

# Tandem transmetallation and oxidative addition reactions of $[\text{Sn}(\text{R})_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2]$ with transition metal complexes of the Group 9

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## Abstract

The reactions of  $[\text{Sn}(\text{Ph})_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2]$  with *trans*- $[\text{M}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$   $\text{M} = \text{Ir}, \text{Rh}$  afford the complexes  $[\text{Rh}(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2(\text{SnClPh}_2)]$  (**1**) and  $[\text{Ir}(\text{CO})(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2(\text{SnClPh}_2)]$  (**2**) as final products of two processes, a transmetallation reaction and an oxidative addition process. The crystal structures of both complexes have been determined, showing the rhodium compound to be into a slightly distorted square base pyramidal geometry, while that of the iridium derivative can be described as a distorted octahedron. © 2003 Elsevier B.V. All rights reserved.

**Keywords:** Phosphorus–sulfur proligands; Transmetallation; Oxidative addition; Transition metal complexes; Crystal structures; Catalysis

## 1. Introduction

Polydentate ligands incorporating both thiolate and tertiary phosphine donor ligands have been focus of intensive research in the recent years as their combination is likely to confer unusual structures [1], properties [2] (unusual oxidation states and enhanced solubility) and unusual reactivities on their metal complexes [3], making these species excellent candidates for further studies in reactivity. This is particularly true in the case of compounds with elements of the groups 8–10, due to the importance these metals have as catalyst in multiple organic transformations [4]. Moreover, the presence of these ligands in the coordination sphere of transition metal complexes may render interesting behaviors in solution, as these ligands can be capable of full or partial de-ligation (hemilability) [5], being able to provide important extra coordination sites for incoming substrates during a catalytic process [5]. On the other hand, reactions employing organometallic intermediates or starting materials have claimed an important place in

modern organic synthesis, allowing transformations otherwise difficult to make by traditional synthetic methods [4]. Among these processes, reactions involving the formation of C–C bonds have been recognized as one of the most important power tools in modern organic synthesis [6], being in this context worth to mention the Stille reaction [7] which involves organometallic tin complexes as starting materials and where a transmetallation process is the rate-determining step [7]. Another process which has gained considerable attention in the recent years is the rhodium-catalyzed addition of organometallic reagents to carbon-heteroatom [8], double bonds (e.g. aldehydes, imines, etc.), reactions which commonly involve organorhodium complexes as active species generated by transmetallation with organometallic reagents such as tin [9]. Thus, following our current interest [10] in the design and synthesis of new complexes containing the  $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-SH}$ <sup>1</sup> (*phPSH*) hybrid proligand, we would like to report our findings on the reactivity of the organometallic tin(IV) compounds  $[\text{Sn}(\text{R})_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2]$  with Rh(I) and Ir(I) complexes.

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<sup>1</sup> Diphenyl (phenyl-2-thiol)phosphine.

## 2. Experimental

### 2.1. Materials and methods

Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using conventional Schlenk glassware, solvents were dried using established procedures and distilled under dinitrogen immediately prior to use. The IR spectra were recorded on a Nicolet-Magna 750 FT-IR spectrometer as nujol mulls. The  $^1\text{H}$  NMR (300 MHz) spectra were recorded on a JEOL GX300 spectrometer. Chemical shifts are reported in ppm down field of TMS using the solvent ( $\text{CDCl}_3$ ,  $\delta = 7.27$ ) as internal standard.  $^{31}\text{P}$  NMR (121 MHz) spectra were recorded with complete proton decoupling and are reported in ppm using 85%  $\text{H}_3\text{PO}_4$  as external standard. Elemental analyses were determined on a Perkin–Elmer 240. Positive-ion FAB mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol (NOBA) matrix using 3 keV xenon atoms. Mass measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material or, alternatively, by electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions. The proligand ( $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-SH}$ ) *phPSH* [11] and the complexes  $[\text{Sn}(\text{Ph})_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2]$  [12] and *trans*- $[\text{M}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$   $\text{M} = \text{Rh}$  [13],  $\text{Ir}$  [14] were prepared according to the published procedures.

### 2.2. Synthesis of $[\text{Rh}(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2(\text{SnClPh}_2)]$ (**1**)

To a solution of *trans*- $[\text{Rh}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$  (40 mg, 0.058 mmol) in  $\text{CH}_2\text{Cl}_2$ , a solution (30 ml,  $\text{CH}_2\text{Cl}_2$ ) of  $[\text{Sn}(\text{Ph})_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2]$  (50 mg, 0.058 mmol) was added under stirring, the resulting yellow solution was allowed to stir overnight, after this time the solvent was taken off under vacuum and the residue recrystallized from  $\text{CH}_2\text{Cl}_2$ -*n*-hexane pair of solvents, to afford a deep red microcrystalline powder of **1**. Yield 75.3%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.86–6.81 (m, Ph, 38H);  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ),  $\delta$  60.63 (d,  $^1J_{(\text{Rh-P})} = 131.76$  Hz,  $^2J_{(117,119)\text{Sn,P}} = 192$  Hz). Elem. Anal. Calc. for  $\text{C}_{48}\text{H}_{38}\text{ClP}_2\text{RhS}_2\text{Sn}$ : C, 55.77; H, 3.84. Found: C, 55.64; H, 3.82%. MS-FAB<sup>+</sup> [ $\text{M}^+$ ] = 997 *m/z*.

### 2.3. Synthesis of $[\text{Ir}(\text{CO})(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2(\text{SnClPh}_2)]$ (**2**)

The title compound was synthesized and purified in a similar manner to that of complex **1** from  $[\text{Sn}(\text{Ph})_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2]$  (50 mg, 0.058 mmol) and *trans*- $[\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$  (45 mg, 0.058 mmol) as source of iridium. Yield 74.4%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),

$\delta$  7.86–6.15 (m, Ph, 38H);  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ),  $\delta$  25.37 ( $^{\text{cis}}J_{(\text{P-P})} = 11.28$  Hz,  $^2J_{(117,119)\text{Sn,P}} = 198.65$  Hz, P *trans* to S) and  $\delta$  10.48 ( $^{\text{cis}}J_{(\text{P-P})} = 11.28$  Hz,  $^2J_{(117,119)\text{Sn,P}} = 2413.34$  Hz, P *trans* to Sn). Elem. Anal. Calc. for  $\text{C}_{49}\text{H}_{38}\text{ClIrOP}_2\text{S}_2\text{Sn}$ : C, 52.77; H, 3.43. Found: C, 52.69; H, 3.39%. MS-FAB<sup>+</sup> [ $\text{M}^+ - \text{CO}$ ] = 1087 *m/z*.

### 2.4. Data collection and refinement for $[\text{Rh}(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2(\text{SnClPh}_2)]$ (**1**) and $[\text{Ir}(\text{CO})(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2(\text{SnClPh}_2)]$ (**2**)

A crystalline red prism of **1** and a yellow prism of **2** grown independently from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  and  $\text{CH}_2\text{Cl}_2$ -*n*-hexane solvent systems, respectively, were glued each to glass fibers. The X-ray intensity data were measured at 291 K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ( $\lambda = 0.71073$  Å). The detector was placed at a distance of 4.837 cm from the crystals in all cases. A total of 1800 frames were collected with a scan width of  $0.3^\circ$  in  $\omega$  and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data was done using a monoclinic unit cell in both cases to yield a total of 37,082 and 8103 reflections for **1** and **2**, respectively, to a maximum  $2\theta$  angle of  $50.00^\circ$  (0.93 Å resolution), of which 8065 (**1**) and 7737 (**2**) were independent. Analysis of the data showed in both cases negligible decays during data collection. The structures were solved by Patterson method using SHELXS-97 [15] program. The remaining atoms were located via a few cycles of least squares refinements and difference Fourier maps, using the space groups  $P2_1/n$  with  $Z = 4$  for **1** and  $P2_1/c$  with  $Z = 4$  for **2**. Hydrogen atoms were input at calculated positions and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for hydrogen atoms on the phenyl groups using a  $U_{\text{eq}} = 1.2$  Å to precedent atom. The final cycle of refinement was carried out on all non-zero data using SHELXL-97 [16] and anisotropic thermal parameters for all non-hydrogen atoms. The details of the structure determinations are given in Table 1 and selected bond lengths (Å) and angles ( $^\circ$ ) in Tables 2 and 3 for **1** and **2**, respectively. The numbering of the atoms is shown in Figs. 1 and 2, respectively (ORTEP) [17].

## 3. Results and discussion

We have previously reported [12] on the reactivity of organometallic tin(IV) compounds of the type  $[\text{Sn}(\text{R})_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2]$   $\text{R} = \text{Ph}$ ,  $\text{Bu}^n$  or  $\text{Bu}^l$  with transition metal complexes of the group 10, we have found that from all the possible fashions this metallo-ligands may coordinate (Scheme 1) they undergo

Table 1

Summary of crystal structure data for complexes [Rh(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>(SnClPh<sub>2</sub>)] (1) and [Ir(CO)(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>(SnClPh<sub>2</sub>)] (2)

Empirical formula	C <sub>48</sub> H <sub>38</sub> ClP <sub>2</sub> RhS <sub>2</sub> Sn(1)	C <sub>49</sub> H <sub>38</sub> ClP <sub>2</sub> IrS <sub>2</sub> SnO (2)
Formula weight	1040.98	1115.19
Temperature	291(2) K	291(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions	<i>a</i> = 9.797(3) Å, $\alpha$ = 90° <i>b</i> = 19.863(5) Å, $\beta$ = 92.106(6)° <i>c</i> = 23.558(6) Å, $\gamma$ = 90°	<i>a</i> = 12.8027(12) Å, $\alpha$ = 90° <i>b</i> = 25.351(4) Å, $\beta$ = 108.197(7)° <i>c</i> = 14.264(2) Å, $\gamma$ = 90°
Volume	4581(2) Å <sup>3</sup>	4397.9(10) Å <sup>3</sup>
<i>Z</i>	4	4
Density (calculated)	1.509 g/cm <sup>3</sup>	1.684 g/cm <sup>3</sup>
Absorption coefficient	1.159 mm <sup>-1</sup>	3.856 mm <sup>-1</sup>
<i>F</i> (000)	2100	2184
Crystal size	0.20 × 0.10 × 0.04 mm	0.40 × 0.24 × 0.06 mm
$\theta$ range for data collection	1.73° – 25.00°	1.70°–25.01°
Index ranges	–11 ≤ <i>h</i> ≤ 11, –23 ≤ <i>k</i> ≤ 23, –27 ≤ <i>l</i> ≤ 27	0 ≤ <i>h</i> ≤ 15, 0 ≤ <i>k</i> ≤ 30, –16 ≤ <i>l</i> ≤ 16
Reflections collected	37,082	8103
Independent reflections	8065 [ <i>R</i> <sub>int</sub> = 0.2418]	7737 [ <i>R</i> <sub>int</sub> = 0.0578]
Completeness to $\theta$ = 25.00°	100%	99.8%
Max. and min. trans.	0.9534 and 0.8330	0.8016 and 0.3077
Absorption correction	Integration	Integration
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	8065/4/509	7737/0/515
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.537 <sup>a</sup>	0.917 <sup>a</sup>
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0466, <i>wR</i> 2 = 0.0660 <sup>a</sup>	<i>R</i> 1 = 0.0405, <i>wR</i> 2 = 0.0790 <sup>a</sup>
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1931, <i>wR</i> 2 = 0.0864 <sup>b</sup>	<i>R</i> 1 = 0.0683, <i>wR</i> 2 = 0.0849 <sup>b</sup>
Largest diff. peak and hole	0.694 and –0.325 e Å <sup>-3</sup>	1.296 and –1.742 e Å <sup>-3</sup>

<sup>a</sup>  $S = [w((F_o)^2 - (F_c)^2)^2 / (n - p)]^{1/2}$ , where *n* is the number of reflections and *p* is the total number of parameters.<sup>b</sup>  $R1 = |F_o - F_c| / |F_o|$ ,  $wR2 = [w((F_o)^2 - (F_c)^2)^2 / w(F_o)^2]^{1/2}$ .

Table 2

Selected bond lengths and angles for [Rh(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>(SnClPh<sub>2</sub>)] (1)

Bond lengths (Å)		Angles (°)	
Rh(1)–P(1)	2.264(3)	P(1)–Rh(1)–P(2)	102.45(10)
Rh(1)–P(2)	2.277(3)	P(1)–Rh(1)–S(2)	172.63(11)
Rh(1)–S(2)	2.314(3)	P(2)–Rh(1)–S(2)	84.74(10)
Rh(1)–S(1)	2.316(3)	P(1)–Rh(1)–S(1)	85.37(10)
Rh(1)–Sn(1)	2.5790(12)	P(2)–Rh(1)–S(1)	169.76(10)
Sn(1)–C(43)	2.057(11)	S(2)–Rh(1)–S(1)	87.30(10)
Sn(1)–C(37)	2.126(10)	P(1)–Rh(1)–Sn(1)	105.85(8)
Sn(1)–Cl(1)	2.393(3)	P(2)–Rh(1)–Sn(1)	107.97(8)
Sn(1)–S(2)	2.917(3)	S(2)–Rh(1)–Sn(1)	72.97(7)
		S(1)–Rh(1)–Sn(1)	75.66(8)
		C(43)–Sn(1)–C(37)	108.7(4)
		C(43)–Sn(1)–Cl(1)	98.7(4)
		C(37)–Sn(1)–Cl(1)	98.3(3)

transmetallation reactions instead, giving place to the stereoselective formation of the corresponding square planar derivatives *cis*-[M(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>] M = Ni, Pd, Pt with the concomitant formation of the tin(IV) halide [Sn(R)<sub>2</sub>(Cl)<sub>2</sub>] R = Ph, Bu<sup>n</sup> or Bu<sup>t</sup> as by products (Scheme 2). We have postulated before that the product of the reaction may actually be dependant of the number of halides available to be transmetallated in the starting material, thus we carried out reactions of the tin(IV) complexes [SnR<sub>2</sub>(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>] with the Vaska's type

Table 3

Selected bond lengths and angles for and [Ir(CO)(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>(SnClPh<sub>2</sub>)] (2)

Bond lengths (Å)		Angles (°)	
Ir(1)–C(51)	1.881(8)	C(51)–Ir(1)–P(2)	95.7(2)
Ir(1)–P(2)	2.3193(19)	C(51)–Ir(1)–S(2)	173.5(2)
Ir(1)–S(2)	2.3950(18)	P(2)–Ir(1)–S(2)	86.19(6)
Ir(1)–P(1)	2.4000(19)	C(51)–Ir(1)–P(1)	93.5(2)
Ir(1)–S(1)	2.4165(19)	P(2)–Ir(1)–P(1)	99.55(7)
Ir(1)–Sn(1)	2.6520(6)	S(2)–Ir(1)–P(1)	92.39(7)
Sn(1)–C(37)	2.150(8)	C(51)–Ir(1)–S(1)	92.6(2)
Sn(1)–C(43)	2.166(8)	P(2)–Ir(1)–S(1)	171.11(7)
Sn(1)–Cl(1)	2.408(2)	S(2)–Ir(1)–S(1)	85.22(7)
O(1)–C(51)	1.130(9)	P(1)–Ir(1)–S(1)	83.12(7)
		C(51)–Ir(1)–Sn(1)	93.1(2)
		P(2)–Ir(1)–Sn(1)	93.32(5)
		S(2)–Ir(1)–Sn(1)	80.48(5)
		P(1)–Ir(1)–Sn(1)	164.86(4)
		S(1)–Ir(1)–Sn(1)	82.99(5)
		C(37)–Sn(1)–C(43)	100.1(3)
		C(37)–Sn(1)–Cl(1)	102.1(3)
		C(43)–Sn(1)–Cl(1)	100.0(3)
		O(1)–C(51)–Ir(1)	178.2(7)

(*trans*-[M(Cl)(CO)(PPh<sub>3</sub>)<sub>2</sub>] M = Ir, Rh) derivatives of rhodium and iridium.

We have also probed that the product of the reaction of [Sn(R)<sub>2</sub>(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>] with [M(Cl)<sub>2</sub>(NCC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>] M = Pd, Pt or NiCl<sub>2</sub>·6H<sub>2</sub>O is irrespective of the R

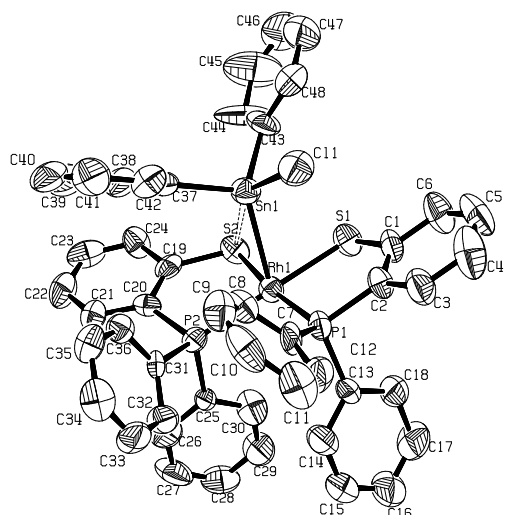


Fig. 1. An ORTEP representation of the structure of [Rh(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>(SnClPh<sub>2</sub>)] (**1**) at 50% of probability showing the atom labeling scheme.

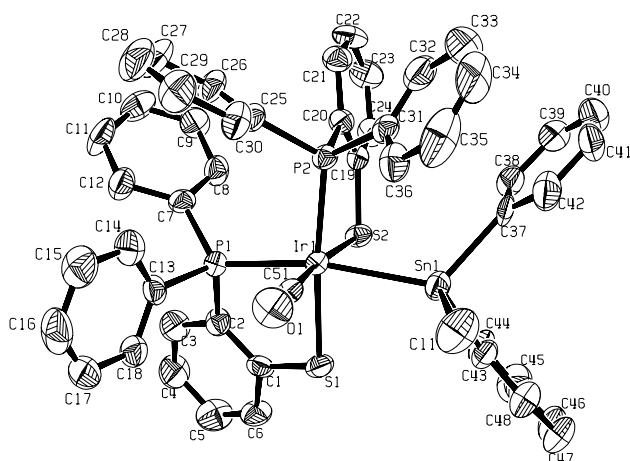
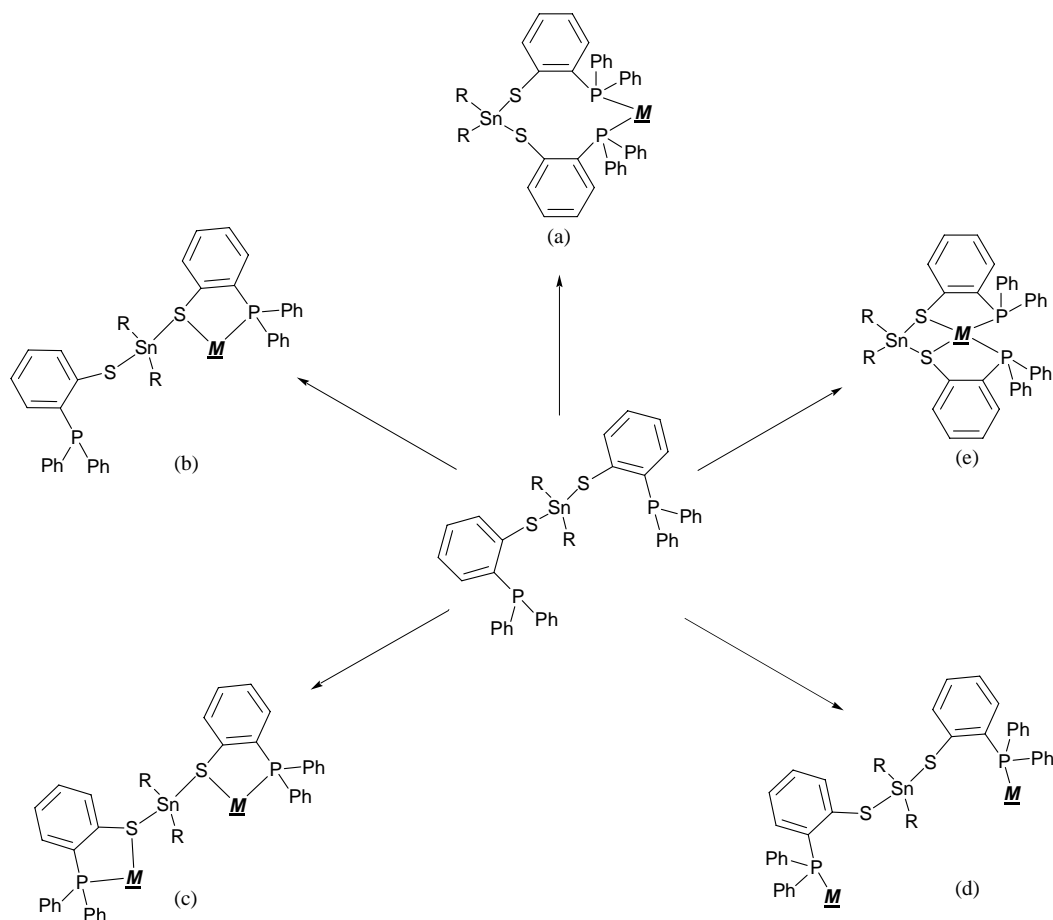


Fig. 2. An ORTEP representation of the structure of [Ir(CO)(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>(SnClPh<sub>2</sub>)] (**2**) at 50% of probability showing the atom labeling scheme.

group in the tin complexes. Thus, in the present case we decide to carry out the reactions only with the phenyl derivative. In this way, by reacting [SnPh<sub>2</sub>(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>] with *trans*-[M(Cl)(CO)(PPh<sub>3</sub>)<sub>2</sub>] M = Ir, Rh in a 1:1 molar ratio the complexes [Rh(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>(SnClPh<sub>2</sub>)] (**1**) and [Ir(CO)(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>(SnClPh<sub>2</sub>)] (**2**) have been obtained as red or yellow microcrystalline powders, respectively. The infrared spectra of **1** exhibit several bands corresponding to the aromatic rings present in the *phPS*<sup>-</sup> ligands; however, the more valuable information in this spectrum is the absence of the absorption due to the presence of the carbonyl ligand, thus indicating that this substituent has been lost in the process. Similar analysis for **2** exhibits a very intense and sharp absorption at 2032.44 cm<sup>-1</sup> due to the ν(C=O) which is on the range for Ir(III) complexes [18]. In both

cases, the analysis by <sup>1</sup>H NMR is not very informative since only signals for all the different sets of aromatic rings in both molecules are observed. However, the analysis by <sup>31</sup>P NMR is more illustrative, in the case of **1** a doublet at δ60.63 ppm symmetrically flanked by <sup>117,119</sup>Sn satellites can be clearly observed, this doublet presenting a coupling constant of <sup>1</sup>J<sub>(Rh-P)</sub> = 131.76 Hz, the fact that we are observing only one signal in the spectra is consistent with the proposed formulation for **1** where the two phosphorus nuclei are magnetically equivalent, moreover the fact that the value of <sup>2</sup>J<sub>(<sup>117,119</sup>Sn,P)</sub> is 192 Hz is consistent with a structure in which the tin atom is in a *cis* disposition to the phosphine substituents [19]. On the other hand, the <sup>31</sup>P NMR spectrum of **2** shows two different sets of signals corresponding to an AB nuclei system, these signals are located at δ 25.37 (P *trans* to S) and δ 10.48 (P *trans* to Sn) ppm, with the corresponding tin satellites whose difference in separations suggest that one phosphorus is *trans* to tin (<sup>2</sup>J<sub>(<sup>117,119</sup>Sn,P)</sub> = 2413.34 Hz) while the other one (<sup>2</sup>J<sub>(<sup>117,119</sup>Sn,P)</sub> = 198.65 Hz) must be opposite to a ligand with weaker *trans* influence (sulfur in this case) [20]. Analysis by FAB<sup>+</sup>-mass spectrometry for **1** exhibits a peak at 997 *m/z* in the spectrum corresponding to the molecular ion [M<sup>+</sup>], another important peak due to the loss of the SnClPh<sub>2</sub> fragment is observed at 689 *m/z* [M<sup>+</sup>-SnClPh<sub>2</sub>]. The mass spectrum of **2** presents a similar fragmentation pattern; however, in this case the molecular ion is not observed, instead a peak corresponding to [M<sup>+</sup>-CO] can be observed at 1087 *m/z*, further loss of the SnClPh<sub>2</sub> fragment is observed at 779 *m/z* [M<sup>+</sup>-SnClPh<sub>2</sub>].

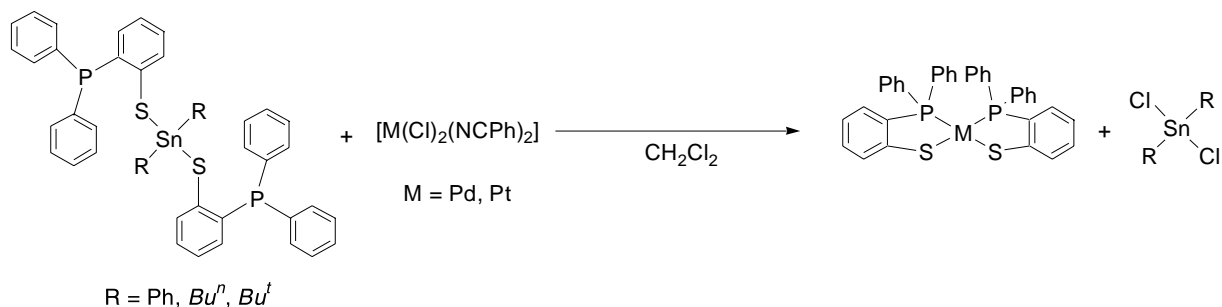
In both cases we were able to obtain crystals suitable for single crystal X-ray diffraction analysis, thus confirming unambiguously the identity and stereochemistry of both complexes. In the case of **1** analysis of the red crystals reveals a rhodium center in a distorted square pyramidal environment (Fig. 1) with two *phPS*<sup>-</sup> ligands arranged in a *cis* conformation and at the top completing the pyramid the SnCl(Ph)<sub>2</sub> moiety. The main distortion is located in the Rh-Sn bond (maximum distortion observed at Sn(1)-Rh(1)-S(1) 75.66°), this distortion being due in part to the steric hindrance of the aromatic rings in the molecule; however, the more important contribution is due to an interaction of the tin atom with one of the sulfurs (Sn(1)-S(2) 2.917 Å) of the *phPS*<sup>-</sup> ligands. The *cis* conformation observed in this case as it was the case for the complexes *cis*-[M(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>] M = Ni, Pd, Pt obtained by the same route evidences once more the stereoselectivity of this process [12]. All other bond distances and angles are within the expected values. Complex **2**, on the other hand, exhibits an iridium center located into a slightly distorted octahedral structure (Fig. 2), with two *phPS*<sup>-</sup> ligands occupying different positions within the octahedron which accounts for the two magnetically different phosphorus nuclei detected in

Scheme 1. Possible coordination modes of the metalloligands  $[\text{Sn}(\text{R})_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2]$ .

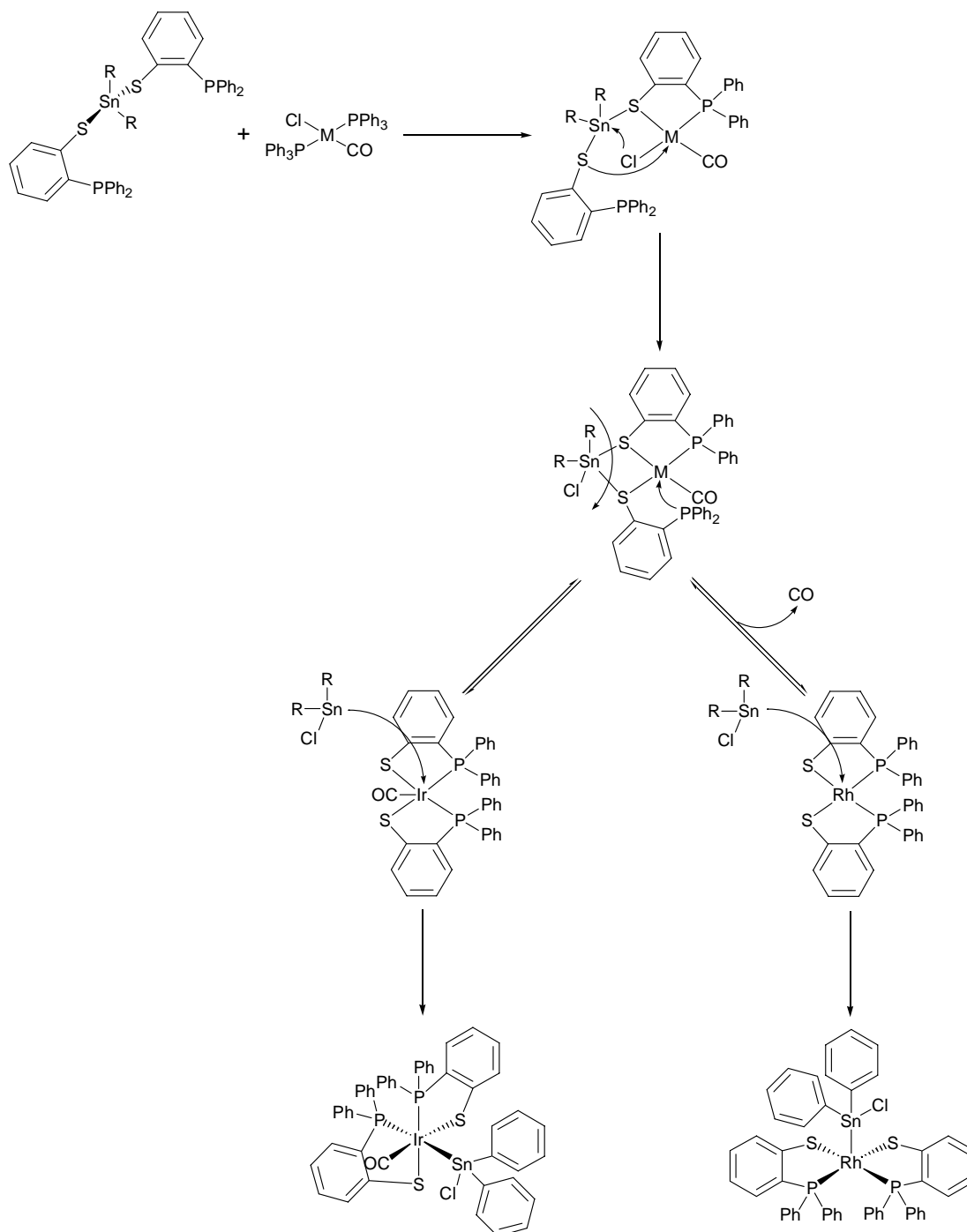
the  $^{31}\text{P}$  NMR experiments, the coordination sphere around the Ir center is completed by the CO ligand *trans* to S(2) and the moiety  $\text{SnClPh}_2$  *trans* to P(1). The distance  $\text{Ir}(1)\text{-P}(2)$  2.3193(19) Å (P *trans* to S) is slightly shorter in comparison with those observed in  $[\text{Ir}(\text{pr}^i\text{PS})_3]$  2.348 Å [3h]; however, the  $\text{Ir}(1)\text{-P}(1)$  (P *trans* to Sn) is considerably longer 2.4000(19) Å, this difference being the reflex of the difference in *trans* influence of the substituents *trans* to the P atoms, being stronger in the case of tin [20]. In all other respects the values for the rest of bond distances and angles are within the expected values. The fact that we are not obtaining the *cis* conformation,

in this case, may be related with the size of the iridium atom which can allow the better distribution of both ligands in the coordination sphere minimizing the steric constraints within the system. The fact that in this case we have the presence of the CO molecule and not in **2** it is related with the facility that Rh has to eliminate CO in a given process [21], fact that in turns makes it such a good catalyst for a wide variety of transformations [22].

It is likely that analogously to what we have observed for the reactions of  $[\text{Sn}(\text{R})_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2]$  with  $[\text{M}(\text{Cl})_2(\text{NCC}_6\text{H}_5)_2]$  M = Pd, Pt or  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , the first step in the formation of **1** and **2** would be the



Scheme 2.



Scheme 3. A proposal of the probable steps involved in the formation of the complexes  $[\text{Rh}(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2(\text{SnClPh}_2)]$  (**1**) and  $[\text{Ir}(\text{CO})(\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-S})_2(\text{SnClPh}_2)]$  (**2**).

transmetalation process to afford an intermediate which on the losing of the tin moiety this would be added to the metal center to afford the more stable Rh(III) or Ir(III) complexes (Scheme 3).

Efforts aimed to take advantage of the presented processes for applications in organic synthesis are currently under development in our laboratory.

#### 4. Supplementary material

Supplementary data for complex **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre. Copies of this information are available free of charge on request from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-

336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk> quoting the deposition numbers CCDC 215671 and 215672.

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