)	93.09(17)	Cl(1)-Sn-Cl(2)	94.68(5)	Br(1)-Sn-Br(2)	92.56(3)	Br(1)-Sn-Br(2)	95.26(2)
F(2)-Sn(1)-F(3)	94.21(17)	F(1) - Sn(1) - Ru(1)	120.47(12)	Cl(2)-Sn-Cl(3)	95.73(5)	Br(2)-Sn-Br(3)	95.47(7)	Br(2)-Sn-Br(3)	94.32(2)
F(2)-Sn(1)-Ru(1)	127.21(12)	F(3) - Sn(1) - Ru(1)	119.21(12)	Cl(2)-Sn-Ru	122.69(3)	Br(2)-Sn-Ru	128.72(3)	Br(2)-Sn-Ru	122.77(3)
P(3)-Ru(2)-Sn(2)	94.52(4)	P(2) - Ru(2) - Sn(2)	94.37(4)	P(2)-Ru-Sn	93.75(5)	P(2)-Ru-Sn	97.25(3)	P(2)-Ru-Sn	100.20(3)
F(4) - Sn(2) - F(5)	93.96(17)	F(4) - Sn(2) - F(6)	93.38(17)	Cl(1)-Sn-Cl(3)	92.88(5)	Br(1)-Sn-Br(3)	94.98(3)	Br(1)-Sn-Br(3)	101.07(2)
F(5)-Sn(2)-F(6)	93.8(17)	F(4) - Sn(2) - Ru(2)	94.37(4)	Cl(1)-Sn-Ru	114.02(4)	Br(1)-Sn-Ru	114.02(2)	Br(1)-Sn-Ru	112.31(3)
F(5)-Sn(2)-Ru(2)	117.79(13)	F(6)-Sn(2)-Ru(2)	121.59(13)	Cl(3)-Sn-Ru	108.90(4)	Br(3)-Sn-Ru	122.85(3)	Br(3)-Sn-Ru	125.34(3)

The results of <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy were unexceptional since no great differences were observed in the chemical shifts comparing with other reported results [5,6]. On the other hand, the <sup>119</sup>Sn NMR chemical shifts revealed interesting aspects of the bonding scheme in the compounds described here.

It was expected, the greater the halogen electronegativity, the lesser the shielding effect at the Sn centre. For the Cl and Br containing derivatives the chemical shifts,  $\delta$  -68 (t) for 2 and -139 (t) for 3 are in accordance with the deshielding effect caused for the electronegativity of the halogens. However, compound 1 shows an abnormal value for the <sup>119</sup>Sn resonance,  $\delta$  –357. In our opinion the <sup>119</sup>Sn chemical shift in this compound is heavily affected by an anomalous  $\pi$  contribution in the bonding scheme at the Sn(II) centre. In order to counterbalance the strong electronic withdraw inductive effect of the fluorine atom, the Sn centre forms a  $\pi$ -back bond with the Ru atom, stronger than in the other derivatives, which increases the shielding effect on the <sup>119</sup>Sn nucleus. Another indication for this is the higher  ${}^{2}J_{(3^{1}P-1^{19}Sn)}$  coupling constant, 500 Hz, which indicates a closer approach of Sn and P in 1 in the P-Ru-Sn system. In fact the Ru-Sn bond is a bit shorter in 1 compared to the others.

Concerning the infrared spectroscopic studies, the most important signals observed in the spectra were the  $v_{(Sn-X)}$ , 490 cm<sup>-1</sup> {X = F}, 290 and 272 cm<sup>-1</sup> {X = Cl} and 265 and 260 cm<sup>-1</sup> {X = Br}. In contrast to the <sup>119</sup>Sn NMR chemical shifts, the IS obtained from studies of <sup>119</sup>Sn Mössbauer spectroscopy

In contrast to the <sup>119</sup>Sn NMR chemical shifts, the IS obtained from studies of <sup>119</sup>Sn Mössbauer spectroscopy revealed an increasing in the IS values with the decreasing of the halogen electronegativity, 1.53 mm s<sup>-1</sup> (1), 1.98 mm s<sup>-1</sup> (2) and 2.10 mm s<sup>-1</sup>(3). The Mössbauer experiments revealed that the  $\pi$ -bond contribution to the bonding scheme does not cause a great change in the Mössbauer spectroscopic data, as expected, since the IS parameters depends only of the *s*-electrons density. The second set of data, QS 2.17 mm s<sup>-1</sup> (1), 1.93 mm s<sup>-1</sup> (2) and 1.79 mm s<sup>-1</sup> (3) showed differences in the symmetry of charge distribution.

# 3.2. Reactions of $[Ru(\eta-C_5H_5)(dppe)N_3]$ with $SnX_2$ (X = F, Cl and Br)

The compound  $[Ru(\eta-C_5H_5)(dppe)N_3]$  was prepared by reacting  $[Ru(\eta-C_5H_5)(dppe)Cl]$  [12] with NaN<sub>3</sub> [13].

Similar reactions with equimolar amounts of  $SnX_2$ {X = F, Cl, Br} afforded [Ru( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(dppe)SnF<sub>3</sub>] (4), [Ru( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(dppe)SnCl<sub>3</sub>] (5) and [Ru( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(dppe)-SnBr<sub>3</sub>] (6). These compounds were also isolated as airand moisture-stable crystalline solids and gave satisfactory elemental analysis and melting points 270–272, 255–257 and 252–254 °C.



The X-ray crystallographic determination of compound 6 served to compare structural features of compounds 6 with 3 (Fig. 3).

Compound 6 displays shorter Ru–P and Ru–Sn bonds, 2.2889 (av.) and 2.5649(4) Å versus 2.3519 (av.) 2.5854(7) observed for 3, respectively. Also a smaller P– Ru–P angle, 82.91(4)°, is revealed for 6 compared to the same angle in 3, 102.00(4)°. It is tentatively explained considering that the two phenyl groups bonded to the phosphorous and the bidentate nature of dppe renders it a less hindered ligand than PPh<sub>3</sub>. It causes smaller P– Ru–P angles in 6, as pointed to by the structural determination. The decrease in the steric effect permits a closer approach of the groups effecting shorter Ru–P and Ru–Sn bonds.

The <sup>119</sup>Sn NMR results show that in all the dppe containing derivatives the <sup>119</sup>Sn chemical shifts, (4)  $\delta$  -345 (q), (5)  $\delta$  -22 (t) and (6)  $\delta$  -111 (t), locates in higher frequency indicating a decrease in the electronic density at the Sn atom. It is also reflected in the smaller <sup>119</sup>Sn-<sup>31</sup>P coupling constants, 444, 390 and 373 Hz, respectively.

The Sn(II) chemical shift in **1–6** is not far from the signal exhibited by other Ru–Sn based compounds, such as  $[Ru(SnCl_3)_6]^{4-}$ ,  $\delta -34.6$  [14],  $[Ru(SnCl_3)_5Cl]^{4-}$ ,  $\delta -167.9$  (equatorial), -149.2 (axial),  $[Ru(SnCl_3)_5(MeCN)]^{3-}$ ,  $\delta -70.6$  (equatorial), -103.9 (axial) [15] and *cis*-[Ru(CO)<sub>4</sub>(SnMe\_3)<sub>2</sub>],  $\delta -207.$ 

The changing of ligands caused no differences in the infrared data since in each compound the signals corresponding to  $v_{(Sn-X)}$ , were observed at 493 cm<sup>-1</sup> {X = F}, 291 and 276 cm<sup>-1</sup> {X = Cl} and 256 and 257 cm<sup>-1</sup> {X = Br}, which are coincident with the previous results.

Also no great changes were observed in the <sup>119</sup>Sn Mössbauer spectroscopic data. The IS values, 1.59, 1.98 and 2.05 mm s<sup>-1</sup> and QS data, 2.19, 1.94, 1.80 mm s<sup>-1</sup> obtained for the dppe derivatives are very close to the



Table 3
Methanol conversion into methyl acetate catalysed by compounds $1-6$

[Catalyst] $(10^{-3} \text{ mol } 1^{-1})$	Rate of methyl acetate formation $(10^{-4} \text{ mol } l^{-1} \text{ h}^{-1})$						
	1	2	3	4	5	6	
1.00	4.4	6.7	4.4	2.4	1.2	1.1	
0.50	2.5	3.6	2.0	2.3	1.0	1.0	
0.25	1.2	2.3	1.2	2.0	0.6	0.5	
0.10	0.6	1.7	0.6	1.3	0.6	0.6	

 $PPh_3$  derivatives, indicating little change in the *s*-electronic density at the Sn centre.

#### 3.3. Catalysis reactions

Compounds 1-6 showed to be active in the catalytic process of obtaining acetic acid from methanol. The catalytic cycle described here can be more interesting than Monsanto's because it needs only methanol as starting material and uses less expensive material (Ru + Sn vs. Rh) without a corrosive iodide promoter [16]. The only product observed was acetic acid detected as methyl acetate. Neither formaldehyde, which is supposed to be the intermediate in methanol conversion to acetic acid [14], nor methyl formate, possible product of formaldehyde dimerisation, was detected in all cases. We believe that the nature of the phosphorus-containing ligand, the nature of the halogen as well as the presence of the Ru–Sn bond exerts a strong influence on the catalytic activity of complexes (Table 3).

The order of catalytic activity of the complexes follows the halogen electronegativity, the  $SnF_3$  bearing derivatives being far more efficient than the others. It seems to be related to the more efficient  $\pi$ -back donation from the Ru fragment to the Sn centre in the  $SnF_3^-$  containing products. It is possible that such a bonding scheme generates an extra positive density of charge in the Ru atom, which could facilitate a coordination to the oxygen atom of the methanol.

#### 4. Supplementary material

Tables of atom positions and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 166690, 166691, 166692 and 166693 for compounds **1**, **2**, **3** and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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#### References

- T. Blackmore, M.I. Bruce, F.G.A. Stone, J. Chem. Soc. A (1971) 2376.
- [2] (a) G. Domazetis, B. Tarpez, D. Dolphim, B.R. James, J. Chem. Soc., Chem. Commun. (1980) 939;
  (b) G. Domazetis, B.R. James, B. Tarpez, D. Dolphim, ACS Symp. Ser. 78 (1981) 152.
- [3] (a) G. Stedman, J. Chem. Soc. (1960) 1702;
- (b) A. Haim, H. Taube, Inorg. Chem. 2 (1963) 1199.
- [4] (a) R.F. Ziolo, Z. Dori, J. Am. Chem. Soc. 90 (1968) 6560;
  (b) A.P. Gaughan, K.S. Bowman, Z. Dori, Inorg. Chem. 11 (1972) 601.
- [5] M.I. Bruce, M.G. Humphrey, A.G. Swincer, R.C. Wallis, Aust. J. Chem. 37 (1984) 1747.
- [6] E.M. Moura, M.H. Dickman, H.G.L. Siebald, G.J. Gama, Polyhedron 18 (1999) 2899.
- [7] (a) O.V. Gusev, T.A. Peganova, M.A. Ievlev, A.G. Kropotova, K.A. Lyssenko, P.V. Petrovskii, Y.F. Oprunenko, N.A. Ustynyuk, J. Organomet. Chem. 622 (2001) 221; (b) T. Lee, S.W. Lee, H.G. Jang, S.O. Kang, J. Ko, Organometallics 20 (2001) 741; (c) Y. Ishikawa, M.S. Liao, C.R. Cabrera, Surf. Sci. 463 (2000) 66; (d) W.M. Teles, N.L. Speziali, C.A.L. Filgueiras, Polyhedron 19 (2000) 739; (e) E.V. Gusevskaya, E.N. dos Santos, R. Augusti, J. Mol. Catal. A Chem. 152 (2000) 15; (f) R.D. Hoffmann, D. Kussmann, U.C. Rodewald, Z. Naturforsch., Teil B 54 (1999) 709; (g) W.M. Teles, N.G. Fernandes, A. Abras, C.A.L. Filgueiras, Transition Met. Chem. 24 (1999) 321; (h) M.C. Janzen, H.A. Jenkins, L.M. Rendina, Inorg. Chem. 38 (1999) 2123[8] (a) R.O. Gould, W.J. Sime, T.A. Stephenson, J. Chem. Soc., Dalton Trans. (1978) 76; (b) J.D. Korp, I. Bernal, Inorg. Chem. 20 (1961) 4065; (c) L.J. Farrugia, B.R. James, C.R. Lassigne, E.J. Wells, Inorg. Chim. Acta 53 (1981) L261; (d) L.J. Farrugia, B.R. James, C.R. Lassigne, E.J. Wells, Can. J. Chem. 60 (1982) 1304; (e) B. Moreno, S. Sabo-Etienne, F. Dahan, B. Chaudret, J. Organomet. Chem. 498 (1995) 139; (f) M. Akita, R. Hua, T. Oku, M. Tanaka, Y. Moro-oka, Organometallics 15 (1996) 4162;

(g) R.D. Adams, D.A. Katahira, Organometallics 1 (1982) 53;

(h) M. Elder, D. Hall, J. Chem. Soc. A (1970) 245.

- [9] G. Consiglio, F. Morandini, G. Ciani, M.K. Kretschmer, J. Am. Chem. Soc. 105 (1983) 1391.
- [10] G.M. Sheldrick, SHELXL 5.0, Siemens Analytical Instruments, Madison, WI, 1994.
- [11] G.M. Sheldrick, SHELXL 96, University of Göttingen, Göttingen, Germany, 1996.
- [12] In the synthesis of  $[Ru(\eta-C_5H_5)(dppe)C]]$ , another species,  $[{Ru(\eta-C_5H_5)Cl}_2(\mu-dppe)_2]$ , in the chair and boat conformation was also obtained. However, only the first one was employed in the synthesis of **4**, **5** and **6**.
- [13] (a) In the exchange of  $Cl^-$  for  $N_3^-$ , using the chair and boat conformers, we observed the formation of only the chair conformer which was fully characterised by elemental analysis,

multinuclear NMR spectroscopy as well as by X-ray crystal-lography;

(b) Ref. [4b];

- (c) E.M. Moura, H.G.L. Siebald, G.M. de Lima, unpublished results.
- [14] H. Moriyama, T. Aoki, S. Shimoda, Y. Saito, J. Chem. Soc., Chem. Commun. (1982) 500.
- [15] N.W. Alcock, J.H. Nelson, J. Chem. Soc., Dalton Trans. (1982) 2415.
- [16] (a) T. Yamakawa, M. Hiroi, S. Shinoda, J. Chem. Soc., Dalton Trans. (1994) 2265;
  - (b) S. Shinoda, T. Ohnishi, T. Yamakawa, Catal. Surv. Jpn. 1 (1997) 25;
  - (c) T. Blackmore, M.I. Bruce, F.G.A. Stone, J. Chem. Soc. A (1971) 2376.