# Bimetallic ruthenium–tin chemistry: Synthesis and molecular structure of arene ruthenium complexes containing trichlorostannyl ligands

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## ARTICLE INFO

## ABSTRACT

A series of neutral, anionic and cationic arene ruthenium complexes containing the trichlorostannyl ligand have been synthesised from $SnCl_2$ and the corresponding arene ruthenium dichloride dimers $[(\eta^6\text{-arene})Ru(\mu_2\text{-Cl})Cl]_2$ (arene = $C_6H_6$, $Pr^iC_6H_4Me$). While the reaction with triphenylphosphine and stannous chloride only gives the neutral mono(trichlorostannyl) complexes $[(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SnCl_3)Cl]$ (1) and $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru(PPh_3)(SnCl_3)Cl]$ (2), the neutral di(trichlorostannyl) complex $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru(NCPh)(SnCl_3)_2]$ (3) could be obtained for the para-cymene derivative with benzonitrile as additional ligand. By contrast, the analogous reaction with the benzene derivative leads to a salt composed of the cationic mono(trichlorostannyl) complex $[(\eta^6\text{-}C_6H_6)Ru(NCPh)_2(SnCl_3)]^+$ (5) and of the anionic tris(trichlorostannyl) complex $[(\eta^6\text{-}C_6H_6)Ru(SnCl_3)_3]^-$ (6). On the other hand, $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru(\mu_2\text{-Cl})Cl]_2$ reacts with $SnCl_2$ and hexamethylenetetramine hydrochloride or 18-crown-6 to give the anionic di(trichlorostannyl) complex $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru(SnCl_3)_2Cl]^-$ (4), isolated as the hexamethylenetetrammonium salt or the chloro-tin 18-crown-6 salt. The single-crystal X-ray structure analyses of 1, 2, $[(CH_2)_6N_4H][4]$, $[(18\text{-crown-6})SnCl][4]$ and $[5][6]$ reveal for all complexes a pseudo-tetrahedral piano-stool geometry with ruthenium–tin bonds ranging from 2.56 (anionic complexes) to 2.60 Å (cationic complex).

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## 1. Introduction

The insertion of tin dichloride into metal–halogen bonds is known for many years [1]. While the reaction of $SnX_2$ with palladium and platinum complexes has been extensively studied [2], the analogous reaction with ruthenium derivatives has only been observed sparingly, in spite of the rich chemistry of this metal. So far, apart from some cyclopentadienyl ruthenium trichlorostannyl complexes [3], only a few arene ruthenium complexes containing trichlorostannyl ligands have been reported (Chart 1). Thus, the reaction of anhydrous $SnCl_2$ with the racemic chloro complex $[(\eta^6\text{-}C_6H_6)RuMe(R\text{-}Ph_2PNHCHMePh)Cl]$ affords the trichlorostannyl derivative $[(\eta^6\text{-}C_6H_6)RuMe(R\text{-}Ph_2PNHCHMePh)(SnCl_3)]$, which can be easily resolved into the diastereoisomers by crystallisation [4]. The phosphine derivatives $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru\{P(OMe)_3\}(SnCl_3)_2]$ and $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru(PPh_3)(SnCl_3)Cl]$ have been synthesised from $SnCl_2$ and the corresponding chloro complexes $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru\{P(OMe)_3\}Cl_2]$ and $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru(PPh_3)Cl_2]$ [5], and cationic arene ruthenium trichlorostannyl complexes of the

general formula $[(\eta^6\text{-}C_6H_6)RuMe(\eta^2\text{-}S_2C)(SnCl_3)]^+$ (arene = $C_6H_6$, $Pr^iC_6H_4Me$, $C_6Me_6$; R = cyclohexyl or isopropyl) are accessible from the corresponding chloro complexes, too [6].

On the other hand, mixtures of $SnCl_2$ and $RuCl_3\cdot nH_2O$ were found to show interesting catalytic properties: The dehydrogenating coupling of methanol to give acetic acid was reported to be catalysed by a binary $RuCl_3/SnCl_2$ composite catalyst [7]. Given this catalytic perspective, it was interesting to prepare well-defined Ru–Sn complexes and to study their structures and properties. In the present paper, we report on the synthesis and structural characterisation of neutral arene ruthenium complexes containing one and two trichlorostannyl ligands, of anionic arene ruthenium complexes containing two and three trichlorostannyl ligands as well as of a cationic arene ruthenium complex containing one trichlorostannyl ligand.

## 2. Results and discussion

### 2.1. Synthesis and characterisation of the neutral arene ruthenium complexes 1–3

The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu_2\text{-Cl})Cl]_2$ (arene = $C_6H_6$, $Pr^iC_6H_4Me$) react with two equivalents of
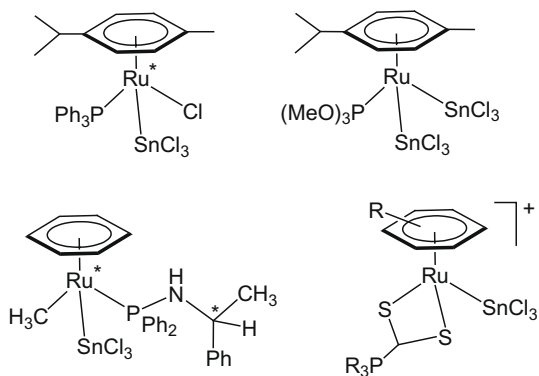
**Chart 1.** Known mononuclear trichlorostannyl arene ruthenium complexes [4–6].

triphenylphosphine and with two equivalents of anhydrous stannous chloride in refluxing tetrahydrofuran to give the neutral mono(trichlorostannyl) complexes $[(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SnCl_3)Cl]$ (**1**) and $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru(PPh_3)(SnCl_3)Cl]$ (**2**), see Scheme 1. Even an excess of tin chloride does not lead to the expected di(trichlorostannyl) derivatives. In the mono(trichlorostannyl) complexes **1** and **2**, the ruthenium atom is stereogenic, due to the coordination of four different ligator atoms, therefore the enantiomeric complexes are isolated as a racemic mixture.

However, a di(trichlorostannyl) derivative could be obtained with benzonitrile as two-electron ligand and with *para*-cymene as six-electron ligand: Thus, $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru(\mu_2\text{-}Cl)Cl]_2$ reacts with benzonitrile and with four equivalents of tin chloride to give the neutral di(trichlorostannyl) complex $[(\eta^6\text{-}Pr^iC_6H_4Me)\text{-}Ru(NCPh)(SnCl_3)_2]$ (**3**), see Scheme 2. Compound **3** is obtained in modest yields as a red crystalline solid.

The molecular structures of the benzene derivative **1** and of the known *para*-cymene analogue **2** [5] have been established by single-crystal X-ray structure analysis. The complexes show a typical piano-stool geometry with the metal centre being coordinated by an arene, a triphenylphosphine, a chloro and a trichlorostannyl ligand. The molecular structures of **1** and **2** are shown in Fig. 1. A series of selected geometrical parameters for **1** and **2** are presented in Table 1. The metal centres in **1** and **2** are stereogenic. However,
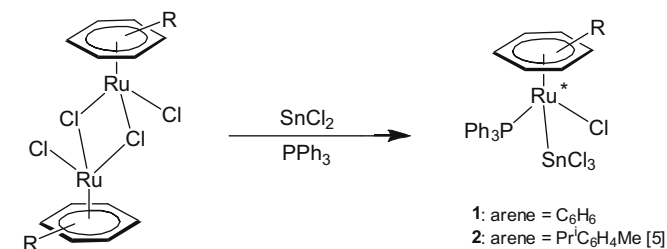


**Scheme 1.** Synthesis of the neutral mono(trichlorostannyl) complexes **1** and **2**.
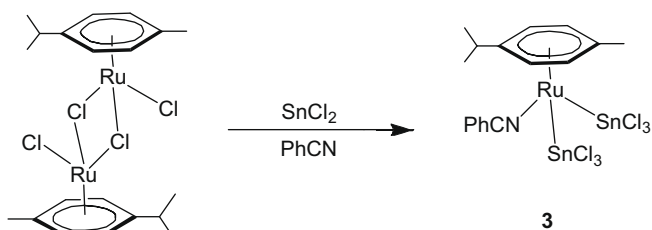


**Scheme 2.** Synthesis of the neutral di(trichlorostannyl) complex **3**.

while **1** crystallised as racemic crystals with the centrosymmetric space groups $P2_1/n$, **2** crystallises as a racemic mixture of enantiopure crystals with the non-centrosymmetric space group $Pca2_1$. The Ru–Sn bond distances are comparable to those found in other arene–Ru–Sn complexes [4–6]. As far as **3** is concerned, the crystal quality was not good enough for a single-crystal X-ray structure analysis; however, the X-ray data set obtained confirms the molecular structure proposed on the basis of the spectroscopic (IR, NMR, MS) and micro-analytical data.

### 2.2. Synthesis and characterisation of the ionic arene ruthenium complexes **4**–**6**

The dinuclear *para*-cymene ruthenium complex $[(\eta^6\text{-}Pr^iC_6H_4Me)$ $Ru(\mu_2\text{-}Cl)Cl]_2$ reacts with an excess of tin chloride and two equivalents of hexamethylenetetramine hydrochloride or 18-crown-6 in refluxing ethanol to give the anionic di(trichlorostannyl) complex $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru(SnCl_3)_2Cl]^-$ (**4**), isolated as the hexamethylenetetrammonium salt or the chloro-tin 18-crown-6 salt (Scheme 3). Both salts were fully characterised by spectroscopic and analytical methods as well as by single-crystal X-ray structure analysis. The molecular structures of $[(CH_2)_6N_4H][\mathbf{4}]$ and $[(18\text{-crown-6})SnCl][\mathbf{4}]$ are presented in Figs. 2 and 3, respectively. Selected bond lengths and angles are listed in Table 2.

The single-crystal structure analyses of the salts, $[(CH_2)_6N_4H][\mathbf{4}]$ and $[(18\text{-crown-6})SnCl][\mathbf{4}]$, show the ruthenium atom in **4** to possess a *pseudo*-tetrahedral geometry with the metal centre being coordinated by a *para*-cymene, a chloro and two trichlorostannyl ligands. The average Ru–Sn distances are slightly shorter in **4** ($\approx 2.56$ Å) than in the neutral complexes **1** and **2** ($\approx 2.59$ Å). The Ru–Cl distances, however, are almost identical in **1**, **2** and **4**. In the cation $[(18\text{-crown-6})SnCl]^+$, the tin atom is coordinated to a chloride and to all oxygen atoms of the crown ether, the Sn–O bond lengths ranging from 2.597(3) to 2.872(3) Å, while the Sn–Cl distance is 2.3978(11) Å. These distances are comparable to those found in the salts $[(18\text{-crown-6})SnCl]Cl$ and $[(18\text{-crown-}6)SnCl]ClO_4$ [8].

In contrast to the reaction of $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru(\mu_2\text{-}Cl)Cl]_2$ with benzonitrile and tin chloride which leads to the neutral *para*-cymene ruthenium di(trichlorostannyl) benzonitrile complex **3** (see Section 2.1), the benzene analogue $[(\eta^6\text{-}C_6H_6)Ru(\mu_2\text{-}Cl)Cl]_2$ reacts with benzonitrile and tin chloride under the same conditions to give a salt composed of the cationic mono(trichlorostannyl) complex $[(\eta^6\text{-}C_6H_6)Ru(NCPh)_2(SnCl_3)]^+$ (**5**) and of the anionic tris(trichlorostannyl) complex $[(\eta^6\text{-}C_6H_6)Ru(SnCl_3)_3]^-$ (**6**), see Scheme 4. Salt [**5**][**6**] was fully characterised by spectroscopic and analytical methods as well as by single-crystal X-ray structure analysis. The molecular structure of [**5**][**6**] is presented in Fig. 4 and selected bond lengths and angles are listed in Table 2.

The single-crystal structure analysis of the salt [**5**][**6**] shows both, the cation $[(\eta^6\text{-}C_6H_6)Ru(NCPh)_2(SnCl_3)]^+$ (**5**) and the anion $[(\eta^6\text{-}C_6H_6)Ru(SnCl_3)_3]^-$ (**6**), to be a typical arene ruthenium piano-stool complex. In cation **5**, the ruthenium atom is coordinated to a benzene, a trichlorostannyl and two benzonitrile ligands, while in anion **6**, the ruthenium atom is coordinated to a benzene and three trichlorostannyl ligands. The Ru–Sn bond length in the mono(trichlorostannyl) cation **5** [2.598(2)] is longer than in the tris(trichlorostannyl) anion **6** [2.546(2)–2.562(2)]. On the other hand, the centroid–Ru distance in **5** [1.712 Å] is shorter than in **6** [1.736 Å].

As far as the catalytic potential of the bimetallic ruthenium–tin complexes obtained in this study is concerned, no noticeable activity could be established so far: No conversion was observed with $[(CH_2)_6N_4H][\mathbf{4}]$ as potential catalyst in the reaction of methanol to give acetic acid or ethyl acetate at 140 °C, nor did **1** or **2** catalyse the coupling of methanol with carbon dioxide to give dimethyl car-
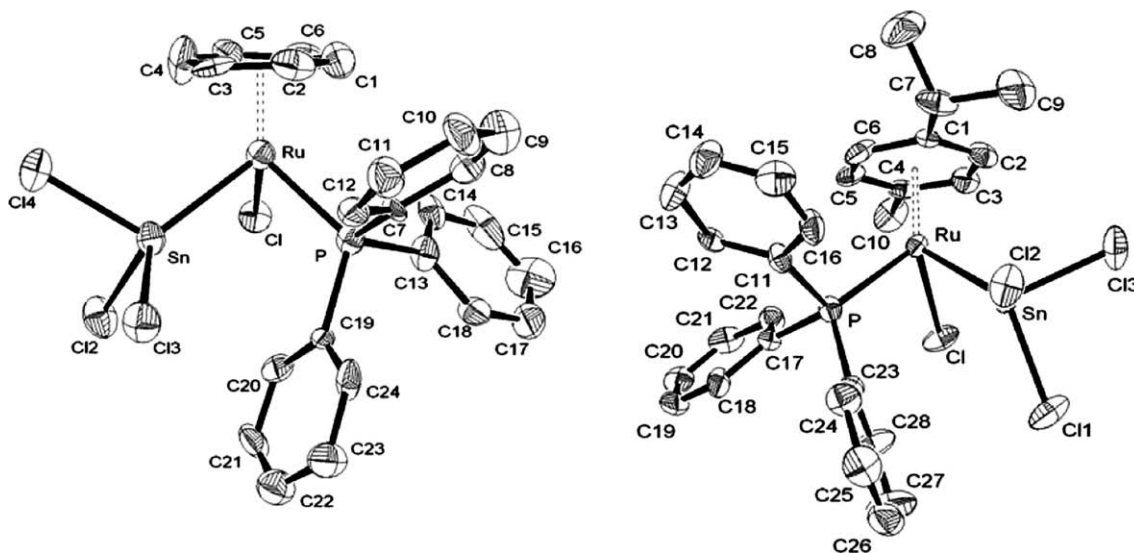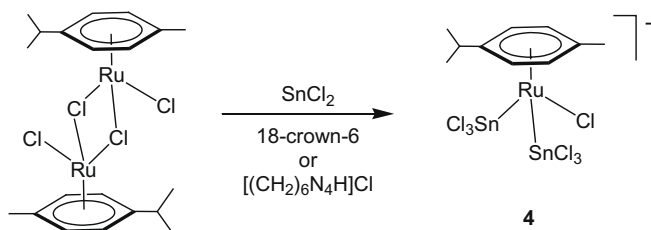
Fig. 1. ORTEP drawings of **1** (left) and **2** (right) at 50% probability level ellipsoids with hydrogen atoms omitted for clarity.

**Table 1**
Selected bond lengths (Å) and angles (°) for neutral complexes **1** and **2**.

|  | **1** | **2** |
|---|---|---|
| *Distances (Å)* | | |
| Ru–Sn | 2.5977(14) | 2.5830(9) |
| Ru–Cl | 2.399(3) | 2.386(2) |
| Ru–P | 2.347(3) | 2.343(3) |
| *Angles (°)* | | |
| Sn–Ru–Cl | 86.66(9) | 83.10(7) |
| Sn–Ru–P | 92.67(9) | 90.91(8) |
| Cl–Ru–P | 89.90(13) | 87.60(9) |



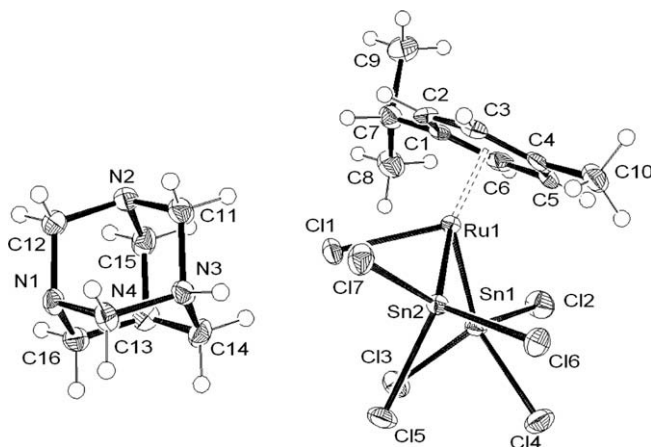Scheme 3. Synthesis of the anionic di(trichlorostannyl) complex **4**.



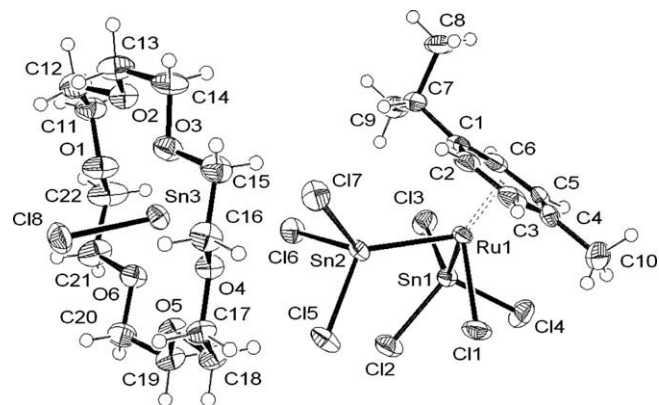Fig. 2. ORTEP drawing of [(CH₂)₆N₄H][**4**] at 50% probability level ellipsoids.



Fig. 3. ORTEP drawing of [(18-crown-6)SnCl][**4**] at 50% probability level ellipsoids, with solvent molecule omitted for clarity.

bonate at 148 °C and 180 bar. These compounds had been chosen for these reactions because of their solubility in methanol or in supercritical carbon dioxide.

A comparison of the anionic, neutral and cationic arene ruthenium trichlorostannyl complexes shows a systematic trend in the Ru–Sn bond lengths: The longest Ru–Sn being found in the cationic complex **5** [2.598(2) Å], while the shortest Ru–Sn is observed in the anionic complex **6** [2.546(2) Å], the Ru–Sn distances in the neutral complexes **1** and **2** being in between. All ruthenium–tin bond lengths are about 0.2 Å shorter than the sum of the covalent Ru and Sn radii (1.46 + 1.39 = 2.85 Å) [9], in line with the other structurally characterised arene ruthenium trichlorostannyl derivatives [4–6].

## 3. Experimental

### 3.1. General

All reagents were purchased either from Aldrich or Fluka and used as received. The starting materials [(η⁶-arene)Ru(μ₂-Cl)Cl]₂ [10] as well as the known complex [(η⁶-Pr$^i$C₆H₄Me)Ru(PPh₃) (SnCl₃)Cl] (**2**) [5] were synthesized according to literature methods. The salt [(CH₂)₆N₄H]Cl was prepared from hexamethylenetetramine and aqueous HCl (2 M) in ethanol solution by a slight

**Table 2**
Selected bond lengths (Å) and angles (°) for anion **4** in [(CH₂)₆N₄H][**4**] and [(18-crown-6)SnCl][**4**] as well as for [**5**][**6**].

| | [(CH₂)₆N₄H][**4**] | [(18-crown-6)SnCl][**4**] | [**5**] | [**6**] |
|---|---|---|---|---|
| *Distances (Å)* | | | | |
| Ru–Sn(1) | 2.5687(6) | 2.5614(5) | 2.598(2) | 2.546(2) |
| Ru–Sn(2) | 2.5605(6) | 2.5673(4) | | 2.549(2) |
| Ru–Sn(3) | | | | 2.562(2) |
| Ru–Cl | 2.4075(14) | 2.3904(11) | | |
| Ru–N(1) | | | 2.10(2) | |
| Ru–N(2) | | | 2.04(2) | |
| *Angles (°)* | | | | |
| Sn(1)–Ru–Sn(2) | 89.46(2) | 88.664(14) | | 90.08(6) |
| Sn(1)–Ru–Sn(3) | | | | 88.87(6) |
| Sn(2)–Ru–Sn(3) | | | | 88.97(6) |
| Sn(1)–Ru–Cl | 80.53(4) | 82.50(4) | | |
| Sn(2)–Ru–Cl | 88.49(4) | 87.01(3) | | |
| Sn–Ru–N(1) | | | 82.4(4) | |
| Sn–Ru–N(2) | | | 85.3(4) | |
| N(1)–Ru–N(2) | | | 87.5(8) | |

variation of a published method [11]. NMR spectra were recorded on a Bruker AMX 400 spectrometer using the residual proton resonance of the deuterated solvent as internal standard. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer FTIR 1720-X spectrometer. Elemental analyses were performed by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland) or by the Mikroelementaranalytisches Laboratorium, ETH Zürich (Switzerland). Electrospray mass spectra were performed by the Department of Chemistry of the University of Fribourg (Switzerland).

### 3.2. Preparation of the neutral arene ruthenium complexes 1–3

#### 3.2.1. [(η⁶-C₆H₆)Ru(PPh₃)(SnCl₃)Cl] (1)

To a solution of [(η⁶-C₆H₆)Ru(μ₂-Cl)Cl]₂ (50 mg, 0.1 mmol) in 10 mL of CH₂Cl₂, triphenylphosphine (53 mg, 0.2 mmol) was added. The reaction mixture was heated under reflux for 1 h. Then

the solvent was evaporated, and the residue was washed with hexane (3 × 2 mL) and dried *in vacuo*. The solid obtained was dissolved in THF (10 mL) and SnCl₂ (41 mg, 0.2 mmol) was added. The solution was heated under reflux overnight. Then the solution was concentrated to approximately half of the volume, which caused the crystallisation of the red product. Yield 89.5 mg (64%). ¹H NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) = 7.68 − 7.45 (m, 15H, C₆H₅), 5.92 (s, 6H, C₆H₆); ¹³C{¹H} NMR (100 MHz, acetone-$d_6$): $\delta$ (ppm) = 133.41, 133.31, 130.51, 130.49, 128.28, 128.17, 91.28, 91.25; ³¹P{¹H} NMR (162 MHz, acetone-$d_6$): $\delta$ (ppm) = 28.3 (s, Sn satellites, $J$ = 848 Hz); ¹¹⁹Sn NMR (149 MHz, acetone-$d_6$): $\delta$ (ppm) = −205.8 (d, $J_{Sn-P}$ = 760 Hz); IR (cm⁻¹): 3435 (w), 3075 (m), 2925 (w), 1704 (m), 1623 (w), 1481 (m), 1435 (m), 1187 (m), 1147 (m), 1092 (m), 999 (m), 850 (m), 823 (m), 749 (m), 697 (m), 607 (m), 527 (m), 512 (m), 500 (m); ESI-MS (positive mode): m/z = 741.0 [**1**+K]⁺; *Anal.* Calc. for C₂₄H₂₁Cl₄PRuSn·0.5 THF: C, 42.31; H, 3.41. Found: C, 42.03; H, 3.60%.

#### 3.2.2. [(η⁶-PrⁱC₆H₄Me)Ru(NCPh)(SnCl₃)₂] (3)

To a solution of [(η⁶-PrⁱC₆H₄Me)Ru(μ₂-Cl)Cl]₂ (150 mg, 0.25 mmol) in 10 mL of THF, SnCl₂ (230 mg, 1.0 mmol) and benzonitrile (1 mL, 9.7 mmol) were added. The reaction mixture was stirred at room temperature for 16 h. Then the solvent was evaporated and the residue washed with hexane (2 × 5 mL) and dried *in vacuo*. Poor quality crystals were obtained by slow diffusion of toluene in CH₂Cl₂ solution of **3**. Yield 58.3 mg (14%). ¹H NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) = 7.85 (m, 3H, C₆H₅), 7.70 (m, 2H, C₆H₅), 6.58 (d, 2H, C₆H₄), 6.46 (d, 2H, C₆H₄), 2.94 (sept, 1H, C**H**(CH₃)₂), 2.43 (s, 3H, CH₃), 1.36 (d, 6H, CH(C**H**₃)₂); ¹³C{¹H} NMR (100 MHz, acetone-$d_6$): $\delta$ (ppm) = 136.11, 134.17, 132.97, 130.65, 112.82, 111.04, 106.03, 90.69, 32.54, 23.03, 19.71; ¹¹⁹Sn NMR (149 MHz, acetone-$d_6$): $\delta$ (ppm) = −63.2; IR (cm⁻¹): 3444 (s), 3067 (w), 2968 (w), 2929 (w), 2254 (w), 1593 (w), 1503 (w), 1470 (m), 1447 (m), 1379 (w), 1201 (w), 1178 (w), 1056 (w), 1031 (w), 874 (w), 762 (m), 683 (m), 547 (w); ESI-MS (positive mode): m/z = 604.8 [**3**−SnCl₃+CH₃CN]⁺; *Anal.* Calc. for C₁₇H₁₉Cl₆NRuSn₂: C, 25.89; H, 2.43. Found: C, 26.02; H, 2.57%.
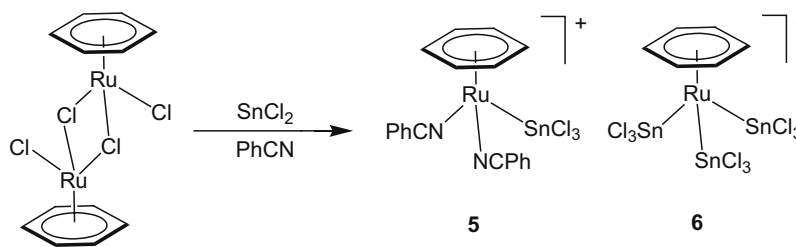


**Scheme 4.** Synthesis of the cationic mono(trichlorostannyl) complex **5** and the anionic tris(trichlorostannyl) complex **6** in the form of the salt [**5**][**6**].
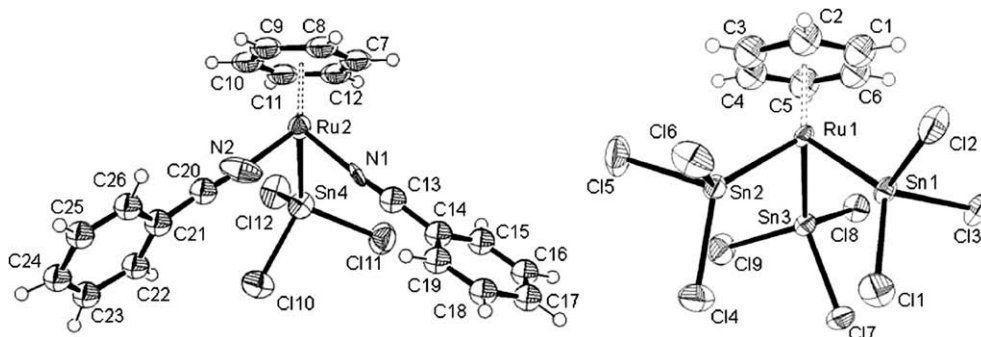


**Fig. 4.** ORTEP drawing of [**5**][**6**] at 50% probability level ellipsoids with solvent molecules omitted for clarity.

## 3.3. Preparation of ionic arene ruthenium complexes 4–6

### 3.3.1. $[(CH_2)_6N_4H][(\eta^6\text{-}Pr^iC_6H_4Me)Ru(SnCl_3)_2Cl]$ ($[(CH_2)_6N_4H][4]$)

To a solution of $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru(\mu_2\text{-}Cl)Cl]_2$ (50 mg, 0.08 mmol) in 10 mL of ethanol, $SnCl_2$ (111 mg, 0.49 mmol) and hexamethylenetetramine hydrochloride (29 mg, 0.16 mmol) were added. Then the reaction mixture was kept in an ultrasonic bath for 5 min, before being refluxed for 1 h. Then the precipitate was filtered and washed with hexane (2 × 5 mL) and dried *in vacuo*. Crystals were obtained by slow diffusion of dioxane in $CHCl_3$ solution of $[(CH_2)_6N_4H][4]$. Yield 86 mg (62%). $^1H$ NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) = 6.00 (d, 2H, $C_6H_4$), 5.90 (d, 2H, $C_6H_4$), 5.15 (s, 12H, $CH_2$), 2.85 (br, 1H, NH), 2.77 (sept, 1H, $CH(CH_3)_2$), 2.14 (s, 3H, $CH_3$), 1.25 (d, 6H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, acetone-$d_6$): $\delta$ (ppm) = 109.90, 102.04, 87.58, 85.86, 73.43, 31.69, 22.88, 18.99; $^{119}Sn$ NMR (149 MHz, acetone-$d_6$): $\delta$ (ppm) = −167.2; IR (cm$^{-1}$): 3444 (s), 3174 (m), 2965 (w), 2928 (w), 1460 (m), 1386 (m), 1360 (m), 1269 (m), 1260 (m), 1068 (m), 1021 (m), 1014 (m), 1005 (m), 975 (m), 823 (m), 814 (m), 656 (w), 647 (w); ESI-MS: m/z = 722.7 [4]$^-$; *Anal.* Calc. for $C_{16}H_{27}Cl_7N_4RuSn_2$: C, 22.29; H, 3.16; N, 6.50. Found: C, 21.91; H, 3.03; N, 6.16%.

### 3.3.2. $[(18\text{-}crown\text{-}6)SnCl][(\eta^6\text{-}Pr^iC_6H_4Me)Ru(SnCl_3)_2Cl]$ ($[(18\text{-}crown\text{-}6)SnCl][4]$)

To a solution of $[(\eta^6\text{-}Pr^iC_6H_4Me)Ru(\mu_2\text{-}Cl)Cl]_2$ (50 mg, 0.08 mmol) in 10 mL of ethanol, $SnCl_2$ (148 mg, 0.66 mmol) and 18-crown-6 (43 mg, 0.16 mmol) were added. The reaction mixture was kept in an ultrasonic bath for 5 min, before being refluxed for 5 min. After cooling, the precipitate was filtered and washed with ethanol (3 × 5 mL) and dried *in vacuo*. Crystals were obtained by slow diffusion of toluene in an acetone solution of $[(18\text{-}crown\text{-}6)SnCl][4]$. Yield 139 mg (75%). $^1H$ NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) = 5.99 (d, 2H, $C_6H_4$), 5.90 (d, 2H, $C_6H_4$), 3.91 (s, 24H, $CH_2$), 2.78 (sept, 1H, $CH(CH_3)_2$), 2.15 (s, 3H, $CH_3$), 1.25 (d, 6H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, acetone-$d_6$): $\delta$ (ppm) = 110.00, 102.00, 87.75, 87.65, 86.14, 85.91, 70.70, 31.75, 22.96, 19.07; $^{119}Sn$ NMR (149 MHz, acetone-$d_6$): $\delta$ (ppm) = −167.0 ($SnCl_3$), −786.5 ($SnCl$); IR (cm$^{-1}$): 2918 (m), 2876 (w), 2830 (w), 1495 (w), 1470 (m), 1435 (w), 1349 (m), 1285 (m), 1247 (m), 1092 (vs), 967 (s), 834

(m), 755 (w), 737 (w), 695 (w); ESI-MS (negative mode): m/z = 722.6 [4]$^-$; *Anal.* Calc. for $C_{16}H_{27}Cl_7N_4RuSn_2$: C, 23.19; H, 3.36. Found: C, 22.84; H, 3.15%.

### 3.3.3. $[(\eta^6\text{-}C_6H_6)Ru(NCPh)_2(SnCl_3)][(\eta^6\text{-}C_6H_6)Ru(SnCl_3)_3]$ ($[5][6]$)

To a solution of $[(\eta^6\text{-}C_6H_6)Ru(\mu_2\text{-}Cl)Cl]_2$ (150 mg, 0.30 mmol) in 10 mL of THF, $SnCl_2$ (271 mg, 1.20 mmol) and benzonitrile (1 mL, 9.70 mmol) were added. The reaction mixture was stirred at room temperature for 16 h. Then the solvent was evaporated, and the residue was washed with cyclohexane (2 × 5 mL) and dried *in vacuo*. Crystals were obtained by slow diffusion of toluene in an acetone solution of $[5][6]$. Yield 260 mg (59%). $^1H$ NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) = 7.74 (m, 4H, $C_6H_5$), 7.69 (m, 2H, $C_6H_5$), 7.55 (m, 4H, $C_6H_5$), 5.96 (s, 6H, $C_6H_6$), 5.93 (s, 6H, $C_6H_6$); $^{13}C\{^1H\}$ NMR (100 MHz, acetone-$d_6$): $\delta$ (ppm) = 134.05, 133.19, 130.30, 129.32, 88.13, 87.50, 87.18; $^{119}Sn$ NMR (149 MHz, acetone-$d_6$): $\delta$ (ppm) = −164.2 (6), −201.8 (5); IR (cm$^{-1}$): 3444 (s), 3066 (m), 2273 (w), 1595 (w), 1508 (w), 1489 (w), 1447 (m), 1434 (m), 1203 (w), 1179 (w), 834 (m), 752 (m), 681 (m), 616 (w), 543 (m); ESI-MS (negative mode): m/z = 852.3 [6]$^-$ (positive mode); m/z = 511.8 [5−NCPh]$^+$; *Anal.* Calc. for $C_{26}H_{22}Cl_{12}N_2Ru_2Sn_4\cdot C_6H_{12}$: C, 24.81; H, 2.21; N, 1.81. Found: C, 25.09; H, 2.09; N, 2.05%.

## 3.4. Single-crystal X-ray structure analyses

Crystals of complexes **1**, **2**, $[(CH_2)_6N_4H][4]$, $[(18\text{-}crown\text{-}6)SnCl][4]\cdot CHCl_3$ and $[5][6]\cdot CHCl_3$ were mounted on a Stoe Image Plate Diffraction system equipped with a $\phi$ circle goniometer, using Mo K$\alpha$ graphite monochromated radiation ($\lambda$ = 0.71073 Å) with $\phi$ range 0–200°. The structures were solved by direct methods using the program SHELXS-97 [12]. Refinement and all further calculations were carried out using SHELXL-97 [13]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on $F^2$. Crystallographic details are summarised in Table 3. Figures of complexes **1**, **2**, $[(CH_2)_6N_4H][4]$, $[(18\text{-}crown\text{-}6)SnCl][4]$ and $[5][6]$ were drawn with ORTEP-32 [14].

**Table 3**
Crystallographic and structure refinement parameters for complexes **1**, **2**, $[(CH_2)_6N_4H][4]$, $[(18\text{-}crown\text{-}6)SnCl][4]\cdot CHCl_3$ and $[5][6]\cdot CHCl_3$.

| | **1** | **2** | **$[(CH_2)_6N_4H][4]$** | **$[(18\text{-}crown\text{-}6)SnCl][4]$** | **$[5][6]$** |
|---|---|---|---|---|---|
| Chemical formula | $C_{24}H_{21}Cl_4PRuSn$ | $C_{28}H_{29}Cl_4PRuSn$ | $C_{16}H_{27}Cl_7N_4RuSn_2$ | $C_{23}H_{39}Cl_{11}O_6RuSn_3$ | $C_{27}H_{23}Cl_{15}N_2Ru_2Sn_4$ |
| Formula weight | 701.94 | 758.04 | 862.02 | 989.57 | 1584.12 |
| Crystal system | Monoclinic | Orthorhombic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ (no. 14) | $Pca2_1$ (no. 29) | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) | $C2/c$ (no. 15) |
| Crystal colour and shape | Orange block | Orange rod | Orange block | Orange block | Red block |
| Crystal size | 0.27 × 0.22 × 0.19 | 0.24 × 0.22 × 0.16 | 0.16 × 0.14 × 0.11 | 0.25 × 0.22 × 0.17 | 0.20 × 0.17 × 0.16 |
| $a$ (Å) | 9.3947(8) | 14.755(3) | 17.0131(15) | 9.7192(6) | 44.152(9) |
| $b$ (Å) | 21.3604(18) | 10.540(2) | 9.0899(6) | 13.7110(6) | 12.260(2) |
| $c$ (Å) | 14.0666(13) | 18.510(4) | 18.0126(15) | 31.393(2) | 17.625(4) |
| $\beta$ (°) | 104.173(10) | | 106.754(10) | 97.198(5) | 91.43(3) |
| $V$ (Å$^3$) | 2736.9(4) | 2878.6(10) | 2667.4(4) | 4150.5(4) | 9538(3) |
| $Z$ | 4 | 4 | 4 | 4 | 8 |
| $T$ (K) | 173(2) | 173(2) | 173(2) | 173(2) | 173(2) |
| $D_{calc}$ (g cm$^{-3}$) | 1.704 | 1.749 | 2.147 | 2.014 | 2.206 |
| $\mu$ (mm$^{-1}$) | 1.924 | 1.836 | 3.132 | 2.883 | 3.544 |
| Flack parameter | | 0.14(4) | | | |
| Scan range (°) | 2.37 < $\theta$ < 26.04 | 2.37 < $\theta$ < 25.93 | 2.33 < $\theta$ < 26.06 | 1.31 < $\theta$ < 25.15 | 1.75 < $\theta$ < 25.46 |
| Unique reflections | 5378 | 5078 | 5230 | 7410 | 6184 |
| Reflections used [$I > 2\sigma(I)$] | 1778 | 3052 | 3800 | 5223 | 2239 |
| $R_{int}$ | 0.1408 | 0.0786 | 0.0769 | 0.0566 | 0.1018 |
| Final $R$ indices [$I > 2\sigma(I)$]$^*$ | 0.0647, $wR_2$ 0.1212 | 0.0414, $wR_2$ 0.0891 | 0.0374, $wR_2$ 0.0820 | 0.0256, $wR_2$ 0.0463 | 0.0578, $wR_2$ 0.1055 |
| $R$ indices (all data) | 0.1640, $wR_2$ 0.1349 | 0.0798, $wR_2$ 0.0965 | 0.0564, $wR_2$ 0.0862 | 0.0483, $wR_2$ 0.0438 | 0.1479, $wR_2$ 0.1201 |
| Goodness-of-fit | 0.748 | 0.806 | 0.907 | 0.811 | 0.668 |
| Maximum, Minimum $\Delta\rho$ (e Å$^{-3}$) | 1.275, −0.915 | 0.627, −1.338 | 1.053, −1.434 | 0.832, −0.964 | 0.818, −1.254 |

$^*$ Structures were refined on $F_0^2$: $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

### 3.5. Catalytic runs

For the dehydrogenating coupling of methanol, 17 mg of $[(CH_2)_6N_4H][4]$ were dissolved in 20 mL of $CH_3OH$ or in a mixture of 10 mL of $CH_3OH$ and 10 mL of $CH_3CN$; then the solution was heated in an autoclave to 140 °C for 24–72 h. After cooling, the solution was analysed by $^1H$ NMR spectroscopy. For the coupling of methanol with carbon dioxide, a solution of 107 mg of **1** or 102 mg of **2** in 20 mL of $CH_3OH$ was pressurised with $CO_2$ (35 g). The reactor was heated to 148 °C (the pressure mounting to 180 bar) for 24 h. After pressure release the solution was analysed by GC.

## 4. Supplementary materials

CCDC 743657, 743658, 743659, 743660 and 743661 contain the supplementary crystallographic data for compounds **1**, **2**, $[(CH_2)_6N_4H][4]$, $[(18\text{-crown-}6)SnCl][4]\cdot CHCl_3$ and $[5][6]\cdot CHCl_3$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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