REACTIVITY OF [$SnPh_3(\eta^1$-2-PyS)] TOWARDS Pt AND Ni COMPLEXES

V. D. de Castro[1], C. A. L. Filgueiras[2], G. M. de Lima*[1]
M. T. P. Gambardella[3] and N. L. Speziali [4]

[1] Laboratorio de Química de Coordenação e Organometálica do Estanho - Departamento de Química - UFMG, Belo Horizonte - MG, 31270-901, Brazil <gmlima@dedalus.lcc.ufmg.br>
[2] Instituto de Química, UFRJ, C.P. 68563, 21945-970 Rio de Janeiro - RJ, Brazil
[3] Instituto de Química de São Carlos - Universidade de São Paulo – São Carlos – SP, 13560-250, Brazil
[4] Departamento de Fisica – UFMG, Belo Horizonte – MG, 31270-901, Brazil

Abstract
The reaction of [$SnPh_3(\eta^1$-2-PyS)] (**1**) with both [cis-$Pt(PPh_3)_2Cl_2$] and [$Pt(PPh_3)_2(C_2H_4)$] yielded the same platinum derivative, [trans-$Pt(PPh_3)_2(\eta^1$-2-PyS)$_2$] (**2**). The tin-containing products were identified as $SnPh_3Cl$ and Sn_2Ph_6 for the first and second reactions, respectively. The same experiment with [cis-$Ni(PPh_3)_2Cl_2$] led to the formation of an insoluble product Ni(2-PyS)$_2$ and of [$SnPh_3(OPPh_3)Cl$] (**3**). Compounds **(1)**, **(2)** and **(3)** were studied by i.r., NMR spectroscopies and their X-ray structures were revised.

1. Introduction

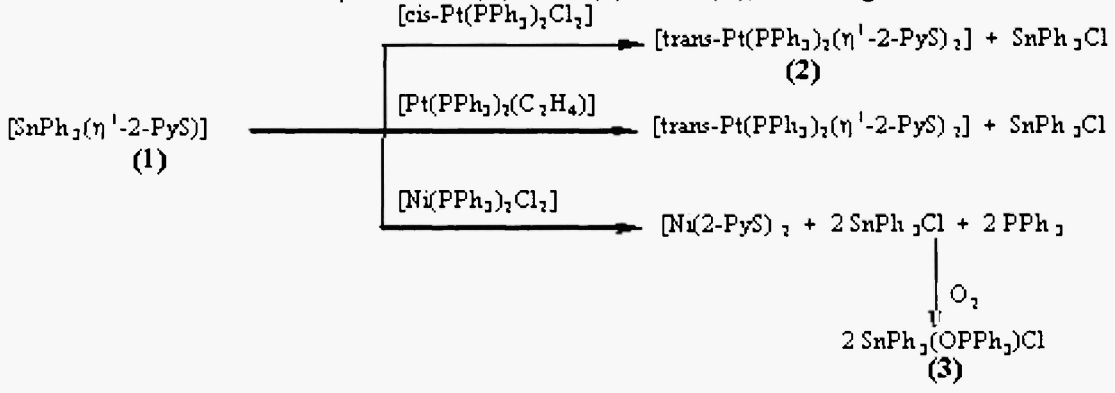
For many years the major uses of Sn metal was in the can-making and food-packing industries and solder for electrical and electronic industries. In the 1950s there was an increased consumption of this metal in the form of organotin(IV) derivatives. Such compounds achieved great importance in modern industry due to their extensive range of biological and chemical properties, which depend strongly upon the number and nature of the organic group attached to the metal centre. After the earliest commercial application in the PVC industries, organotin(IV) compounds were employed in the preparation of commercially-available biocidal materials {antibacterial, antifungal, pesticidal, antimicrobial, etc} [1]. Today their wide uses range from pharmacological to nano-technological areas, as precursors in the preparation of semiconductor materials such as nanometric SnS [2]. Recently they are playing an important role in the catalytic process of CO_2 fixation [3].

Since the discovery of cisplatinum, platinum-containing compounds are the main metal-based antitumor drugs in use. However, at the beginning of the last decade some organotin(IV) complexes were found to have similar biological activities. Those derivatives where the Sn(IV) atom bears 2,6-dicarboxypyridyl and 2-thiopyridyl groups were tested and showed promising activity against mammary tumor and colon carcinoma, displaying an activity higher than carboplatin and cisplatin. [4].

In view of our interest in the chemical and biological features of sulphur-having ligands and their metallic complexes, the synthesis of 2-thiopyridyl heterometallic complexes with both Sn(IV) and Pt(II) was attempted, in order to investigate the pharmacological activity of the derivatives. Herein we report the synthesis of [$SnPh_3(\eta^1$-2-PyS)] (Py = pyridine) and its reactions with Pt(II), Pt(0) and Ni(II) complexes.

2. Results and discussion

Compound **(1)** was prepared by reacting 2-PySK with $SnPh_3Cl$. After a proper characterisation it was used in reactions with complexes of Pt(II) and Pt(0) and Ni(II), according to Scheme 1.



Scheme 1 – Reactions of $SnPh_3(\eta^1$-2-PyS)

The subsequent reactions yielded: [trans-$Pt(PPh_3)_2(\eta^1$-2-$PyS)_2$] **(2)**, [$Ni(2\text{-}PyS)_2$] and as tin-containing products $SnPh_3Cl$, Sn_2Ph_6 and $SnPh_3OPPh_3$ **(3)**.

Compound **(1)** was previously structurally authenticated and our results are in accordance to those found in the literature.

The ^1H and ^{13}C NMR spectra were unexceptional since the expected signals corresponding to pyridyl and phenyl rings were observed. The ^{119}Sn NMR study revealed a resonance at δ -121 with $^1J_{(^{119}Sn\text{-}^{13}C)}$ = 567 Hz, which is characteristic of ^{119}Sn atom in a tetrahedral environment. The ^{119}Sn Mössbauer parameters also agree with a tetrahedral geometry at the Sn(IV) centre, δ = 1.25 $mm.s^{-1}$ and Δ = 1.59 $mm.s^{-1}$. In spite of the differences of the NMR and the ^{119}Sn Mössbauer experiments, the former was performed in solution and the latter was conducted in the solid state, the results suggest that the structure in the solid state is kept in solution. The i.r. spectroscopic study exhibited ν(Sn-S) at $360cm^{-1}$.

Compound **(2)** was first prepared by the reaction of [$Pt(2\text{-}PyS)_2$] with PPh_3 [5]. In our case a coordination of the Pt(II) and Pt(0) to the S donor centre was expected, forming a heterobimetallic complex. Surprisingly, in both reactions, Scheme 1, the thiolate groups were transferred to the Pt atom, yielding the same Pt(II) product, [trans-$Pt(PPh_3)_2(\eta^1$-2-$PyS)_2$], **(2)**. In experiment 1 the Sn compound was identified as $SnPh_3Cl$, which was characterised by elemental analysis and ^{119}Sn NMR spectroscopy, δ -46. The second reaction led to the formation of Sn_2Ph_6, also characterised by elemental analysis and ^{119}Sn NMR studies, δ-146 $^1J_{(^{119}Sn\text{-}^{117}Sn)}$ 4495Hz, in agreement with the literature [6]. The resonance found in the ^1H and ^{13}C NMR spectra confirmed the presence of the pyridyl and phenyl groups. The ^{31}P NMR study revealed three signals, δ -4.9, 7.8 {$^1J_{(^{31}P\text{-}^{195}Pt)}$ 3866 Hz} and 29.7. According to the previous report the three signals were assigned to the presence of three different phosphorus species in solution, [trans-$Pt(PPh_3)_2(\eta^1$-2-$PyS)_2$], [$Pt(PPh_3)(\eta^2$-2-$PyS)(\eta^1$-2-$PyS)$] and free PPh_3.[6] The parameters obtained by the X-ray crystallographic study did not reveal new features of **(2)**.

The reaction of [$SnPh_3(\eta^1$-2-$PyS)$] with [$Ni(PPh_3)_2Cl_2$] produced two products, a green and insoluble material, presumably [$Ni(2\text{-}PyS)_2$] and an unexpected organotin derivative, [$SnPh_3OPPh_3Cl$]. This reaction followed a pathway different from the previous one. In the two previous reactions the PPh_3 group remained attached to the Pt(II), perhaps in view of the size of the metal, which is sufficient to arrange the ligands in a square. In the case of Ni(II) it is not possible to accommodate all the donor centres around a square, thus there is an elimination of PPh_3 which is transferred to the Sn atom, scheme 1. Due to its poor solubility and high thermal stability (it did not melt up to 350°C), the compound [$Ni(2\text{-}PyS)_2$] may present a polymeric chain structure with bridging S-C-N intermolecular bonds. The minimal formula of the Ni(II) derivative, on the basis of the satisfactory elemental analysis (C, H, N and Ni) can be assigned as [$Ni(2\text{-}PyS)_2$].

In the solution remained an Sn-containing derivative which was expected to be [$SnPh_3PPh_3Cl$]. However, there was an insertion of oxygen into the Sn-P bond yielding [$SnPh_3OPPh_3Cl$] instead. The same compound was obtained by stirring $SnPh_3Cl$ with PPh_3 for 24 hours in air.

The previous structural analysis of **(3)** was not satisfactory [7]. Our X-ray data showed small differences in terms of a, b, c measurements. Also the final error reported here, 3.6% is smaller than the presented in the previous work, 5.44 %.

3. Experimental

3.1 Material and procedures

Experimental work was carried out under an atmosphere of dry nitrogen employing vacuum line techniques. All solvents were distilled prior to use. The chemicals were obtained from Aldrich or Strem Companies or prepared according to literature procedures. NMR spectra were recorded at 400 MHz ^1H, 100.62 MHz $^{13}C\{^1H\}$, 162.0 MHz $^{31}P\{^1H\}$, 86.0 MHz ^{195}Pt, 149.1 MHz ^{119}Sn using a Bruker DRX-400 and DPX-200 spectrometers equipped with an 89mm wide-bore magnet. ^{13}C and ^1H shifts are reported relative to $SiMe_4$; ^{119}Sn relative to $SnMe_4$, ^{31}P relative to H_3PO_4 85 % in D_2O and ^{195}Pt relative to K_2PtCl_4 in HCl.

3.2 X-ray structure determination of crystalline (1), (2) and (3)

The data were collected using a Enraf-Nonius CAD4 diffractometer at a temperature of 298K. The structures were solved by SIR-92 [8] and the refinements were carried out using SHELXL97 [9], minimizing on the weighted R factor *w*R2. Further details are given in Table 1. All non-H atoms were anisotropic. The Ortep drawing shows the non-H atoms as 20% thermal vibration ellipsoids.

3.3 Synthesis of [$SnPh_3(h^1$-2-PyS)]

To a round-bottom-flask containing KH (0.82 g, 20.4 mmols), previously washed with n-hexane, were added 50 mL of thf and 2-PySH (2.22 g, 20,0 mmols) dissolved in the same solvent.

After 3.5 hours under stirring the yellow colour of 2-PySH had completely disappeared and an the insoluble white solid formed. This was filtered off, washed with thf (3x20mL) and dried under vacuum. A solution of $SnPh_3Cl$ (7.70 g, 20.0 mmols) was added to a suspension of the white solid in thf and left stirring for 4 hours. The volatiles were removed under vacuum and the resultant white solid was washed with n-hexane and recrystallised in a 1:1 mixture of thf and acetonitrile. Yield 31 % (2.85 g, 6.20 mmol). X-ray quality crystals were obtained by slow evaporation of the same solution. Mp 104-106 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz), δ 8.2 – 8.1, 7.5 – 7.4, 7.0 – 6.9 (Py), δ 7.9 – 7.8, 7.5 – 7.4 (Ph); ^{13}C{^{1}H} NMR ($CDCl_3$, 100.61 MHz), 160, 148, 137, 123, 119 (Py), 141 [J^1($^{119/117}$Sn-^{13}C) = 583 Hz], 137 [J^2($^{119/117}$Sn-^{13}C) = 44 Hz], 129, 128 [J^3($^{119/117}$Sn-^{13}C) = 59 Hz] (Ph); ^{119}Sn NMR ($CDCl_3$, 149.089 MHz) δ −121 [$^1J_{(^{119/117}Sn-^{13}C)}$ = 567 Hz]; ν(Sn-S) 360 cm^{-1}. Elemental analysis for $C_{23}H_{19}NSSn$ calc(exp): C 59.88(60.02), H 3.86(3.91), N 3.04(3.04).

3.4 Reaction of [$SnPh_3(\eta^1$-2-PyS)] with [cis-$Pt(PPh_3)_2Cl_2$]

To a Schlenk-flask containing [$SnPh_3(\eta^1$-2-PyS)] (137.9 mg, 0.30 mmol) dissolved in thf (10 mL) was added [cis-$Pt(PPh_3)_2Cl_2$] (114.5 mg, 0.15 mmols) also in thf (10 mL). A colour change from white to yellow was observed in the solution with no precipitation. After 17 hours stirring about 70 % of the solvent was removed under vacuum and n-hexane was added causing the precipitation of a yellow crystalline solid, [trans-$Pt(PPh_3)_2(\eta^1$-2-PyS)$_2$]. The remaining solution was removed by a cannula, from which a white solid was isolated. This solid was later identified as $SnPh_3Cl$. X-ray quality crystals were obtained by recrystalisation from an acetronitrile solution of **(2)**. Yield 90 % (126.98 mg, 0.14 mmol). Mp 218 (d) °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz), δ 7.4 - 6.7 (Py), δ 7.9 - 7.6, 7.3 (Ph); ^{31}P{^{1}H} NMR ($CDCl_3$, 161.923 MHz), δ -4.9, 7.82 [$J^1_{(^{31}P-^{195}Pt)}$ = 3866 Hz and 29.7, ^{195}Pt NMR ($CDCl_3$, 85.996 MHz), δ -4026 [J^1(^{31}P-^{195}Pt) = 3870 Hz; ν(Pt-S) 410 cm^{-1}. Elemental analysis for $C_{46}H_{38}N_2P_2S_2Pt$: C 58.70(58.78), H 3.63(4.07), N 2.83(2.98). Carrying out a similar reaction with [$Pt(PPh_3)_2(C_2H_4)$] (116.8 mg, 0.16 mmols) the same product was obtained in lower yield 74 % (111.3 mg, 0.12 mmol). In this case the Sn product was identified as [Sn_2Ph_6]. M.p. 229-230°C. ^{119}Sn NMR ($CDCl_3$, 149.089 MHz) δ-146 $^1J_{(^{119}Sn-^{117}Sn)}$ 4495Hz.

3.5 Reaction of [$SnPh_3(\eta^1$-2-PyS)] with [$Ni(PPh_3)_2Cl_2$]

The same procedure used in 2.4 was employed in the reaction of [$SnPh_3(\eta^1$-2-PyS)] (74.7 mg, 0.16 mmol) with [$Ni(PPh_3)_2Cl_2$] (106.2 mg, 0.16 mmols). After 16 hours stirring about 70 % of the solvent was removed under vacuum and n-nexane was added causing the precipitation of a green solid, [$Ni(2\text{-PyS})_2$]. The remaining solution was removed by a cannula, from which a white solid was isolated. This solid was later identified as [$SnPh_3(OPPh_3)Cl$] **(3)**. X-ray quality crystals were obtained from a toluene solution of **(3)**. Yield 76 %. Analysis of [$Ni(2\text{-PyS})_2$]. Mp > 350 °C. Elemental analysis for $C_{10}H_8S_2N_2Ni$ calc(exp): C 43.1(44.5), H 2.87(2.91), N 10.0(11.2). Analysis of [$SnPh_3(OPPh_3)Cl$] (81.7 mg, 0.12 mmol). Elemental analysis for $C_{36}H_{30}OPClSn$ calc(exp): C 65.1(67.5), H 4.55(4.61). Mp 166-168°C. ν(Sn - Cl) 269 cm^{-1}; ν(P = O) 1152 e 1111 cm^{-1}.

4. Supplementary data

Crystallographic data for the strucutural analysis for the complexes discussed here have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, and are available on request quoting the deposition numbers CCDC 166210 **(1)**, 166205 **(2)** and 166204 **(3)**.

5. Acknowledgment

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6. References

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