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The Role of the Trichlorostannyl Ligand in Tin-Ruthenium Arene Complexes: Experimental and Computational Studies

Miroslav Novák,^[a] Marek Bouška,^[a] Libor Dostál,^[a] Michael Lutter,^[b] Klaus Jurkschat,^[b] Jan Turek,^{[c]*} Frank De Proft,^[c] Zdeňka Růžicková,^[a] Roman Jambor^{[a]*}

Abstract: A set of neutral and ionic ruthenium arene trichlorostannyl complexes is reported. The tin(II) compounds L^1SnCl (**1**, $L^1 = [2-(CH_2NEt_2)-4,6-(tBu)_2C_6H_2]^-$) and $[L^2SnCl][SnCl_3]$ (**2**, $L^2 = 2,6-[(CH_3)C=N(C_6H_3-2,6-IPr_2)_2]C_5H_3N$) show a rather different reactivity towards the ruthenium complex $[(\eta^6\text{-cymene})RuCl]_2(\eta\text{-Cl})_2$. As a consequence, the neutral complex $[Ru(\eta^6\text{-cymene})(L^1SnCl)Cl_2]$ (**4**) and the ionic compound $[L^2SnCl][Ru(\eta^6\text{-cymene})(SnCl_3)_2Cl]$ (**8**) were isolated. The insertion reaction of **4** with $SnCl_2$ provided the neutral trimetallic ruthenium complex $[Ru(\eta^6\text{-cymene})(L^1SnCl)(SnCl_3)Cl]$ (**6**). Analogous ruthenium complexes $[Ru(\eta^6\text{-cymene})(L^3PPh_2)Cl_2]$ (**5**) and $[Ru(\eta^6\text{-cymene})(L^3PPh_2)(SnCl_3)Cl]$ (**7**) containing the phosphane ligand L^3PPh_2 (**3**, $L^3 = \{2,6-IPr_2-(C_6H_3)NH\}^-$) were also prepared in order to evaluate the donor-acceptor strength of the tin(II)- and phosphorus-containing ligands. The structural characterization and DFT calculations of the above-mentioned complexes suggest a strong influence of the $[SnCl_3]^-$ moiety on the Ru-E interaction ($E = Sn, P$). The influence of the trichlorostannyl ligand on the Ru-E interaction in the complexes **4** - **7** was further evaluated with a distortion/interaction analysis.

dimethoxymethane,^[5e] carbene-carbene coupling reactions^[5f] or the methylation of alkylamines.^[5g] Apart from the cyclopentadienyl ruthenium trichlorostannyl complexes, only a few arene ruthenium complexes containing trichlorostannyl ligands have been reported so far (Figure 1A).^[6]

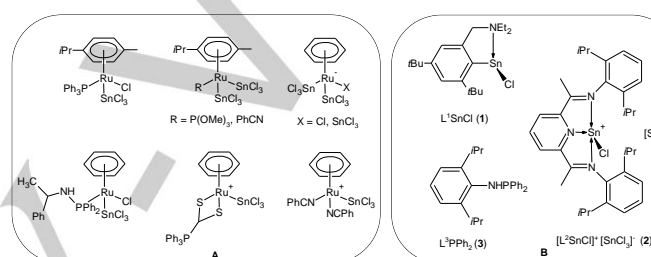


Figure 1. (A) Examples of arene ruthenium complexes containing the trichlorostannyl moiety; (B) Donor ligands used in this study.

Introduction

Ru/Sn based alloys have shown efficient catalytic properties in particular in the hydrogenation of various organic substrates.^[1] A binary $RuCl_3/SnCl_2$ composite catalyst was found as an interesting catalytic system for the dehydrogenating conversion of methanol to acetic acid.^[2] As a result, the syntheses and structural studies of well-defined Ru–Sn complexes are of current interest. Despite of the well-established insertion reaction of tin dichloride into metal–halogen bonds,^[3] the reaction of $SnCl_2$ with ruthenium derivatives has only been observed scarcely.^[4] Among these, the cyclopentadienyl ruthenium trichlorostannyl complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{phosphane})_2Ru(SnCl_3)]$ have been synthesized^[5] and tested as catalysts for the preparation of methyl acetate from methanol,^[5b-d] selective electrochemical oxidation of methanol to

While the reaction of the anhydrous $SnCl_2$ with an appropriate arene ruthenium chloride complex yielding the corresponding trichlorostannyl derivatives is rather straightforward, the particular role of the $SnCl_3$ moiety in these complexes has not been clearly specified. Nevertheless, it is believed that its high π -acceptor character removes the electron density from the ruthenium atom, which enhances its ability to interact with organic substrates.^[7]

Therefore, we decided to investigate tin containing arene ruthenium complexes in more detail. Both the C,N-chelated stannylene L^1SnCl (**1**), where L^1 is $[2-(CH_2NEt_2)-4,6-(tBu)_2C_6H_2]^-$ and the salt $[L^2SnCl][SnCl_3]$ (**2**), where L^2 is $2,6-[(CH_3)C=N(C_6H_3-2,6-IPr_2)_2]C_5H_3N$,^[8a] containing a N,N,N-chelated tin(II) cation were used as potential donor ligands, where the tin atom can coordinate to the ruthenium atom *via* the lone pair of electrons. Similarly, amidophosphane L^3PPh_2 (**3**), where L^3 is $\{2,6-IPr_2-(C_6H_3)NH\}^-$, was recently applied to synthesize the analogous Ru complex $[Ru(\eta^6\text{-cymene})(L^3PPh_2)Cl_2]$,^[9] and therefore this compound was used in this study to compare the donor ability of the tin and phosphorus atoms in appropriate arene ruthenium complexes (Figure 1B). Moreover, insertion reactions of the above-mentioned ruthenium complexes stabilized by various donor ligands with $SnCl_2$ were also studied.

As a result of their different reactivity, the present paper reports the syntheses, structural characterization and DFT calculations of the bi- and trimetallic neutral arene ruthenium complexes with one trichlorostannyl ligand, as well as the anionic arene ruthenium complex containing two trichlorostannyl ligands.

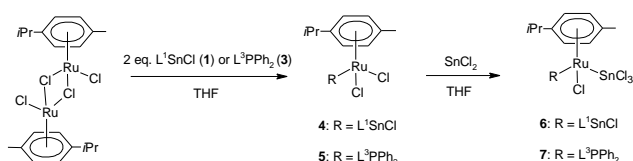
- [a] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, 53210 Pardubice, Czech Republic.
E-mail: roman.jambor@upce.cz, <http://www.upce.cz>
- [b] Lehrstuhl für Anorganische Chemie II, Technische Universität Dortmund, 44221 Dortmund, Germany
- [c] Eenheid Algemene Chemie (ALGC), Member of the QCMM VUB-UGent Alliance Research Group, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium;
E-mail: jturek@vub.ac.be, <http://we.vub.ac.be/~algc/index.html>

Crystallographic details and NMR data are given in Supporting information.

Results and Discussion

Synthesis and NMR studies of Ru complexes

The reaction of L^1SnCl (**1**)^[10] and L^3PPh_2 (**3**)^[9] with $[(\eta^6\text{-cymene})RuCl]_2(\mu\text{-Cl})_2$ gave the corresponding complexes $[Ru(\eta^6\text{-cymene})(L^1SnCl)Cl_2]$ (**4**) and $[Ru(\eta^6\text{-cymene})(L^3PPh_2)Cl_2]$ (**5**),⁹ respectively (Scheme 1). Furthermore, the insertion of $SnCl_2$ into the Ru-Cl bond in **4** and **5** provided the trimetallic and bimetallic neutral ruthenium complexes $[Ru(\eta^6\text{-cymene})(L^1SnCl)(SnCl_3)Cl]$ (**6**) and $[Ru(\eta^6\text{-cymene})(L^3PPh_2)(SnCl_3)Cl]$ (**7**) containing one trichlorostannyl ligand (Scheme 1). The insertion reaction into the remaining Ru-Cl bond in **6** and **7** by an excess of $SnCl_2$ did not proceed.



Scheme 1. Synthesis of the neutral arene ruthenium complexes **4** - **7**.

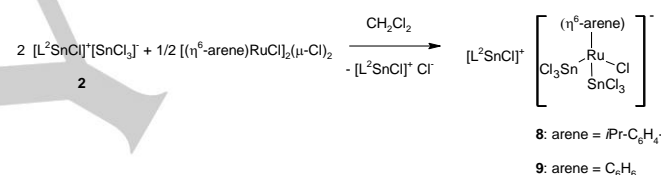
The present compounds are orange (**6**, **7**) to red (**4**) crystalline materials, which are well soluble in chlorinated solvents.

The 1H NMR spectrum of **4** showed an AB spin system for the NCH_2 protons at δ_A 4.04 and δ_B 4.18 with J_{AB} being approximately 7 Hz. The ring protons of the cymene ligand in **4** constitute an AA'BB' spin system at δ_A 5.52, $\delta_{A'}$ 5.57, δ_B 5.67 and $\delta_{B'}$ 5.71 with J_{AB} being approximately 5 Hz as the consequence of asymmetric tin atom. Accordingly, the ^{13}C NMR spectrum showed for the cymene moiety two signals at δ 82.5 and 84.1 ppm for the $C_{2,6}$ and two signals at δ 84.4 and 84.8 ppm for the $C_{3,5}$ carbon atoms. The ^{119}Sn NMR spectrum of **4** showed one signal at δ -14.6 being shifted upfield relative to **1** (δ 269.4).^[10] The NMR data obtained for compound **5** agree well with the data published earlier.^[9] However, the molecular structure of **5** was not yet determined (see discussion below).

The 1H NMR spectrum of **6** showed an AX spin system for the NCH_2 protons at δ_A 3.89 and δ_X 4.25 with J_{AB} being approximately 11 Hz. In the 1H NMR spectra of **6** and **7**, the ring protons of the cymene ligand constitute a well-resolved AA'BB' spin system at δ_A 5.80, $\delta_{A'}$ 5.88, δ_B 6.07 and $\delta_{B'}$ 6.12 with J_{AB} being approximately 5 Hz in **6** (similarly 5.24, 5.44, 5.79 and 6.09 in **7**) as a result of the three different substituents on the Ru(II) atom. In addition, the 1H NMR spectrum of **6** revealed also second set of signals with lower intensity (an AX spin system for the NCH_2 protons at δ_A 3.89 and δ_X 4.39 with $J_{AB} = 15$ Hz and AA'BB' spin system at δ_A 5.94, $\delta_{A'}$ 5.96, δ_B 6.05 and $\delta_{B'}$ 6.02 with $J_{AB} = 4$ Hz of the ring protons of the cymene ligand) proving the existence of second diastereomer in solution. In analogy to compound **4**, the ^{13}C NMR spectra showed for the cymene moiety signals at δ 84.0 and 84.9 ppm ($C_{2,6}$ carbon atoms, **6**) and at δ 86.5 and 88.7 ppm ($C_{3,5}$ carbon atoms **6**) (86.4, 86.9, 91.1 and 92.1 for **7**). The ^{119}Sn NMR spectra showed a singlet at δ -191.2 for **6** and a doublet at δ -198.5 for **7** ($^2J(^{119}Sn, ^{31}P) =$

678 Hz), clearly demonstrating the presence of the $SnCl_3$ substituent in both complexes. The values are close to those found for $[(\eta^6\text{-cymene})Ru(PPh_3)(SnCl_3)(Cl)]$ (δ -205.8, 704 Hz).^[6b] In addition, the ^{119}Sn NMR spectrum of **6** also showed a signal at δ 110.1, that corresponds to the coordinated L^1SnCl moiety. The downfield shift of this signal from δ -14.6 in **4** to δ 110.1 in **6** can be thus attributed to the insertion of the $SnCl_2$ into the Ru-Cl bond. The latter also suggests a strong influence of the $SnCl_3$ moiety on the L^1SnCl coordination ability in the parent Ru complexes. The ^{119}Sn NMR spectrum of **6** revealed also second set of signals with lower intensity at δ -191.2 and 143.9 of second diastereomer in solution. The $^{31}P\{^1H\}$ NMR spectrum of **7** revealed a signal at δ 79.4 flanked with satellites ($^2J(^{119}Sn, ^{31}P) = 665$ Hz) being shifted downfield in comparison with the parent compound **5** containing Ru-Cl bonds only (δ 57.9).^[9]

In contrast to the reactivity of the stannylene **1**, the treatment of $[L^2SnCl][SnCl_3]$ (**2**),^[8] as a possible tin containing donor ligand, with $[(\eta^6\text{-cymene})RuCl]_2(\mu\text{-Cl})_2$ and $[(\eta^6\text{-benzene})RuCl]_2(\mu\text{-Cl})_2$ gave the ionic ruthenium complexes $[L^2SnCl][Ru(\eta^6\text{-cymene})(SnCl_3)_2Cl]$ (**8**) and $[L^2SnCl][Ru(\eta^6\text{-benzene})(SnCl_3)_2Cl]$ (**9**), respectively, where an arene ruthenium anion contains two trichlorostannyl ligands (Scheme 2).



Scheme 2. Synthesis of the anionic ruthenium complexes **8** and **9**

The 1H NMR spectrum of **8** showed the ring protons of the cymene ligand resonating as two doublets at δ 5.77 and 5.87 ppm. For **9**, a singlet resonance of the benzene protons was observed at δ 5.83 ppm. The ^{119}Sn NMR spectra showed one signal at δ -160.2 for **8** and at δ -151.1 for **9**, demonstrating the equivalency of both $SnCl_3$ substituents in the arene ruthenium anions, while a second signal at δ -423.1 (for **8**) and δ -423.0 (for **9**) unambiguously validates the existence of the $[L^2SnCl]^+$ cation.^[8] The former signals are shifted downfield in comparison to the signals of the $SnCl_3$ moieties in the neutral complexes **6** and **7**. They are close to the values found in the related arene ruthenium anions (ranging from δ -164.0 to -167.2 ppm).^[6a] The latter, upfield shifted, signals are close to the value found for the $[L^2SnCl]^+$ moiety (δ -423.1).^[8a] The ionic character of **9** and the formation of $[Ru(\eta^6\text{-benzene})(SnCl_3)_2Cl]^-$ anion has been also corroborated by the ESI/MS spectrum (positive mode), showing a mass cluster centered at $m/z = 636.2$. It is assigned to the $[L^2SnCl]^+$ cation. In the negative mode, a mass cluster centered at $m/z = 666.5$ was observed and assigned to the $[Ru(\eta^6\text{-benzene})(SnCl_3)_2Cl]^-$ anion.

Solid state structures

The molecular structures of the complexes **4** – **7** and **9** were determined by X-ray diffraction analysis. Single crystals of **4**·2CHCl₃, **5**·CH₂Cl₂, **6**, **7**·CH₂Cl₂ and **9**·1.5 CH₂Cl₂, suitable for X-ray analysis, were obtained by a slow solvent evaporation from saturated solutions of **4** – **7** and **9** in the corresponding solvents. The molecular structures of **4**·2CHCl₃ and **5**·CH₂Cl₂ are shown in Figure 2, selected bond distances and bond angles are given in Table 1 and the crystallographic parameters can be consulted in Table S1 (see SI).

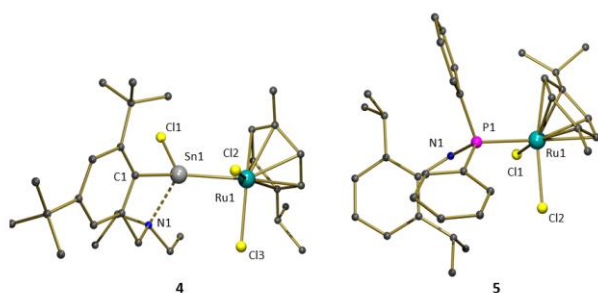


Figure 2. Pov Ray presentation of the molecular structures of **4**·2CHCl₃ and **5**·CH₂Cl₂. Hydrogen atoms and solvent molecules are omitted for clarity.

Both compounds **4**·2CHCl₃ and **5**·CH₂Cl₂ show a typical piano-stool geometry. The geometry at the ruthenium center is essentially octahedral with *cis* interligand angles in the range of 82.85(2) – 89.13(2)° in **4**·2CHCl₃ and 85.56(2) – 90.45(2)° in **5**·CH₂Cl₂, respectively. Both chlorine atoms, mutually in *cis* positions (Cl2-Ru1-Cl3 = 85.26(3)° in **4**·2CHCl₃ and Cl1-Ru1-Cl1 = 85.56(2)° in **5**·CH₂Cl₂) are coordinated *cis* to the donating atom with Sn1-Ru1-Cl3 of 89.13(2)° and Sn1-Ru1-Cl2 of 82.85(2)° in **4**·2CHCl₃ and with P1-Ru1-Cl1 = 88.93(2)° and P1-Ru1-Cl2 = 90.45(2)° in **5**·CH₂Cl₂, respectively. The Ru1-Sn1 distance (2.6006(3) Å) in **4**·2CHCl₃ and the Ru1-P1 distance (2.3729(6) Å) in **5**·CH₂Cl₂, respectively, is essentially similar to those found in the related stannylene^[11] and phosphane-arene ruthenium complexes.^[5,6] The tin atom in **4**·2CHCl₃ is four-coordinated by N1, C1, Cl1 and Ru1 atoms and exhibits a distorted tetrahedral environment. The C1-Sn1-Cl1 angle of 107.39(7)° differs from that found in the parent organostannylene **1** (93.99 (12)°),^[10] which may be attributed to the coordination of the Sn1 atom to the Ru1 atom.

The molecular structures of **6** and **7**·CH₂Cl₂ are shown in Figure 3, selected bond distances and bond angles are given in Table 1 and the crystallographic parameters can be consulted in Table S1 (see SI).

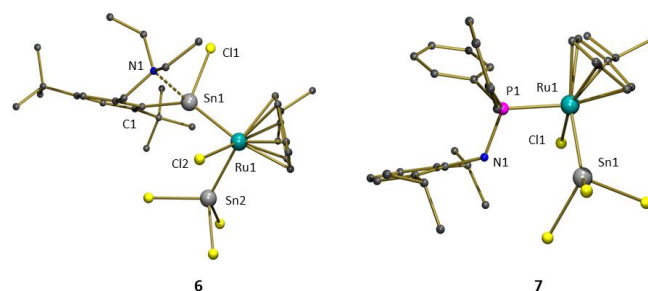


Figure 3. Pov Ray presentation of the molecular structures of **6** and **7**·CH₂Cl₂. Hydrogen atoms and solvent molecules are omitted for clarity.

Table 1. Selected bonding distances [Å] and angles [°] in **4** – **7** and **9**.

	4 ·2CHCl ₃ (E = Sn1)	5 ·CH ₂ Cl ₂ (E = P1)	6 (E = Sn1)	7 ·CH ₂ Cl ₂ (E = P1) ^[a]	9 ·1.5CH ₂ Cl ₂
Ru-E	2.6006(3)	2.3729(5)	2.5963(3)	2.3351(7)/ 2.3320(7) ^[a]	-
Ru-SnCl ₃	-	-	2.5738(3)	2.5675(3)/ 2.5697(3) ^[a]	2.5756(7) 2.5648(7)
Ru-Cl	2.4516(8) 2.4241(8)	2.4181(6) 2.3982(5)	2.4371(5)	2.3946(7)/ 2.3993(8) ^[a]	2.4146(17)
E-Ru-Cl	82.85(2) 89.13(2)	88.93(2) 90.45(2)	87.04(1)	88.68(3)/ 88.99(3) ^[a]	-
E-Ru-SnCl ₃	-	-	89.66(1)	92.79(2) /93.50(2) ^[a]	-
Cl-Ru-SnCl ₃	-	-	76.85(1)	82.54(2)/ 81.08(2) ^[a]	89.18(5) 82.38(5)
Cl ₃ Sn-Ru-SnCl ₃	-	-	-	-	89.33(2)

[a] two independent molecules

The ruthenium atom is a stereogenic center in both complexes **6** and **7**·CH₂Cl₂ due to the coordination of four different ligand atoms and thus the complexes are isolated as racemic mixtures. The complexes show a typical piano-stool geometry with the ruthenium center being coordinated by the arene, chloro, trichlorostannyl and stannylene (**6**) or phosphane (**7**·CH₂Cl₂) ligand. The octahedral geometry at the ruthenium atom is very similar to the starting complexes **4**·2CH₂Cl₂ and **5**·CH₂Cl₂ with *cis* interligand angles in the range of 76.85(1) – 89.66(1)° for **6** and 81.08(2) – 93.50(2)° for **7**·CH₂Cl₂. However, the Ru-E distances are clearly affected by the insertion reaction. Thus, the Ru1-Sn1 distance in the trichlorostannyl-substituted complex **6** (2.5963(3) Å) is slightly shorter in comparison to complex **4**·2CH₂Cl₂ (2.6006(3) Å). Similarly, the Ru1-P1 distance (2.3320(7)/2.3351(7) Å) in **7**·CH₂Cl₂ is shorter than in the starting complex **5**·CH₂Cl₂ (2.3729(5) Å). In both complexes **6** and

$7 \cdot \text{CH}_2\text{Cl}_2$, the Ru-SnCl₃ distances (2.5738(3) Å in **6** and 2.5675(3)/2.5697(3) Å in $7 \cdot \text{CH}_2\text{Cl}_2$) are somewhat shorter than those found for other neutral arene-Ru-Sn complexes (the range of 2.5977(3) - 2.5830(9) Å).^[6]

While crystalline material suitable for X-ray analysis was not obtained in the case of **8**, the molecular structure of **9**, as its dichloromethane solvate $9 \cdot 1.5\text{CH}_2\text{Cl}_2$, was determined by X-ray diffraction analysis (see Figure 4). Selected interatomic distances and angles are given in Table 1 and the crystallographic parameters are summarized in Table S1 (see SI).

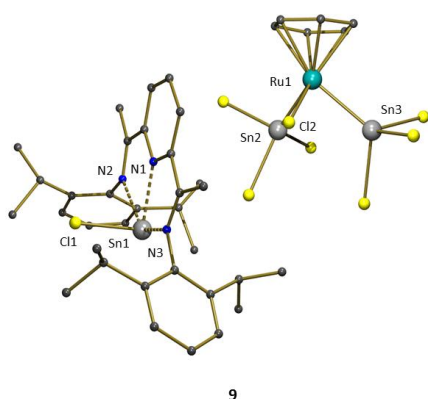


Figure 4. Pov Ray presentation of the molecular structure of $9 \cdot 1.5\text{CH}_2\text{Cl}_2$. Hydrogen atoms and solvent molecules are omitted for clarity.

The molecular structure of the ionic arene ruthenium complex $9 \cdot 1.5\text{CH}_2\text{Cl}_2$ showed the presence of the $[\text{L}^2\text{SnCl}]^+$ cation that compensates the $[\text{Ru}(\eta^6\text{-benzene})(\text{SnCl}_3)_2\text{Cl}]^-$ anion with a typical piano-stool geometry. In the $[\text{L}^2\text{SnCl}]^+$ cation, the geometry resembles that of the complex $[\text{L}^2\text{SnCl}][\text{SnCl}_3]$ reported by Roesky et al.^[8a] The Sn(1) atom is four-coordinated by three nitrogen atoms showing relatively strong N→Sn interactions with distances ranging between 2.305(5) (Sn1–N1) and 2.439(5) Å (Sn1–N3) and by one chlorine atom (Sn1–Cl1 2.416(2) Å). The ruthenium atom is coordinated by the arene, chloro and two trichlorostannyl ligands. Both Ru-SnCl₃ distances (2.5648(7) and 2.5756(7) Å) fall into the range found for the anionic arene-Ru trichlorostannyl complexes (range of 2.546(2) - 2.5673(4) Å)^[6b] and are also comparable to those found in the neutral complexes **6** and $7 \cdot \text{CH}_2\text{Cl}_2$.

Thus, a set of the arene trichlorostannyl ruthenium complexes **6** – **9** allows for the investigation of the strength of the Ru-SnCl₃ interaction. While the trimetallic arene ruthenium complexes **6** and **7** are neutral, the complexes **8** and **9** contain an anionic $[\text{Ru}(\eta^6\text{-arene})(\text{SnCl}_3)_2\text{Cl}]^-$ moiety. Therefore, the lability of the Ru-SnCl₃ bond with respect to the charge of the ruthenium complex can be evaluated. Moreover, a comparison of the complexes **4** and **5** with the related arene trichlorostannyl ruthenium complexes **6** and **7** can reveal the influence of the SnCl₃ group on the Ru-E interaction (E = Sn, P). In order to

investigate all these points in more detail, a thorough DFT computational study was performed for **4** – **7** and **9**.

Computational studies

The geometries of compounds **4–7** and **9** were fully optimized and characterized by the vibrational frequency calculations at the B3LYP/cc-pVDZ(-PP)^[12] level of theory (Figure 5) and subsequently an NBO analysis^[13] was performed. The most relevant geometrical parameters of the studied compounds are listed in Table 2 along with the Wiberg bond indices (WBI)^[14] and the natural population analysis (NPA) charges.^[15]

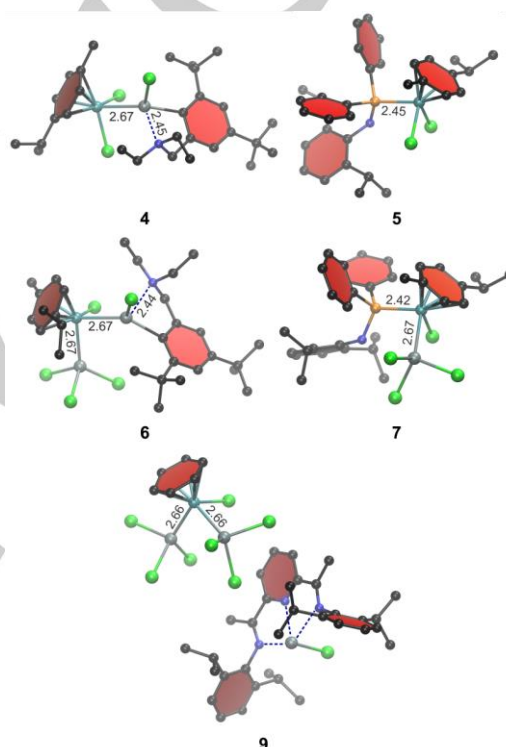


Figure 5. B3LYP/cc-pVDZ(-PP) optimized geometries of compounds **4–7** and **9** (Hydrogen atoms were omitted for clarity) along with selected distances (in Å).

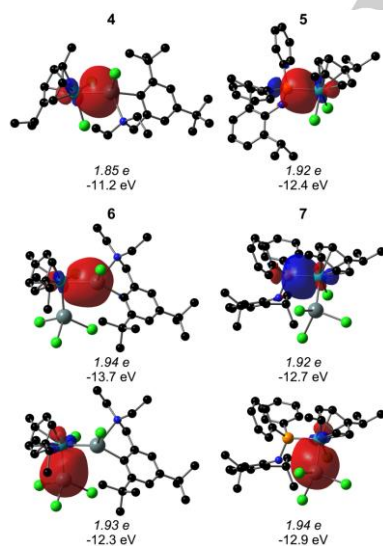
The $\text{WBI}_{\text{Ru-E}}$ for the Ru-Sn and Ru-P interaction, respectively, is predicted to be around 0.7 in the compounds **4–7**, pointing to a significant degree of covalency of the Ru-E bond. Similar $\text{WBI}_{\text{Ru-Sn}}$ values were found for the interaction of the Ru atom with the SnCl₃ fragment in the compounds **6** and **7**, suggesting a similar strength and nature of both Ru-E and Ru-Sn interactions. The calculated NPA charges revealed that the Ru-E bonds are highly polarized in the complexes **4** and **5**, with charges on the ruthenium atoms of -0.55e and -0.34e, respectively.

Table 2. Relevant bond distances (*r*, Å), Wiberg bond indices (*W*) and NPA atomic charges (*q*, e) for compounds **4–7** and **9**.

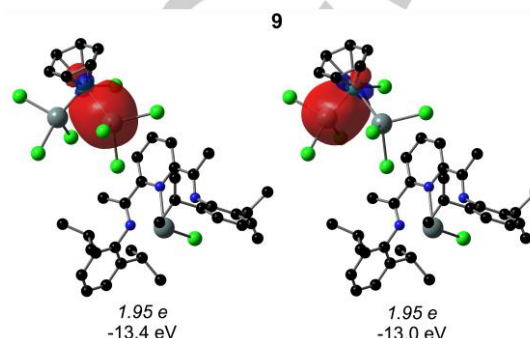
	4	5	6	7	9
	(E=Sn)	(E=P)	(E=Sn)	(E=P)	
<i>r</i> _{Ru-E}	2.668	2.449	2.668	2.416	-
<i>r</i> _{Ru-Sn} ^[a]	-	-	2.668	2.671	2.657/2.668
<i>W</i> _{Ru-E}	0.73	0.75	0.75	0.76	-
<i>W</i> _{Ru-Sn} ^[a]	-	-	0.71	0.71	0.73/0.72
<i>q</i> _{Ru}	-0.55	-0.34	-1.02	-0.78	-1.02
<i>q</i> _E	1.65	1.45	1.65	1.45	-
<i>q</i> _{Sn} ^[a]	-	-	1.51	1.52	1.53/1.53

^[a]Sn atom of the SnCl₃ fragment

The insertion of the SnCl₂ into the Ru-Cl bond increases the charge on the ruthenium atom to -1.02e and -0.78e in **6** and **7**, respectively. Consequently, this leads to a further polarization of the Ru-E bonds in **6** and **7**. Furthermore, the natural bond orbitals analysis (NBO) of **4** and **5** showed the presence of a σ(Ru-E) bond, which has a significantly higher occupancy and lower orbital energy for the Ru-P bond in **5** (Figure 6). On the other hand, upon insertion of the SnCl₂ into the Ru-Cl bond, a notable increase in occupancy and decrease in orbital energy were found for the Ru-Sn bond in **6**, while only slight changes were revealed in the case of **7**. Finally, the NBO analyses of **6** and **7** indicate that the σ(Ru-Sn) bond between the ruthenium atom and the SnCl₃ moiety is very similar in both compounds (Figure 6).

**Figure 6.** Relevant NBOs (isosurface value: 0.03 a.u.) showing σ(Ru-E) and σ(Ru-Sn) bonds in **4–7** (hydrogen atoms are omitted for clarity). NBO populations and energies are also displayed.

Despite the anionic character of **9**, the structural parameters of the anionic part of the ionic arene ruthenium complex **9**, containing two trichlorostannyl ligands, are very similar to those found for the trimetallic neutral complex **6** (Figure 5, Table 2). Consequently, the NBO analysis of **9**, showing two equivalent σ(Ru-Sn) bonds, resulted in similar values of the NBO populations and energies compared with values obtained for **6** (Figure 7).

**Figure 7.** Relevant NBOs (isosurface value: 0.03 a.u.) showing σ(Ru-Sn) bonds in **9** (Hydrogen atoms were omitted for clarity). NBO populations and energies are also displayed.

The influence of the trichlorostannyl ligand on the Ru-E interaction in the complexes **4–7** can be further evaluated with a distortion/interaction analysis. This analysis is a fragment-based approach in which the total energy of the complex (ΔE_{tot}) is decomposed into two terms: the energy associated to distorting the fragments from their initial equilibrium structures (ΔE_{dist}) and the interaction energy between those fragments (ΔE_{int}):

$$\Delta E_{\text{tot}} = \Delta E_{\text{dist}} + \Delta E_{\text{int}}$$

The fragments were selected as the C,N-chelated stannylene (L^1SnCl) and amidophosphane (L^3PPh_2) ligands, respectively, and the arene ruthenium moiety (ArRu). The results are collected in Table 5. The ΔE_{dist} refers to the distortion energy associated to either the stannylene or the phosphane ligand ($\text{L}^1\text{SnCl}/\text{L}^3\text{PPh}_2$) and ΔE_{int} is the interaction energy computed as follows:

$$\Delta E_{\text{int}} = E_{\text{ArRu}(\text{L}^1\text{SnCl}/\text{L}^3\text{PPh}_2)} - E_{\text{ArRu}} - E_{\text{L}^1\text{SnCl}/\text{L}^3\text{PPh}_2}$$

Table 3. B3LYP/cc-pVDZ(-PP) distortion (ΔE_{dist} in kcal mol⁻¹) and interaction (ΔE_{int} in kcal mol⁻¹) energies computed for compounds **4–7**.

	ΔE_{tot}	ΔE_{dist} ($\text{L}^1\text{SnCl}/\text{L}^3\text{PPh}_2$)	ΔE_{int} (ArRu-fragment)
4	-30.9	1.7	-32.5
5	-38.0	1.5	-39.5
6	-39.5	1.6	-41.2
7	-43.8	2.0	-45.8

Low values of ΔE_{dist} for compounds **4-7**, varying between 1.5 and 2.0 kcal mol⁻¹, suggest that a very small energy is required for the geometrical distortion of both stannylene and phosphane ligands. However, the ΔE_{int} values ranging from -32.5 to -45.8 kcal mol⁻¹ proved that the particular E-Ru interactions between the arene ruthenium fragment and the stannylene or phosphane ligands are very stabilizing. In line with the NBO analysis, the P-Ru interaction energy in **5** is about 7 kcal mol⁻¹ more stabilizing than the Sn-Ru interaction in **4**. Furthermore, the interaction energy in the ruthenium trichlorostannyl complexes **6** and **7** decreases to -41.2 and -43.8 kcal mol⁻¹ (cf. -32.5 and -39.5 kcal mol⁻¹ for **4** and **5**), respectively, proving thus the stabilizing effect of the SnCl₃ ligand on the strength of Ru-E interaction resulting from the increased negative charge on the ruthenium atom.

Conclusions

A set of neutral and ionic ruthenium arene trichlorostannyl complexes was prepared. While the stannylene L¹SnCl (**1**) reacts with [(η⁶-cymene)RuCl]₂(μ-Cl)₂ as a neutral donor ligand yielding the complex [Ru(η⁶-cymene)(L¹SnCl)Cl₂] (**4**), the ionic compound [L²SnCl][SnCl₃] (**2**) provided the ionic product [L²SnCl][Ru(η⁶-cymene)(SnCl₃)₂Cl] (**8**). The insertion reaction of SnCl₂ with **4** yielded the neutral trimetallic ruthenium complex [Ru(η⁶-cymene)(L¹SnCl)(SnCl₃)Cl] (**6**). Analogous complexes [Ru(η⁶-cymene)(L³PPh₂)Cl₂] (**5**) and [Ru(η⁶-cymene)(L³PPh₂)(SnCl₃)Cl] (**7**) containing the phosphane ligand L³PPh₂ (**3**) were prepared and therefore the donor-acceptor interaction of the tin(II) and phosphorus atoms with the ruthenium atoms was studied. The influence of the trichlorostannyl ligand on the Ru-E interaction in the complexes **4-7** was evaluated by structural characterization as well as by DFT calculations. The calculated NPA charges revealed highly polarized Ru-E bonds in both complexes **4** and **5** with a charge on the ruthenium atom of -0.55e in **4** and -0.34e in the phosphane-containing analogue **5**. Moreover, the insertion of SnCl₂ into the Ru-Cl bond increases the negative charge on the ruthenium atom in **6** and **7** to -1.02e and -0.78e, respectively. The influence of the trichlorostannyl ligand on the Ru-E interaction in the complexes **4-7** was further evaluated with a distortion/interaction analysis. The ΔE_{int} values were calculated for compounds **4** and **5** and showed that the Ru-P interaction energy in **5** is about 7 kcal mol⁻¹ more stabilizing than the Ru-Sn interaction in **4**. Furthermore, the interaction energy in the ruthenium trichlorostannyl complexes **6** and **7** decreases to -41.2 and -45.8 kcal mol⁻¹, respectively. It is evident that the insertion of SnCl₂ resulted in an increase of the negative charge on the ruthenium center and as a consequence, the Ru-E (E = Sn, P) interaction is stronger in **6** and **7**. The stabilization effect of the [SnCl₃]⁻ moiety is stronger for the stannylene-Ru interaction in complexes **4** and **6**, where the ΔE_{int} value rises from -32.5 to -41.2 kcal mol⁻¹.

Experimental Section

General Methods. The starting compounds **1-3** and **5** were prepared according to the literature.^[8-10] All reactions were carried out under argon, using standard Schlenk techniques. The starting complexes [(η⁶-benzene)RuCl]₂(μ-Cl)₂ and [(η⁶-cymene)RuCl]₂(μ-Cl)₂ and SnCl₂ were purchased from Sigma Aldrich. Solvents were dried by standard methods, distilled prior to use. The ¹H, ¹³C, ³¹P, and ¹¹⁹Sn NMR spectra were recorded at ambient temperature with a Bruker Avance 500 spectrometer. The chemical shifts δ are given in ppm and referenced as follows: ¹H: residual internal CHCl₃ (δ = 7.27 ppm); ¹³C: internal CDCl₃ (δ = 77.3 ppm); ³¹P: external H₃PO₄ (δ = 0.00 ppm); ¹¹⁹Sn: external SnMe₄ (δ = 0.00 ppm).

Synthesis of [Ru(η⁶-cymene)(L¹SnCl)Cl₂] (4**).** A THF (15 ml) solution of **1** (0.37 g, 0.86 mmol) with [(η⁶-cymene)RuCl]₂(μ-Cl)₂ (0.26 g, 0.43 mmol) was stirred for 2 h. The resulting solution was evaporated to dryness and the solid residue was washed with toluene/hexane. The insoluble red solid was characterized as **4** (0.54 g, 85%). M.p. 218-219 °C. ¹H NMR (CDCl₃, 500.13 MHz): δ = 1.12 (t, 3H, CH₃(Et), ³J(¹H,¹H) = 7.2 Hz), 1.19 (t, 3H, CH₃(Et), ³J(¹H,¹H) = 7.2 Hz), 1.25 (d, 6H, CH₃(iPr,cymene), ³J(¹H,¹H) = 7.8 Hz), 1.26 (s, 9H, tBu), 1.51 (s, 9H, tBu), 2.37 (s, 3H, CH₃(cymene)), 2.96 (sept. 1H, CH(iPr,cymene), ³J(¹H,¹H) = 7.8 Hz), 3.03 (m, 1H, CH₂(Et)), 3.19 (m, 1H, CH₂(Et)), 3.53 (m, 1H, CH₂(Et)), 3.72 (m, 1H, CH₂(Et)), 4.04 and 4.18 (AX system, 2H, CH₂N), 5.52 and 5.67 (AX system, 2H, ArH(cymene)), 5.57 and 5.71 (AX system, 2H, ArH(cymene)) 6.99 (s, 1H, ArH), 7.39 (s, 1H, ArH) ppm. ¹³C{¹H} NMR (CDCl₃, 125.77 MHz): δ = 7.6, 12.3 (CH₃(Et)), 18.3 (CH₃(cymene)), 22.4, 22.8 (CH₃(iPr,cymene)), 30.5 (CH(iPr,cymene)), 31.2 (CH₃(tBu)), 32.8 (CH₃(tBu)), 34.7 (C(tBu)), 36.9 (C(tBu)), 46.9, 47.8 (CH₂(Et)), 59.4 (CH₂N), 82.5, 84.1, 84.4, 84.8, 96.8, 104.1 (Ar-C(cymene)), 121.3, 124.1, 140.9, 142.9, 152.3, 157.6 (Ar-C) ppm. ¹¹⁹Sn{¹H} NMR (CDCl₃, 186.36 MHz): δ = -14.6 ppm. C₂₉H₄₆Cl₃NRuSn (734.82): calcd. C 47.40, H 6.31, found C 46.95, H 6.25.

Synthesis of [Ru(η⁶-cymene)(L¹SnCl)(SnCl₃)Cl] (**6**).

A THF (15 ml) solution of **4** (0.48 g, 0.65 mmol) with SnCl₂ (0.13 g, 0.65 mmol) was stirred for 24 h at room temperature. The resulting solution was evaporated to dryness and the solid residue was washed with toluene/hexane to provide an orange solid, which was re-crystallized from CH₂Cl₂ solution to give **6** as suitable material for X-ray diffraction analysis (0.54 g, 85%). M.p. 225-227 °C. ¹H NMR (CDCl₃, 500.13 MHz): δ = 1.09 (t, 3H, CH₃(Et), ³J(¹H,¹H) = 7.2 Hz), 1.28 (d, 6H, CH₃(iPr,cymene), ³J(¹H,¹H) = 7.6 Hz), 1.29 (s, 9H, tBu), 1.47 (t, 3H, CH₃(Et), ³J(¹H,¹H) = 7.2 Hz), 1.50 (s, 9H, tBu), 2.17 (s, 3H, CH₃(cymene)) 2.84 (sept. 1H, CH(iPr,cymene), ³J(¹H,¹H) = 7.6 Hz), 3.00 (m, 1H, CH₂(Et)), 3.08 (m, 1H, CH₂(Et)), 3.45 (m, 1H, CH₂(Et)), 3.78 (m, 1H, CH₂(Et)), 3.89 and 4.25 (AX system, 2H, CH₂N), 5.80 and 6.07 (AX system, 2H, ArH(cymene)), 5.88 and 6.12 (AX system, 2H, ArH(cymene)) 7.03 (s, 1H, ArH), 7.48 (s, 1H, ArH) ppm. ¹³C{¹H} NMR (CDCl₃, 125.77 MHz): δ = 6.5, 12.7 (CH₃(Et)), 18.6 (CH₃(cymene)), 22.0, 22.6 (CH₃(iPr,cymene)), 30.5 (CH(iPr,cymene)), 31.2 (CH₃(tBu)), 32.6 (CH₃(tBu)), 33.3 (C(tBu)), 34.8 (C(tBu)), 37.6 (CH₂(Et)), 44.6 (CH₂(Et)), 59.2 (CH₂N), 84.0, 84.9, 86.5, 88.7, 97.0, 114.0 (Ar-C(cymene)), 121.8, 125.0, 139.3, 145.2, 153.2, 157.2, 158.1 (Ar-C) ppm. ¹¹⁹Sn{¹H} NMR (CDCl₃, 186.36 MHz): δ = -191.2 (SnCl₃), 110.1 (L¹SnCl) ppm. C₂₉H₄₆Cl₅NRuSn₂ (924.44): calcd. C 37.68, H 5.02; found C 37.47, H 4.98.

Synthesis of [Ru(η⁶-cymene)(L³PPh₂)(SnCl₃)Cl] (**7**).

A THF (15 ml) solution of **5** (0.87 g, 1.30 mmol) with SnCl₂ (0.25 g, 1.30 mmol) was stirred for 24h at room temperature. The resulting

solution was evaporated to dryness and the solid residue was washed with toluene/hexane to provide orange solid, which was re-crystallized from CH_2Cl_2 / hexane solution at $+4^\circ\text{C}$ to give **7** (0.90 g, 81%). M.p. $213-215^\circ\text{C}$. ^1H NMR (CDCl_3 , 500.13 MHz): δ = 0.49 (d, 6H, $\text{CH}_3(\text{iPr})$, $^3J(\text{H}, \text{H})$ = 6.5 Hz), 0.56 (d, 6H, $\text{CH}_3(\text{iPr})$, $^3J(\text{H}, \text{H})$ = 6.5 Hz), 1.13 (s, 3H, $\text{CH}_3(\text{cymene})$), 1.18 (d, 3H, $\text{CH}_3(\text{iPr}, \text{cymene})$, $^3J(\text{H}, \text{H})$ = 7.0 Hz), 1.30 (d, 3H, $\text{CH}_3(\text{iPr}, \text{cymene})$, $^3J(\text{H}, \text{H})$ = 7.0 Hz), 2.55 (sept, 1H, $\text{CH}(\text{iPr}, \text{cymene})$, $^3J(\text{H}, \text{H})$ = 7.0 Hz), 3.09 (sept, 1H, $\text{CH}(\text{iPr})$, $^3J(\text{H}, \text{H})$ = 6.5 Hz), 4.68 (d, 1H, NH , $^2J(\text{H}, \text{P})$ = 11.5 Hz), 5.24 and 5.79 (AX system, 2H, $\text{ArH}(\text{cymene})$), 5.44 and 6.09 (AX system, 2H, $\text{ArH}(\text{cymene})$), 6.73 (d, 2H, ArH , $^3J(\text{H}, \text{H})$ = 7.5 Hz), 6.94 (t, 1H, ArH , $^3J(\text{H}, \text{H})$ = 7.5 Hz), 7.33-7.51 (m, 8H, ArH), 7.78 (m, 2H, ArH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125.77 MHz): δ = 16.2, 22.3 ($\text{CH}_3(\text{iPr}, \text{cymene})$), 23.2 ($\text{CH}_3(\text{cymene})$), 23.9 ($\text{CH}(\text{iPr})$), 28.1 ($\text{CH}_3(\text{iPr})$), 30.5 ($\text{CH}(\text{iPr}, \text{cymene})$), 86.4, 86.9, 91.1, 92.1, 97.8, 120.7 ($\text{Ar-C}(\text{cymene})$), 123.2, 126.9, 127.3, 128.1, 130.1, 131.0, 133.3, 134.7, 135.1, 137.1, 147.8, 147.9 (Ar-C) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 202.40 MHz): δ = 79.4 ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3 , 186.36 MHz): δ = -198.5 (SnCl_3 , $^2J(\text{H}, \text{P})$ = 665 Hz). $\text{C}_{34}\text{H}_{42}\text{Cl}_4\text{NPRuSn}$ (857.27): calcd. C 47.64, H 4.94; found C 47.28, H 4.75.

Synthesis of $[\text{L}^2\text{SnCl}][\text{Ru}(\eta^6\text{-cymene})(\text{SnCl}_3)_2\text{Cl}]$ (**8**).

A CH_2Cl_2 (30 ml) solution of **3** (0.60 g, 0.7 mmol) was added with stirring to $[(\eta^6\text{-cymene})\text{RuCl}]_2(\mu\text{-Cl})_2$ (0.1 g, 0.175 mmol) at room temperature. The reaction mixture was further stirred for additional 24 h. The solution was filtered and the filtrate was concentrated to a volume of approximately 10 ml. Storing it overnight at 4°C gave the orange solid of **8** (0.43 g, 91%). M.p. 208.3°C with dec.; ^1H NMR (CDCl_3 , 500.13 MHz): δ = 1.16 (d, 12H, $\text{CH}(\text{CH}_3)_2$, $^3J(\text{H}, \text{H})$ = 8.0 Hz), 1.23 (d, 12H, $\text{CH}(\text{CH}_3)_2$, $^3J(\text{H}, \text{H})$ = 8.0 Hz), 1.25 (d, 6H, iPr , cymene , $^3J(\text{H}, \text{H})$ = 6.0 Hz), 2.15 (s, 3H, iPr , cymene), 2.64 (s, 6H, $(\text{CH}_3)_2\text{C}=\text{N}$), 2.75 (sept, 4H, $\text{CH}(\text{CH}_3)_2$, $^3J(\text{H}, \text{H})$ = 8.0 Hz), 2.86 (sept, 1H, iPr , cymene , $^3J(\text{H}, \text{H})$ = 6.0 Hz), 5.77 and 5.88 (dd, 4H, $\text{ArH}(\text{cymene})$), 7.30-7.39 (m, 6H, ArH), 8.61 (d, 2H, ArH , $^3J(\text{H}, \text{H})$ = 8.5 Hz), 8.93 (t, 1H, ArH , $^3J(\text{H}, \text{H})$ = 8.5 Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125.77 MHz): δ = 18.8 ($\text{CH}_3(\text{iPr})$, cymene), 19.6 ($(\text{CH}_3)_2\text{C}=\text{N}$), 22.8 (CH_3 , cymene), 24.8 ($\text{CH}_3(\text{iPr})$), 25.2 ($\text{CH}_3(\text{iPr})$), 28.4 ($\text{CH}(\text{iPr})$), 29.3 ($\text{CH}(\text{iPr})$), 30.9 ($\text{CH}(\text{iPr})$, cymene), 84.9, 86.5, 102.1, 108.9, 124.9, 125.0, 128.2, 130.8, 136.8, 139.5, 140.4, 147.0, 149.6, 169.3 ($\text{C}=\text{N}$) ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3 , 186.36 MHz): δ = -160.2 (SnCl_3), -423.1 ($[\text{L}^2\text{SnCl}]^+$) ppm. $\text{C}_{43}\text{H}_{57}\text{N}_3\text{Cl}_8\text{RuSn}_3$ (1356.7): calcd. C 38.07, H 4.23; found C 38.25, H 4.35.

Synthesis of $[\text{L}^2\text{SnCl}][\text{Ru}(\eta^6\text{-benzene})(\text{SnCl}_3)_2\text{Cl}]$ (**9**).

A CH_2Cl_2 (30 ml) solution of **3** (0.60 g, 0.7 mmol) was added with stirring to $[(\eta^6\text{-benzene})\text{RuCl}]_2(\mu\text{-Cl})_2$ (0.09 g, 0.175 mmol) at room temperature. The reaction mixture was further stirred for additional 24 h. The solution was concentrated to a volume of approximately 10 ml. Storing it at room temperature for three days provided the orange solid of **9** ($1.5\text{CH}_2\text{Cl}_2$ (0.8 g, 86%). M.p. 221.8°C with decomp.; ^1H NMR (CDCl_3 , 500.13 MHz): δ = 1.14 (d, 12H, $\text{CH}(\text{CH}_3)_2$, $^3J(\text{H}, \text{H})$ = 7.2 Hz), 1.22 (d, 12H, $\text{CH}(\text{CH}_3)_2$, $^3J(\text{H}, \text{H})$ = 7.2 Hz), 2.62 (s, 6H, $(\text{CH}_3)_2\text{C}=\text{N}$), 2.74 (bs, 4H, $\text{CH}(\text{CH}_3)_2$), 5.83 (s, 6H, C_6H_6), 7.15 – 7.31 (m, 6H, ArH), 8.61 (d, 2H, ArH , $^3J(\text{H}, \text{H})$ = 7.8 Hz), 8.91 (t, 1H, ArH , $^3J(\text{H}, \text{H})$ = 7.8 Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125.77 MHz): δ = 19.6 ($\text{CH}_3(\text{iPr})$), 22.8 ($(\text{CH}_3)_2\text{C}=\text{N}$), 24.9 ($\text{CH}(\text{iPr})$), 86.7, 125.3, 128.2, 129.0, 130.7, 136.7, 140.4, 149.6, 169.3 ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3 , 186.36 MHz): δ = -159.1 (SnCl_3), -423.0 ($[\text{L}^2\text{SnCl}]^+$) ppm. ESI/MS: positive part m/z 636.2 $[\text{L}^2\text{SnCl}]^+$; negative part m/z 666.5 $[\text{Ru}(\eta^6\text{-benzene})(\text{SnCl}_3)_2\text{Cl}]$. $\text{C}_{40.5}\text{H}_{52}\text{N}_3\text{Cl}_{11}\text{RuSn}_3$ (1427.94): calcd. C 34.03, H 3.93; found C 35.09, H 3.80.

Crystallography. Single crystals of **4**· 2CHCl_3 , **5**· CH_2Cl_2 , **6**, **7**· CH_2Cl_2 and **9**· $1.5\text{CH}_2\text{Cl}_2$ were obtained by slow evaporation from dichloromethane

(for **5**, **6**, and **9**) or chloroform (for **4**) solutions. Crystals were mounted on a glass fiber with an inert viscous oil and measured on a KappaCCD diffractometer with a CCD area detector by monochromatized MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 150(2) K (**4**· 2CHCl_3 , **5**· CH_2Cl_2 , **6**, **7**· CH_2Cl_2). Intensity data for **9**· $1.5\text{CH}_2\text{Cl}_2$ were collected on an XcaliburS CCD diffractometer (Oxford Diffraction) using Mo-K_α radiation at 110 K. The details pertaining to the data collection and refinement for crystals are given in Table S1 (see Supporting Information). Data reductions were performed with DENZO-SMN (**4**· 2CHCl_3 , **5**· CH_2Cl_2 , **6**, **7**· CH_2Cl_2).^[16] The absorption was corrected by integration methods (**4**· 2CHCl_3 , **5**· CH_2Cl_2 , **6**, **7**· CH_2Cl_2).^[17] Structures were solved by direct methods (Sir92)^[18] (**4**· 2CHCl_3 , **5**· CH_2Cl_2 , **6**, **7**· CH_2Cl_2) and SHELXS-97^[19] (**9**· $1.5\text{CH}_2\text{Cl}_2$), respectively, and refined by full matrix least-square based on F^2 (SHELXL97 and SHELXL2014/6, respectively).^[20] Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{pivot atom})$ or of $1.5 U_{\text{eq}}$ for the methyl moiety with C-H = 0.98, 0.97, and 0.93 Å for methyl, methylene and hydrogen atoms in aromatic rings, respectively. The structure of compound **5** contains a disorder of one of the chlorine atoms in the dichloromethane molecule, the chlorine atom was split into two positions with an occupancy of about 1:1. This disorder has been treated by standard SHELXL software instructions.^[20] CCDC-1511592 (**4**· 2CHCl_3), CCDC-1511593 (**5**· CH_2Cl_2), CCDC-1511594 (**6**), CCDC-1511595 (**7**· CH_2Cl_2) and CCDC-1518855 (**9**· $1.5\text{CH}_2\text{Cl}_2$) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details. All calculations were carried out using Density Functional Theory (DFT) as implemented in the Gaussian09 quantum chemistry program.^[21] Geometry optimizations were carried out at the B3LYP/cc-pVDZ level of theory (for heavier atoms - Ru and Sn - the cc-pVDZ-PP basis set including small-core relativistic pseudopotentials that account also for relativistic effects was used).^[12] The electronic energies were re-evaluated by additional single point calculations on each of all optimized geometries using the triple- ζ -quality cc-pVTZ(-PP) basis set. Analytical vibrational frequencies within the harmonic approximation were computed with the cc-pVDZ basis set to confirm proper convergence to well-defined minima or saddle points on the potential energy surface. Subsequent NBO analysis^[13] and calculation of Wiberg bond indices^[14] were performed at the B3LYP6/cc-pVDZ(-PP) level.

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Keywords: tin • ruthenium • NMR • DFT calculations • complexes

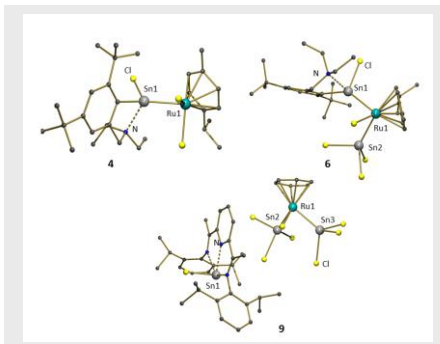
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FULL PAPER

A set of Sn(II)-Ru arene trichlorostannyl complexes was prepared. As a result of different properties of tin(II) donor ligands, either neutral or ionic trimetallic arene ruthenium complexes were isolated. Structurally related phosphane compounds were also prepared and the E – Ru donor-acceptor interactions (E = Sn, P) were studied by DFT calculations. Moreover, the influence of the trichlorostannyl ligand on the Ru-E interaction was evaluated with a distortion/interaction analysis

**Tin-ruthenium complexes**

Miroslav Novák, Marek Bouška, Libor Dostál, Michael Lutter, Klaus Jurkschat, Jan Turek, * Frank De Proft, Zdeňka Růžicková, Roman Jambor*

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