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SnCl₂ insertion into Ir–Cl and Rh–Cl bonds: Synthesis, characterization and catalytic activity of three-legged piano-stool trichlorostannyl iridium and rhodium complexes



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ABSTRACT

Facile insertion reaction of SnCl₂ across pentamethylcyclopentadienyl complexes of Ir(III) and Rh(III) resulted in the formation of Ir–SnCl₃ and Rh–SnCl₃ heterobimetallic complexes. Treatment of SnCl₂ with [Cp*IrCl₂]₂ and [Cp*Ir(NH⁴₂Bu)Cl₂] afforded [Cp*Ir(SnCl₃)₂[SnCl₂(H₂O)₂] (1) and [Cp*Ir(SnCl₃)₃][NH⁴₃Bu] (3), respectively. Similarities in NMR data for complexes 1 and 3 suggested that complex 1 converts to anionic [Cp*Ir(SnCl₃)₃] species in solution via rapid chloride exchange. Similarly, insertion reaction of SnCl₂ with [Cp*Ir(Ph₃)Cl₂] and [Cp*Rh(PPh₃)Cl₂] afforded single insertion complex [Cp*Ir(PPh₃)(SnCl₃) Cl] (2) and double insertion complex [Cp*Rh(PPh₃)(SnCl₃)₂] (4), respectively. All these new complexes were characterized by multinuclear NMR spectroscopy, while complexes 1, 3 and 4 were structurally characterized by single crystal X-ray diffraction technique. Complexes 1–4 were also tested as catalyst for bisarylation of aldehyde with arene and it was observed that only complexes 1 and 3 were active. Scope of this organic reaction was examined for different arenes and heteroarenes and in all the cases very good yields of triarylmethane derivatives were achieved.

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1. Introduction

Transition metal (Tm) complexes having trichlorostannyl (SnCl₃) ligands display remarkable efficacy in various homogenous catalytic organic transformations like hydrogenation, hydro-formylation, polymerization, alkene isomerization, water gas shift reaction and different coupling reaction [1]. Thus designing of such complexes and exploring their catalytic activity still remain as an ongoing field of interest within a broad area of organometallic chemistry. Among the synthetic methods available for constructing Tm–SnCl₃ motif, oxidative addition and insertion reaction are two most widely used pathways. In the oxidative addition approach, a stannic chloride molecule (SnCl₄) is being added to a transition metal complex where the transition metal has a vacant coordination site and it is in relatively lower oxidation state. In this case the metal is getting inserted into a Sn–Cl bond of SnCl₄, thus the formal

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oxidation state of the metal and electron count of the complex increase by two units. Thus the oxidative addition of SnCl₄ to a transition metal complex leads to the generation of 'Cl–Tm–SnCl₃' unit (Eq (1)). Facile oxidative addition reaction is possible with electron-rich, low-valent, and coordinatively unsaturated transition metal complexes favoring two-electron redox couple. Among the others, low-valent d⁸ and d¹⁰ complexes are generally very common which undergo oxidative addition with many substrates. Square planar group 9 (e.g., cobalt, rhodium and iridium in their +1 oxidation state) and group 10 (e.g., nickel, palladium, platinum in their 0 or +2 oxidation state) metal complexes are very much known for their easy approach towards oxidative addition with SnCl₄ [2].

$$[L]Tm + SnCl_4 \xrightarrow{\text{Oxidative Addition}} [L]Tm(Cl) - SnCl_3$$
(1)

$$[L]Tm - Cl + SnCl_2 \xrightarrow{Insertion Reaction} [L]Tm - SnCl_3$$
(2)

On the other hand, a trichlorostannyl ligand is formed from insertion of stannous chloride $(SnCl_2)$ in transition metal-chlorine bond with no change of formal oxidation state of the central metal (Eq (2)). Thus, a formal insertion of $SnCl_2$ into a Tm-Cl bond



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produces a bimetallic 'Tm–SnCl₃' motif where the transition metal can be in low or high oxidation state. For the insertion of a SnCl₂ group into a Tm–Cl bond, one can consider two possible mechanisms. Firstly, the reaction might proceed by coordination of a SnCl₂ molecule, perhaps solvated, to the transition metal, followed by an intramolecular migration of the halide group from the transition metal to the tin atom. Alternatively, the active species might be SnCl₃, produced under the reaction conditions, which could displace halide ions in S_N1 or S_N2 reaction pathways [3].

Moreover, the above synthetic strategies are interesting in view of the fact that they bring desirable electronic features in the multimetallic Tm-SnCl₃ motif for potential application within cooperative catalysis regime. The key features which induce catalytic activity by the Tm–SnCl₃ motif include a high valent and electrophilic transition metal center (Tm), an electrophilic trichlorostannyl group (SnCl₃) and the most importantly the bond between these two fragments. Thus, as a whole the Tm-SnCl₃ moieties can act as a mild and controlled Lewis acid to trigger electrophilic activation and indeed we have delineated success in harnessing catalytic reactivity utilizing the concepts. For example, quite recently we and other research groups [4] have illustrated the unique reactivity of multimetallic catalysts in activating electrophiles, such as benzylic alcohols [5a,5e,5g], propargylic alcohols [5g,6a], allylic alcohols [5f,5g], ethers [5c], aldehydes [5b,5e,6b,6c], aldimines [5i,6d], α , β -unsaturated ketone [5h,6e,6f,6g], α -methyl substituted aryl alkene [5], epoxide [6h,6i] and γ -hydroxy lactams [5d] towards carbon-carbon and carbon-heteroatom bond formation. In view of the above facts, we demonstrate here the formation of Ir-SnCl₃ and Rh-SnCl₃ frameworks via the insertion reaction of SnCl₂ across the half-sandwich complexes of iridium and rhodium. It may be noted that, although examples of insertion of SnCl₂ across Group 10 metal complexes are well known, those across Group 9 metal complexes are relatively rare [7]. In this article we wish to report the synthesis and characterization of some threelegged piano-stool trichlorostannyl complexes of iridium (III) and rhodium (III) via the insertion reaction of SnCl₂ and their catalytic activity towards the alkylation reaction of aromatic aldehyde.

2. Results and discussion

2.1. Synthesis of iridium and rhodium complexes having trichlorostannyl ligands

A multimetallic three-legged piano-stool complex of iridium, $[Cp*Ir(SnCl_3)_2{SnCl_2(H_2O)_2}]$ **1** bearing two trichlorostannyl ligands was synthesized via insertion of SnCl₂ across the Ir–Cl bonds of $[Cp*IrCl_2]_2$ in refluxing 1,2-dichloroethane (Scheme 1). The initially brick-red solution slowly turned greenish yellow on completion of the reaction. Upon slow diffusion of *n*-hexane to this solution, the product **1** crystallized out as greenish yellow blocks in good yield [5d].

This reaction could also be done in chlorinated solvents like dichloromethane at room temperature. But at room temperature the reaction yield was highly compromised. In aromatic solvents



Scheme 1. Insertion Reaction of SnCl₂ across [Cp*IrCl₂]₂.

like benzene or toluene this reaction did not proceed at all. The multimetallic complex **1** is air and moisture stable in solid as well as solution phase but it turned in to an oily paste after prolong exposure to moisture. This complex is soluble in polar solvents like DMSO, DMF, MeCN, MeOH, acetone, hot DCM, and hot DCE; and sparingly soluble in CHCl₃ and insoluble in benzene, toluene or xylene.

Another three-legged piano-stool complex of iridium, $[Cp*Ir(PPh_3)(SnCl_3)Cl]$ **2** having one trichlorostannyl ligand and one triphenylphosphine was synthesized via the insertion reaction of SnCl₂ across $[Cp*Ir(PPh_3)Cl_2]$ in 1,2-dichloroethane at room temperature (Scheme 2). After overnight stirring the color of the solution changes from deep yellow to pale yellow and the product **2** was isolated as yellow powder by precipitating using *n*-hexane. Unfortunately, the various attempt to purely synthesize double insertion iridium complex, $[Cp*Ir(PPh_3)(SnCl_3)_2]$ with two trichlorostannyl ligands and one triphenylphosphine ligand was unsuccessful as the insertion of SnCl₂ across $Cp*Ir(PPh_3)Cl_2$ at higher reaction temperature always afforded the mixture of single and double insertion complexes [8].

An interesting ionic complex of iridium, $[Cp^*Ir(SnCl_3)_3][NH_3^tBu]$ **3** having three trichlorotannyl ligands was synthesized when the insertion reaction of SnCl₂ across $[Cp^*Ir(NH_2^tBu)Cl_2]$ was attempted in 1,2-dichloroethane at refluxing condition (Scheme 3). The complex **3** was obtained as yellow crystals upon slow diffusion of *n*hexane to the yellow solution of 1,2-dichloroethane. Our initial plan was to synthesize the double insertion complex or iridium with an σ -donor ligand like *tert*-butylamine. Instead of getting the desired complex, we came up with an ionic complex of iridium having *tert*butylammonium as the counter cation. The complex **3** is highly soluble in polar solvents like DMSO, DMF, MeCN, MeOH, acetone, DCM, and DCE, CHCl₃ and sparingly soluble in hydrocarbon solvents like benzene, toluene or xylene.

An analogous double insertion rhodium complex, [Cp*Rh (PPh₃)(SnCl₃)₂] **4** was synthesized via the insertion reaction of SnCl₂ across [Cp*Rh(PPh₃)Cl₂] in 1,2-dichloroethane at refluxing condition (Scheme 4). Interestingly, in this case we were unable to isolate any single insertion rhodium complex even carrying out the reaction at room temperature. Very much like the behavior of analogous iridium complex, a mixture of single and double insertion rhodium complex was always isolated.

2.2. NMR spectroscopic analysis of complex 1-4

All NMR spectra were recorded in deuterated acetone at room temperature. All the NMR data are shown in Table 1. The ¹H NMR spectra of **1–4** show characteristic peaks due to $C_5(CH_3)_5$ protons of the iridium or rhodium coordinated pentamethylcyclopentadienyl group at around 1.5–2.5 ppm. While the Cp* peaks are appeared as singlet in the proton NMR spectra for complexes **1** and **3**, for complexes **2** and **4** those are observed as doublet due to the ⁴*J*_{H–P} coupling (coupling constants are in the range of 2.0–3.6 Hz). Due to the long range ⁴*J*_{H–Sn} coupling, the satellite peaks (having the coupling constants of 29–42 Hz) appear in the ¹H NMR spectra of



Scheme 2. Insertion reaction of SnCl₂ across [Cp*Ir(PPh₃)Cl₂].



Scheme 3. Insertion Reaction of SnCl₂ across [Cp*Ir(NH^t₂Bu)Cl₂].



Scheme 4. Insertion reaction of SnCl₂ across [Cp*Rh(PPh₃)Cl₂].

these complexes [9]. For complexes **2** and **4**, the ¹H NMR spectra also have the distinctive aromatic signals due to triphenylphosphine group. In the proton NMR spectrum of complex **3**, the strong singlet at 1.55 ppm and a broad multiplet at 7.78 ppm are also observed due to the counter *tert*-butylammonium cation. The ¹³C NMR spectra for all the complexes show the characteristic signals for methyl and ring carbons of Cp* group at around 8–10 ppm. In addition, for complexes **2** and **4**, the spectra have the signals for coordinated triphenylphosphine in the aromatic region. Similarly for complex **3**, the ¹³C NMR spectra contain the signals at 26.8 and 55.5 ppm for the *tert*-butylammonium group. The ³¹P NMR spectra for complexes $\mathbf{2}$ and $\mathbf{4}$ show the signal at -2 and 40 ppm, respectively. In the ³¹P NMR spectra of **4** the I_{P-Rh} coupling is observed and the coupling constant of 138 Hz is in good agreement with values found in other Rh–P complexes [10]. For both the complexes **1** and **3**, the 119 Sn NMR spectra show the signal at -311 ppm with the ²J_{Sn-Sn} coupling constant of 2.9 kHz. Similarities in NMR spectroscopic data for 1 and 3 suggest that complex 1 converts to the anionic [Cp*Ir(SnCl₃)₃] species in solution via rapid chloride exchange [11].

2.3. Solid state crystal structures of complex 1, 3 and 4

Suitable crystals for X-ray diffraction studies for the complexes crystallized in different crystalline systems and space groups (monoclinic, *P21/a* for **1**, monoclinic *C2/c* for **3** and monoclinic, *P21/ n* for **4**). Structures of the complexes **1**, **3** and **4** were confirmed by X-ray crystallographic analysis. The ORTEP diagrams of 1, 3 and 4 are shown in Figs. 1–3, which illustrate that the basic structural

Table 1

Proton-1, carbon-13, phosphorous-31 and tin-119 data of complexes 1-4.ª

features are similar in all the cases. The principal crystallographic data and refinement parameters are listed in Table 2. Selected structural parameters for these compounds are given in Table 3.

All compounds displays the usual distorted three-legged pianostool geometry as is common to the Cp*M (M = Ir or Rh in +3oxidation state) complexes. The geometry around the central transition metal (M) is formally octahedral with the Cp* ligand occupying three coordination positions and the others three occupied by stannyl or triphenylphosphine ligands. Due to the steric demand of the Cp* group the geometry around the transition metal turns out to be distorted, confirmed by Sn-M-X(X = Sn or P)angles of 88.91(3)° to 95.66(6)°, with remaining Cp(centroid)-M-X angles of 120.49(3)° to 127.86(6)° (Table 3).

The distance between Cp(centroid) and M is of 1.866(4) Å to 1.899(7) Å which lies in the expected range of other known Cp*M complexes. The M-Sn distances, ranging from 2.5507(11) Å to 2.5743(8) Å are short but comparable to other M-Sn distances [5,12]. Dehen and coworkers in 2000 reported a very similar type of complexes of Co(III) having SnCl₃ ligands and they also observed the similar structural pattern in those complexes [13]. In the complex 4, the Rh–P length is 2.357(2) Å which is well within the values expected for this family of compounds.

Due to the same steric requirement of bulky Cp* ligand, the tin atoms (all three tin centers in case of 3 or Sn1, Sn2 in cases of 1 and 4) are also placed in the center of distorted rather than ideal tetrahedral coordination environment in the SnCl₃ groups, confirmed by M-Sn-Cl angles of 110.73(12)°-132.58(7)°, with remaining Cl-Sn-Cl angles of 95.18(10)°-101.28(9)°. In these complexes the Sn-Cl bond distances, ranging from 2.343(3) Å to 2.384(2) Å, are little short but comparable with other known Sn-Cl distances [9,10]. Curiously, one Sn–Cl distance in a SnCl₃ group is slightly longer (in the range of 2.38 Å) than the other two (in the range of 2.35 Å) in all the complexes and this structural behavior was also observed in a very few complexes like in $[(\eta^5-(1S)-1-(6$ methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl) ethane)Fe(CO)₂SnCl₃] reported by McArdle in 1997 and CpRu[η^3 -CH₂C(Me)CHC(Me)O]-(Cl)(SnCl₃) reported by Paz-Sandoval in 2002 [14].

In 1, the Sn3 is five-coordinate with geometry that is best described as trigonal bipyramidal with the two oxygen atoms (O1w and O2w) occupying the axial sites (Fig. 1). The IrSnCl₂ unit is nearly planar with Sn3 only 0.009 Å out of the IrCl₂ plane. However the trigonal bipyramid is significantly distorted toward a square pyramid with Iridium at the axial site, confirmed by the O1w-Sn3-O2w angle of 161.30(3)° and the Cl7-Sn3-Cl8 angle of $104.44(13)^{\circ}$. The Sn–O bond lengths are similar to those (2.276(7)) and 2.344(7) Å) in $[HPt(PEt_3)(SnR_2){Sn(OMe)R_5}_2(SnR_3)]$ (R = p-CH₃C₆H₄) [15] and (2.350(8) and 2.356(8) Å) in W(CO)₅ {SnC1₂(THF)₂} [16].

Complex	δ _H		δς			δ_{P}	δ_{Sn}
	C ₅ (C H ₃) ₅	$P(C_6H_5)_3$	C ₅ (C H ₃) ₅	C ₅ (CH ₃) ₅	P(C ₆ H ₅) ₃		
1	2.29 ^b		10.4	98.0			-311 ^c
2	1.57 ^d	7.50-7.64	7.9	97.4	128.4, 130.9, 134.3, 134.7	-2	NR ^e
3	2.30 ^f		9.9	98.2			-311 ^c
4	1.82 ^g	7.53-7.61	10.0	106.9	128.9, 130.2, 131.8, 134.7	40 ^h	NR

^a Measured at 161.9 MHz (³¹P) or 149.1 MHz (¹¹⁹Sn) in acetone-*d*₆ solvent.

^b ${}^{4}J_{H-Sn} = 28$ Hz.

 $^{c} {}^{2}J_{Sn-Sn} = 2.9$ MHz. $^{d} {}^{4}J_{H-P} = 2.0$ Hz.

NR = not recorded.

 ${}^{f}{}^{4}J_{H-Sn} = 29$ Hz. ${}^{g} {}^{4}J_{H-P} = 3.6$ Hz.

 h $J_{P-Rh} = 138$ Hz.



Fig. 1. ORTEP diagram of $1\makebox{-}3H_2O$ with 50% probability thermal ellipsoids. H atoms are not shown for clarity.

2.4. Catalytic activity

The catalytic activity of **1–4** was evaluated for bisarylation of aldehyde leading to formation of triarylmethane derivatives as the motifs bearing triarylmethane (TRAM) and their heterocyclic analogs can be used to construct a wide range of bioactive molecules, dyes, dendrimers and NLOs [17]. Instead of their usefulness, there are limited numbers of report known in the literature for the clean synthesis of TRAMs via Lewis acid catalyzed alkylation of arenes with aldehyde [14,18]. Usually the aforementioned process suffers limitations in terms of multiple products, high catalyst loading or even stoichiometric amount of Lewis acid and drastic reaction conditions. So, in this section we demonstrate the utility of the Tm–SnCl₃ motifs as in **1–4** for the straightforward synthesis of TRAMs from the aromatic aldehydes and arenes or heteroarenes.

Initially a model study on the bisarylation of 4-nitroben zaldehyde with thiophene was tested for the synthesis of the desired (4-nitrophenyl)-bis-(2-thienyl)methane **6a** (Table 4). It was observed that while the multimetallic Ir–SnCl₃ complexes **1** and **3** had the highest catalytic activity; complexes **2** and **4** are completely inactive. The drastic catalytic activity difference between these two types of complexes may be due to the fact that as strong electron donating ligand like PPh₃ is attached to central transition metal in case of complex **2** and **4**, they lack sufficient electrophilicity to



Fig. 2. ORTEP diagram of $3\cdot\rm H_2O$ with 50% probability thermal ellipsoids. H atoms are not shown for clarity.

perform as Lewis acidic catalyst. The similarity in catalytic activity for complexes **1** and **3** again suggests the fact that **1** converts to the anionic $[Cp^*Ir(SnCl_3)_3]$ species in solution via rapid chloride exchange (**1** and **3** also have similar NMR spectra, see Table 1). Another bimetallic complex from our group, $[(COD)Ir(SnCl_3)Cl(\mu Cl)]_2$, synthesized from the oxidative addition of SnCl₄ across $[(COD)IrCl]_2$ shows moderate catalytic activity (entry 5, Table 4) [**5a**]. The bisarylation reaction was also tried to perform with 5% loading of only $[Cp^*IrCl_2]_2$, only SnCl₂, only SnCl₄ but in no cases merely any yield of the bisarylated product was isolated.

The generality of the bisarylation of aldehyde to form TRAMs **6** were tested with various aromatic aldehydes **5** and arenes or heteroarenes (Table 5). We were delighted to find that very good yields of the TRAMs **6** were obtained with both *para-* and *ortho*-substituted benzaldehydes. It is important to mention that in every case the starting aldehyde was fully consumed.

3. Conclusion

In conclusion, the trichlorostannyl complexes of iridium are found as useful catalysts for the bisarylation of aldehyde to synthesize TRAM derivatives. These complexes were synthesized via insertion reaction of SnCl₂ across the Ir–Cl or Rh–Cl bonds of different iridium or rhodium complexes. All the synthesized complexes well characterized by multinuclear NMR. Three of the complexes were structurally characterized by single crystal X-ray diffraction method. Further, from the NMR analysis and catalytic activity it was revealed that complex **1** may be present in a symmetric ionic form in the solution state.

4. Experimental section

4.1. General

¹H NMR spectra were recorded at 300 K, at 200 MHz and 400 MHz, chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃: δ 7.26 ppm, (CD₃)₂CO: δ 2.05 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling



Fig. 3. ORTEP diagram of 4 with 50% probability thermal ellipsoids. H atoms are not shown for clarity.

Table 3

Selected bond distances (Å) and angles (°) for 1, 3 and 4.

Table 2	
Summary of crystallographic data and structure refinement for complexes 1 3 and 4	4

$1 \cdot 3H_2O$ 3.H20 4 Empirical formula C10H25Cl8IrO5Sn3 C14H29Cl9IrNOSn3 C28H30Cl6PRhSn2 Formula weight 1057.17 1094.70 950.56 Crystal description, Block, green Block, yellow Block, orange color Crystal size (mm) $0.20\times0.14\times0.08~0.18\times0.14\times0.10~0.18\times0.16\times0.12$ Monoclinic Monoclinic Monoclinic Crystal system Space group P21/a C2lcP21/n 9.5026(4) 23.656(5) 11.5482(14) a (Å) b (Å) 34.1358(13) 19.388(5)16.102(2)c (Å) 9.7418(4) 17.985(5)17.997(2)90 90 90 α (°) 90.252(4) 116.922(10) 129.313(8) $\beta(^{\circ})$ γ(°) 90 90 90 V (Å³) 2817.6(2) 6382.0(3) 3346.5(7) 4 8 4 $D_{\text{calc}} (\text{mg/m}^3)$ $\mu (\text{mm}^{-1})$ 2.492 2.279 1.886 8113 7 2 4 1 2 5 1 4 Total no. 42,100 36,445 22,212 reflections Unique reflections 8842 5349 3400 $R_1 = 0.0655$, $R_1 = 0.0365$, Final R indices $R_1 = 0.0405$. $[I > 2\sigma(I)]$ $wR_2 = 0.1523$ $wR_2 = 0.0903$ $wR_2 = 0.0716$ Goodness-of-fit 1.010 1.013 0.892 Largest diff. 1.940/-7.100 0.602/-0.965 0.877/-0.676 peak/hole $(e.Å^{-3})$

constant (Hz), integration. ¹³C NMR spectra were recorded at 54.6 MHz and 100 MHz with proton decoupling at 300 K. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃: δ 77.0 ppm, (CD₃)₂CO: δ 29.9 and 206.7 ppm). ³¹P{¹H} NMR spectra were recorded at 162 MHz and ¹¹⁹Sn^{{1}H} NMR spectra were recorded at 149 MHz. An elemental analyzer was used to collect microanalytical data (C, H, N). Melting points were determined on a melting point apparatus and are uncorrected. Single crystal X-ray crystallographic data were collected using graphite monochromated MoKa radiation $(\lambda = 0.71073 \text{ Å})$ on a diffractometer equipped with CCD area detector at 298 K. The structure was solved by direct method and refined by least square method on F^2 employing WinGX or Olex2 crystallographic package and the relevant programs (SHELX-97 [19] and ORTEP-3 [20]). Non-hydrogen atoms were refined anisotropically and hydrogen atoms on carbon atoms were fixed at calculated positions and refined using a riding model.

All preparations and manipulations have been performed under an inert atmosphere of argon. All solvents used for the synthesis have been dried and distilled by standard methods. Pre-coated silica gel $60F_{254}$ was used for thin layer chromatography (TLC) and silica gel 60-120 and 100-200 mesh was used for column chromatography. Petroleum ether refers to the fraction boiling in the range 60-80 °C. IrCl₃·xH₂O, RhCl₃·xH₂O, 1,2,3,4,5pentamethylcyclopentadiene (Cp*H), triphenylphosphine (PPh₃), tert-butylamine (^tBuNH₂) and SnCl₂·2H₂O were commercially available and were used without further purification. Dry SnCl₂ was prepared from commercially available SnCl₂·2H₂O. [Cp*IrCl₂]₂ [21], [Cp*RhCl₂]₂ [18], Cp*Ir(PPh₃)Cl₂ [22], Cp*Rh(PPh₃)Cl₂ [19], Cp*(^tBuNH₂)Cl₂ [23] were synthesized according to the literature procedure and all physical and spectral data were in accordance with literature data.

4.2. Synthesis and characterization of the complexes

4.2.1. [Cp*Ir(SnCl₃)₂{SnCl₂(H₂O)₂}] (**1**) [5d]

To $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol) in 2 mL of dichloroethane was added anhydrous SnCl₂ (60 mg, 0.3 mmol). The mixture was heated

	1 ·3H ₂ O	$3 \cdot \mathbf{H}_2 \mathbf{O}$	4
M ^a -Cp ^b	1.866(4)	1.872(7)	1.899(7)
M ^a –Sn1	2.5517(9)	2.5507(11)	2.5724(9)
M ^a –Sn2	2.5581(8)	2.5602(10)	2.5743(8)
Ir1–Sn3	2.5660(8)	2.5599(10)	_
Rh1–P1	-	_	2.357(2)
Sn1-Cl1	2.351(3)	2.385(3)	2.380(2)
Sn1-Cl2	2.382(3)	2.365(3)	2.384(2)
Sn1-Cl3	2.359(3)	2.354(3)	2.335(2)
Sn2-Cl4	2.347(3)	2.344(3)	2.363(3)
Sn2–Cl5	2.379(4)	2.365(3)	2.375(2)
Sn2-Cl6	2.351(4)	2.363(3)	2.346(2)
Sn3–Cl7	2.353(3)	2.345(3)	_
Sn3–Cl8	2.343(3)	2.361(3)	-
Sn3–Cl9	_	2.359(3)	_
Sn3-O1w	2.280(8)	_	_
Sn3-O2w	2.271(8)	-	-
Cp ^b -M ^a -Sn1	122.94(3)	122.61(14)	121.26(3)
Cp ^b –M ^a –Sn2	124.95(3)	126.73(14)	120.49(3)
Cp ^b –M ^a –Sn3	124.79(3)	123.01(15)	_
Cp ^b –Rh1–P1	-	-	127.86(6)
Sn1-M ^a -Sn2	92.08(3)	92.20(3)	88.91(3)
Sn2-Ir1-Sn3	91.78(3)	89.34(4)	-
Sn3-Ir1-Sn1	90.50(3)	93.31(3)	_
Sn2-Rh1-P1	-	-	93.13(5)
P1-Rh1-Sn1	-	-	95.66(6)
M ^a –Sn1–Cl1	125.36(10)	115.31(8)	112.25(6)
M ^a -Sn1-Cl2	114.11(9)	118.41(8)	113.53(6)
M ^a -Sn1-Cl3	120.07(11)	127.31(7)	132.58(7)
M ^a –Sn2–Cl4	128.58(10)	120.51(9)	123.71(8)
M ^a –Sn2–Cl5	110.73(12)	121.14(8)	118.64(7)
M ^a -Sn2-Cl6	117.92(11)	118.54(8)	117.59(6)
M ^a –Sn3–Cl7	129.47(10)	115.57(8)	-
M ^a –Sn3–Cl8	126.09(10)	116.69(9)	-
M ^a –Sn3–Cl9	-	125.02(9)	-
Cl1-Sn1-Cl2	96.70(14)	96.63(12)	100.36(8)
Cl2-Sn1-Cl3	97.88(16)	97.70(10)	97.43(9)
Cl3-Sn1-Cl1	97.21(15)	95.27(11)	95.37(9)
Cl4–Sn2–Cl5	96.43(15)	96.10(12)	95.31(9)
Cl5-Sn2-Cl6	99.17(17)	97.38(12)	95.18(10)
Cl6-Sn2-Cl4	98.60(15)	97.81(12)	101.28(9)
Cl7–Sn3–Cl8	104.44(13)	98.84(13)	_
Cl8-Sn3-Cl9	-	97.34(13)	-
Cl9–Sn3–Cl7	-	98.68(11)	-
01w-Sn3-02w	161.30(3)	_	_

 a M = Ir for complexes **1** and **3** or M = Rh for complex **4**. b Centroid of the Cp* ligand.

Table 4

Bisarylation of 4-nitrobenzaldehyde with thiophene: screening of different bimetallic catalysts.^a



Entry	Catalyst	Time, h	Yield of 6a , ^b %
1	$[Cp^*Ir(SnCl_3)_2[SnCl_2(H_2O)_2]](1)$	3	85
2	$[Cp*Ir(PPh_3)(SnCl_3)Cl](2)$	12	Trace
3	$[Cp^*Ir(SnCl_3)_3][NH_3^tBu](3)$	3	83
4	$[Cp^*Rh(PPh_3)(SnCl_3)_2]$ (4)	12	Trace
5	$[CODIr(SnCl_3)Cl(\mu-Cl)]_2$	6	35

^a General conditions: **5a** (0.5 mmol), thiophene (1.5 mmol), catalyst (0.005 mmol), DCE (3 mL).

^b Isolated yield.

Table 5Bisarylation of aldehyde leading to TRAMs catalyzed by 1.ª



Table 5 (continued)



^a General condition: **5** (0.5 mmol), nucleophile (1.5 mmol), **1** (0.005 mmol), DCE (3.5 mL), 80 °C.

^b Isolated yield.

at 80 °C for 3 h. The initially brick red solution slowly turned a greenish yellow color after completion of the reaction. After the mixture was cooled to room temperature, the greenish yellow solution was taken out from the reaction flask and slow diffusion of *n*-hexane to this solution causes greenish yellow block like crystals: yield 90 mg (80%); mp > 300 °C; ¹H NMR (200 MHz, (CD₃)₂CO) δ 2.29 (s, 15H) with tin satellites ($J_{H-Sn} = 29$ Hz); ¹³C NMR (54.6 MHz, (CD₃)₂CO) δ 10.4, 98.0; ¹¹⁹Sn NMR (149 MHz, (CD₃)₂CO) δ –311 with tin satellites ($J_{Sn-Sn} = 2900$ Hz). Anal. Calcd for C₁₀H₂₅Cl₈IrO₅Sn₃ (1057.59): C, 11.36; H, 2.38. Found: C, 11.53; H, 2.56.

4.2.2. [Cp*Ir(PPh₃)(SnCl₃)Cl] (2)

To [Cp*Ir(PPh₃)Cl₂] (33 mg, 0.05 mmol) in 2.5 mL of dichloroethane was added excess anhydrous SnCl₂ (95 mg, 0.5 mmol). The mixture was stirred at RT for 12 h. The initially deep yellow solution slowly turned a pale yellow color after completion of the reaction. The reaction mixture was settled down and then the pale yellow solution was taken out from the reaction flask, *n*-hexane was added to get **2** as yellow powder: yield 35 mg (85%); mp > 300 °C; ¹H NMR (400 MHz, (CD₃)₂CO) δ 1.57 (d, *J* = 2.0 Hz, 15H), 7.50–7.64 (m, 15H); ¹³C NMR (100 MHz, (CD₃)₂CO) δ 7.9, 97.4, 128.4, 130.9, 134.3, 134.7; ³¹P NMR (162 MHz, (CD₃)₂CO) δ –2.0. Anal. Calcd. For C₂₈H₃₀Cl₄IrPSn (849.95): C, 39.55; H, 3.56. Found: C, 39.76; H, 3.69.

4.2.3. $[Cp^*Ir(SnCl_3)_3][NH_3^tBu]$ (3)

To [Cp^{*}Ir(^tBuNH₂)Cl₂] (47 mg, 0.1 mmol) in 3.5 mL of dichloroethane was added excess anhydrous SnCl₂ (190 mg, 1 mmol). The mixture was stirred at 80 °C for 12 h. The initially deep brown solution slowly turned a pale yellow color after completion of the reaction. After the mixture was cooled to room temperature the pale yellow solution was taken out from the reaction flask and slow diffusion of *n*-hexane to this solution causes yellow block like crystals: yield 98 mg (90%); mp > 300 °C; ¹H NMR (400 MHz, (CD₃)₂CO) δ 1.55 (s, 9H), 2.30 (s, 15H) with tin satellites (J_{H-Sn} = 29 Hz), 7.78 (m, 3H); ¹³C NMR (100 MHz, (CD₃)₂CO) δ 9.9, 26.8, 55.5, 98.2; ¹¹⁹Sn NMR (149 MHz, (CD₃)₂CO) δ –311 with tin satellites (J_{Sn-Sn} = 2900 Hz). Anal. Calcd for C₁₄H₂₉Cl₉IrNOSn₃ (1094.61): C, 15.36; H, 2.67; N, 1.28. Found: C, 15.54; H, 2.83; N, 1.44. 4.2.4. [Cp*Rh(PPh₃)(SnCl₃)₂] (4)

To $[Cp^*Rh(PPh_3)Cl_2]$ (57 mg, 0.1 mmol) in 3.5 mL of dichloroethane was added excess anhydrous SnCl₂ (190 mg, 1 mmol). The mixture was stirred at 80 °C for 12 h. The initially red solution slowly turned an orange color after completion of the reaction. After the mixture was cooled to room temperature the orange colored solution was taken out from the reaction flask and slow diffusion of *n*hexane to this solution causes orange colored block like crystals: yield 94 mg (95%); mp > 300 °C; ¹H NMR (200 MHz, (CD₃)₂CO) δ 1.82 (d, *J*_{H-P} = 3.6 Hz, 15H) with tin satellites (*J*_{H-Sn} = 42 Hz), 7.53-7.61 (m, 15H); ¹³C NMR (100 MHz, (CD₃)₂CO) δ 10.0, 106.9, 128.9, 130.1, 131.8, 134.7; ³¹P NMR (162 MHz, (CD₃)₂CO) δ 40.0 (d, *J*_{Rh-P} = 138 Hz). Anal. Calcd for C₂₈H₃₄Cl₆O₂PRhSn₂ (986.75): C, 34.09; H, 3.47. Found: C, 33.95; H, 3.57.

4.3. Representative procedure for the bisarylation of aldehyde catalyzed by **1**

A 10 mL round bottom flask equipped with a magnetic bar was charged with **1** (5.3 mg, 0.005 mmol), 4-nitrobenzaldehyde (75.5 mg, 0.5 mmol), thiophene (125 μ L, 1.5 mmol) and DCE (3.5 mL). The reaction was allowed to continue at 80 °C for 3 h. After completion, solvent was removed and the mixture was subjected to column chromatography over silica gel to afford **6a** as oil in 85% yield.

- 4.3.1. (4-Nitrophenyl)-bis-(2-thienyl)methane (6a) [5b]
- ¹H NMR (200 MHz, CDCl₃) δ 5.97 (s, 1H) 6.83 (d, J = 2.9 Hz, 2H), 6.97 (dd, J = 2.9 and 4.1 Hz, 2H), 7.26 (d, J = 4.1 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 8.18 (d, J = 8.5 Hz, 2H).

4.3.2. (4-Chlorophenyl)-bis-(5-methyl-2-thienyl)methane (**6b**) [5i] ¹H NMR (CDCl₃, 200 MHz) δ 2.36 (s, 6H), 5.59 (s, 1H), 6.52 (s, 4H), 7.15–7.25 (m, 4H).

4.3.3. (4-Chlorophenyl)-bis-(5-methyl-2-furyl)methane (**6c**) [24] ¹H NMR (CDCl₃, 200 MHz) δ 2.28 (s, 6H), 5.35 (s, 1H), 5.79–5.81 (m, 4H), 7.12 (d, 2H, *J* = 8.6 Hz), 7.22 (d, 2H, *J* = 8.6 Hz).

4.3.4. (2-Bromophenyl)-bis-(2-thienyl)methane (6d)

¹H NMR (CDCl₃, 400 MHz) δ 6.32 (s, 1H), 6.80 (d, 2H, *J* = 3.2 Hz), 6.94 (*t*, 2H, *J* = 4.8 Hz), 7.10–7.14 (m, 1H), 7.22–7.27 (m, 4H), 7.57 (d,

1H, I = 8.0 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 46.4, 124.4, 124.8, 126.5, 127.6, 128.7, 130.0, 132.9, 142.9, 146.2. Anal. Calcd For C15H11BrS2 (333.95): C, 53.73; H, 3.31. Found: C, 53.97; H, 3.19.

4.3.5. (Phenyl)-bis-(3-indolyl)methane (6e) [18]

¹H NMR (CDCl₃, 200 MHz) δ 5.90 (s, 1H), 6.61 (d, 2H, J = 1.6 Hz), 7.02 (t, 2H, J = 6.4 Hz), 7.15–7.43 (m, 11H), 7.83 (br, 2H).

4.3.6. (4-Nitrophenyl)-bis-(2,4,6-trimethoxyphenyl)methane (6f) [5b]

¹H NMR (CDCl₃, 400 MHz) δ 3.50 (s, 12H), 3.77 (s, 6H), 6.10 (s, 4H), 6.25 (s, 1H), 7.14 (d, 2H, J = 8.2 Hz), 8.00 (d, 2H, J = 8.2 Hz).

4.3.7. (4-Chlorophenyl)-bis-(2,4,6-trimethoxyphenyl)methane (6g) [18]

¹H NMR (CDCl₃, 200 MHz) δ 3.52 (s, 12H), 3.79 (s, 6H), 6.11 (s, 4H), 6.16 (s, 1H), 6.97 (d, 2H, *J* = 8.6 Hz), 7.11 (d, 2H, *J* = 8.6 Hz).

4.3.8. (2-Chlorophenyl)-bis-(4-methoxyphenyl)methane (6h)

¹H NMR (CDCl₃, 200 MHz) δ 3.78 (s, 6H), 5.84 (s, 1H), 6.82 (d, 4H, J = 8.8 Hz), 6.90–6.95 (m, 1H) 6.97 (d, 4H, J = 8.8 Hz), 7.11–7.19 (m, 2H), 7.33–7.38 (m, 1H); ¹³C NMR (CDCl₃, 54.6 MHz) δ 51.8, 55.2, 113.7, 126.6, 127.6, 129.7, 130.4, 131.0, 134.5, 135.0, 142.3, 158.1. Anal. Calcd For C₂₁H₁₉ClO₂ (338.11): C, 74.44; H, 5.65. Found: C, 74.25; H, 5.80.

4.3.9. (4-Bromophenyl)-bis-(2,4-dimethoxyphenyl)methane (6i) [5i]

 1 H NMR (CDCl₃, 400 MHz) δ 3.69 (s, 6H), 3.79 (s, 6H), 5.95 (s, 1H), 6.37 (dd, 2H. J = 2.2 and 8.4 Hz), 6.46 (d, 2H, J = 2.2 Hz), 6.66 (d, 2H, J = 8.4 Hz), 6.92 (d, 2H, J = 8.4 Hz), 7.34 (d, 2H, J = 8.4 Hz).

4.3.10. (Phenyl)-bis-(2,4,6-trimethoxyphenyl)methane (6j) [18] ¹H NMR (CDCl₃, 200 MHz) δ 3.50 (s, 12H), 3.78 (s, 6H), 6.11 (s, 4H), 6.22 (s, 1H), 7.02–7.06 (m, 3H), 7.13 (d, 2H, J = 6.4 Hz).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jorganchem.2014.06.011.

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