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Journal of Organometallic Chemistry 679 (2003) 101–109

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Transmetallation reactions of $[Sn(R)_2(Ph_2PC_6H_4\text{-}2\text{-}S)_2]$ with metal complexes of the Group 10

Stereoselective synthesis of *cis*-$[M(Ph_2PC_6H_4\text{-}2\text{-}S)_2]$ ($M = Ni, Pd, Pt$)

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Received 6 May 2003; received in revised form 3 June 2003; accepted 6 June 2003

Abstract

The complexes *cis*-$[M(Ph_2PC_6H_4\text{-}2\text{-}S)_2]$ $M = Ni$, Pd, Pt were stereoselectively synthesized by transmetallation reactions of $[M(Cl)_2(NCC_6H_5)_2]$ $M = Pd$, Pt or $NiCl_2 \cdot 6H_2O$ with $[Sn(R)_2(Ph_2PC_6H_4\text{-}2\text{-}S)_2]$ $R = Ph$, ^{n}Bu or ^{t}Bu. The conformation of the Pd and Pt derivatives being unequivocally confirmed by single crystal X-ray diffraction studies showing both metal centers to be into a slightly distorted square planar environment, the main distortion being due to the steric hindrance caused by the aromatic rings in the phosphine moiety.

Keywords: Phosphorus-sulfur ligands; Transmetallation; Transition metal complexes; Crystal structures

1. Introduction

In recent years, attention has increasingly been paid to the coordination chemistry of polydentate ligands incorporating both thiolate and tertiary phosphine donor ligands, as their combination is likely to confer unusual structures and reactivities on their metal complexes [1]. Some of these complexes have been used as models of biologically active centers in metalloproteins such as ferredoxins, nitrogenase, blue copper proteins and metallothioneins [2] or as models for the design of complexes with potential application as radiopharmaceuticals [3]. These complexes have shown an intriguing variety of structures [4] or unusual oxidation states and enhanced solubility [5], making these species excellent candidates for further studies in reactivity. In the specific case of compounds with elements of the groups 8–10 these may be suitable species for catalytic screening. Moreover, the presence of these ligands in the coordination sphere of transition metal complexes may render interesting behaviours in solution as these ligands can be capable of full or partial de-ligation (hemilability) [6], being able to provide important extra coordination sites for incoming substrates during a catalytic process [6]. In this respect, processes involving transmetallation reactions as key steps for a particular catalytic process have been of considerable interest in the recent years and this is particularly true for reactions involving the formation of C–C bonds and of particular interest the Stille reaction [7] which uses organometallic tin complexes as starting materials and where the transmetallation process is the rate-determining step. Thus, following our current interest [8] in the design and synthesis of new complexes containing the $Ph_2PC_6H_4$-2-SH[1] (*ph*PSH) hybrid proligand we would like to report our findings on the reactivity of the organometallic tin(IV) compounds $[Sn(R)_2(Ph_2PC_6H_4\text{-}2\text{-}S)_2]$ with Ni(II), Pd(II) and Pt(II) complexes.

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[1] Diphenyl(phenyl-2-thiol)phosphine.

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doi:10.1016/S0022-328X(03)00538-2

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}H-NMR (300 MHz) spectra were recorded on a JEOL GX300 spectrometer. Chemical shifts are reported in parts per million down field of TMS using the solvent ($CDCl_3$, $\delta = 7.27$) as internal standard. ^{31}P-NMR (121 MHz) spectra were recorded with complete proton decoupling and are reported in parts per million using 85% H_3PO_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 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 ($Ph_2PC_6H_4$-2-SH) *ph*PSH [9] was synthesized according to the published procedure and the complexes [Sn(R)$_2$($Ph_2PC_6H_4$-2-S)$_2$] R = Ph, ^{n}Bu or ^{t}Bu where prepared by a slight modification of the method reported [10]. The starting materials [M(Cl)$_2$(NCC_6H_5)$_2$] M = Pd [11], Pt [12] were prepared according to published procedures.

2.2. Synthesis of the metalloligands [Sn(R)$_2$($Ph_2PC_6H_4$-2-S)$_2$] R = Ph, (**1**) ^{n}Bu (**2**) and ^{t}Bu (**3**)

All complexes were synthesized by a slight modification of the methods reported [10]. Thus as a representative example the experimental procedure for the synthesis of complex **2** is described.

A solution of the proligand $Ph_2PC_6H_4$-2-SH (200 mg, 0.68 mmol) and NEt_3 (71 mg, 0.70 mmol) in dry-methanol (35 ml) was refluxed for 5 min. After this time the heating is stopped and a methanol solution (15 ml) of [Sn(^{n}Bu)$_2$Cl$_2$] (103 mg, 0.34 mmol) was then added. The resulting mixture is refluxed for further 4 h (a gradual cloudiness is observed with time). After this time the solution was cooled to room temperature and the resulting white precipitate is washed twice with methanol (25 ml) and filtered off under vacuum. Yield 61% of a white microcrystalline powder of **2**.

2.2.1. [Sn(Ph)$_2$($Ph_2PC_6H_4$-2-S)$_2$] (*1*)

$Ph_2PC_6H_4$-2-SH (200 mg, 0.68 mmol), NEt_3 (71 mg, 0.70 mmol) and [Sn(Ph)$_2$Cl$_2$] (117 mg, 0.34 mmol). Yield: 80.67%. ^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.65–6.50 (m, Ph, 38H); ^{31}P-NMR (121 MHz, $CDCl_3$), δ −13.10 (s). Anal. Calc. for [$C_{48}H_{38}P_2S_2Sn$]: C, 67.8; H, 4.4. Found: C, 68.5; H, 4.2%. MS-FAB^{+} [M^{+}] = 859 *m*/*z*.

2.2.2. [Sn(^{n}Bu)$_2$($Ph_2PC_6H_4$-2-S)$_2$] (*2*)

Yield: 61.32%. ^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.63–7.00 (m, Ph, 28H), 1.72–0.72 (m, ^{n}Bu, 18H); ^{31}P-NMR (121 MHz, $CDCl_3$), δ −11.70 (s). Anal. Calc. for [$C_{44}H_{46}P_2S_2Sn$]: C, 64.50; H, 5.60. Found: C, 63.70; H, 5.40%. Ms-FAB^{+} [M^{+}] = 819 *m*/*z*.

2.2.3. [Sn(^{t}Bu)$_2$($Ph_2PC_6H_4$-2-S)$_2$] (*3*)

$Ph_2PC_6H_4$-2-SH (200 mg, 0.68 mmol), NEt_3 (71 mg, 0.70 mmol) and [Sn(^{t}Bu)$_2$Cl$_2$] (103 mg, 0.34 mmol). Yield: 95.51%. ^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.77–6.70 (m, Ph, 28H), 1.22 (*s*, ^{t}Bu, 12H), 1.33 (s, ^{t}Bu, 6H); ^{31}P-NMR (121 MHz, $CDCl_3$), δ −11.80 (s). Anal. Calc. for [$C_{44}H_{46}P_2S_2Sn$]: C, 64.50; H, 5.60. Found: C, 62.90; H, 6.00%. MS-FAB^{+} [M^{+}] = 819 *m*/*z*.

2.3. Synthesis of cis-[Pd($Ph_2PC_6H_4$-2-S)$_2$] (*4*)

To a solution of [Sn(R)$_2$($Ph_2PC_6H_4$-2-S)$_2$] (R = Ph, 50 mg, 0.058 mmol, R = ^{n}Bu, 48 mg, 0.058 mmol, R = ^{t}Bu, 48 mg, 0.058 mmol) in CH_2Cl_2 (20 ml), a CH_2Cl_2 solution (30 ml) of [Pd(Cl)$_2$(NCC_6H_5)$_2$] (22 mg, 0.058 mmol) was added under stirring. The resulting mixture was allowed to stir overnight. After this time, formation of a pale yellow precipitated was noticed, the product was filtered off under vacuum and washed twice with methanol. Recrystallization from a double layer solvent system CH_2Cl_2/MeOH afforded complex **4** as a microcrystalline yellow powder. Yield: 87.5%. ^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.71–6.79 (m, Ph, 28H); ^{31}P-NMR (121 MHz, $CDCl_3$), δ, 42.42 (s). Anal. Calc. for [$C_{36}H_{28}P_2S_2Pd$]: C, 64.20; H, 4.00. Found: C: 64.00, H: 4.20%. MS-FAB^{+} [M^{+}] = 692 *m*/*z*.

2.4. Synthesis of cis-[Pt($Ph_2PC_6H_4$-2-S)$_2$] (*5*)

The compound was synthesized and purified in a similar manner to that of complex **4** from [Sn(Ph)$_2$($Ph_2PC_6H_4$-2-S)$_2$] (50 mg, 0.058 mmol) and [Pt(Cl)$_2$(NCC_6H_5)$_2$] (22.3 mg, 0.058 mmol) as the source of platinum. Yield: 80.61%. ^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.73–6.74 (m, Ph, 28H); ^{31}P-NMR (121 MHz, $CDCl_3$), δ, 42.94 (s, J_{P-Pt} 2680 Hz). Anal. Calc. for [$C_{36}H_{28}P_2S_2Pt$]: C, 55.30; H, 3.60. Found: C, 55.90; H, 3.30%. MS-FAB^{+} [M^{+}] = 781 *m*/*z*.

2.5. Synthesis of *cis*-[Ni($Ph_2PC_6H_4$-2-S)$_2$] (**6**)

The title compound was synthesized and purified in a similar manner to that of complex **4** from [Sn(Ph)$_2$($Ph_2PC_6H_4$-2-S)$_2$] (50 mg, 0.058 mmol) and $NiCl_2 \cdot 6H_2O$ (14 mg, 0.058 mmol). Yield: 87.5%. ^1H-NMR (300 MHz, $CDCl_3$), δ 7.76–6.88 (m, Ph, 28H); ^{31}P-NMR (121 MHz, $CDCl_3$), δ, 42.69 (s). Anal. Calc. for [$C_{36}H_{28}P_2S_2Ni$]: C, 67.0; H, 4.3. Found: C, 65.7; H, 4.4%. MS-FAB$^+$ [M^+] = 644 *m/z*.

2.6. Data collection and refinement for [Sn(^{n}Bu)$_2$($Ph_2PC_6H_4$-2-S)$_2$] (2), *cis*-[Pd($Ph_2PC_6H_4$-2-S)$_2$] (4) and *cis*-[Pt($Ph_2PC_6H_4$-2-S)$_2$] (5)

A crystalline colorless prism of **2**, an orange prism of **4** and a yellow prism of **5** grown independently from CH_2Cl_2/MeOH solvent systems were glued to glass fibers. The X-ray intensity data were measured at 293 K for **2** and at 291 K for **4** and **5** 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° in ω and an exposure time of 10 s frame^{-1}. 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 orthorhombic unit cell for **2** or a monoclinic unit cell for **4** and **5** to yield a total of 3658, 26 645 and 6115 reflections, respectively to a maximum 2θ angle of 50.00° (0.93 Å resolution), of which 3658 (**2**), 5879 (**4**) and 5882 (**5**) were independent. Analysis of the data showed in all cases negligible decays during data collection. The structures were solved by Patterson method using SHELXS-97 [13] program. The remaining atoms were located via few cycles of least squares refinements and difference Fourier maps, using the space groups *Pcan* with $Z = 4$ (**2**), $P2_1/n$ with $Z = 4$ (**4**) and $P2_1/n$ with $Z = 4$ (**5**), respectively. 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 $U_{eq} = 1.2$ Å to precedent atom. The final cycle of refinement was carried out on all non-zero data using SHELXL-97 [14] and anisotropic thermal parameters for all non-hydrogen atoms. The details of the structure determinations are given in Table 1. The numbering of the atoms (ORTEP) [15] and selected bond lengths (Å) and angles (°) are shown in Figs. 1–3, respectively.

3. Results and discussion

3.1. Synthesis and characterization of the metalloligands [Sn(R)$_2$($Ph_2PC_6H_4$-2-S)$_2$] R = Ph(**1**), ^{n}Bu(**2**) or ^{t}Bu(**3**)

The three tin(IV) complexes were synthesized by a slight modification of the reported technique [10]. In all cases the complexes where obtained as colorless microcrystalline powders in good yields. Comparative analysis by multinuclear NMR, FAB$^+$-MS and elemental analysis agree well with the proposed formulations, the new complex **2** containing *n*-butyl moieties was also analyzed in a similar manner to that of the phenyl and *tert*-butyl analogues. Crystals of **2** suitable for single crystal X-ray diffraction analysis where obtained by slow evaporation of a saturated solution of **2** in ethanol. The crystal structure (Fig. 1) exhibits the tin center to be in a quasi-perfect tetrahedral environment with C(1)–Sn(1)–S(1)#1 and C(1)#1–Sn(1)–C(1)#1 angles equal to 106.7(3)° and 105.3(3)°, respectively, the *ph*PS$^-$ ligands are coordinated to the tin center as pendant arms with only the sulfur atom attached to the metal, leaving the phosphorus atoms free for further coordination (Fig. 1), this coordination fashion was also confirmed by ^{31}P-NMR experiments where the difference in chemical shifts observed for the free ligand ($\delta = -12.3$ ppm) and that of the coordinated ligand ($\delta = -11.7$ ppm) does not vary considerably ($\Delta\delta = 0.6$ ppm) thus indicating the electronic environment around the phosphorus atoms has remain unaltered. All other bond distances and bond angles are within the expected values and comparable to those observed in the phenyl derivative [Sn(Ph)$_2$($Ph_2PC_6H_4$-2-S)$_2$] [16].

3.2. Transmetallation reactions of [Sn(R)$_2$($Ph_2PC_6H_4$-2-S)$_2$] with metal complexes of the Group 10

The synthesis of the organometallic complexes [Sn(R)$_2$($Ph_2PC_6H_4$-2-S)$_2$] R = Ph, ^{t}Bu and its reactivity with metals of the Group 11 (Ag, Au) have been previously described [10], from all the probable fashions in which these complexes may coordinate (Scheme 1), binding to the corresponding metal by the free phosphorus atoms has been the common denominator. For instance in the particular case of silver and gold, each phosphorus coordinates independently to a metal center (**d** in Scheme 1).

Thus, we decide to explore the reactivity of these potential bidentate metalloligands with starting materials of the Group 10 (Ni, Pd and Pt). In this way, by reacting the complexes [Sn(R)$_2$($Ph_2PC_6H_4$-2-S)$_2$] R = Ph, ^{n}Bu or ^{t}Bu with the starting material [Pd(Cl)$_2$(NCC_6H_5)$_2$] in a 1:1 ratio, the complex *cis*-[Pd($Ph_2PC_6H_4$-2-S)$_2$] (**4**) was obtained irrespectively of the R group, this compound being produced by a

Table 1
Summary of crystal structure data for complexes [Sn(^{n}Bu)$_2$(Ph$_2$PC$_6$H$_4$-2-S)$_2$] (**2**), *cis*-[M(Ph$_2$PC$_6$H$_4$-2-S)$_2$] M = Pd (**4**), Pt (**5**)

Empirical formula	$C_{44}H_{46}P_2S_2Sn$ (**2**)	$C_{36}H_{28}P_2S_2Pd$ (**4**)	$C_{36}H_{28}P_2S_2Pt$ (**5**)
Formula weight	819.56	777.97	866.66
Temperature (K)	293(2)	291(2)	291(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pcan*	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	10.801(1)	15.5474(7)	15.5522(16)
b (Å)	14.854(1)	9.5188(4)	9.538(7)
c (Å)	25.833(2)	22.5548(10)	22.537(12)
α (°)	90	90	90
β (°)	90	91.9180(10)	91.947(10)
λ (°)	90	90	90
V (Å^3)	4144.3(7)	3336.1(3)	3341.3(5)
Z	4	4	4
D_{calc} (g cm^{-3})	1.314	1.549	1.723
Absorption coefficient (mm^{-1})	0.823	0.965	4.607
F(0 0 0)	1688	1576	1704
Crystal size (mm)	0.36 × 0.36 × 0.10	0.28 × 0.12 × 0.10	0.22 × 0.18 × 0.16
θ Range for data collection (°)	2.09–25.00	1.57–25.00	1.57–24.99
Index ranges	$0 \leq h \leq 12$, $0 \leq k \leq 17$, $0 \leq l \leq 30$	$-18 \leq h \leq 18$, $-11 \leq k \leq 11$, $-26 \leq l \leq 26$	$0 \leq h \leq 18$, $0 \leq k \leq 11$, $-26 \leq l \leq 26$
Reflections collected	3658	26 645	6115
Independent reflections	3658 [$R_{int} = 0.0000$]	5879 [$R_{int} = 0.0539$]	5882 [$R_{int} = 0.0500$]
Absorption correction	None	None	Integration
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3658/0/223	5879/0/397	5882/0/398
Goodness-of-fit on F^2	1.020 [a]	0.942 [a]	0.896 [a]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0703$, $wR_2 = 0.1410$ [a]	$R_1 = 0.0383$, $wR_2 = 0.0786$ [a]	$R_1 = 0.0397$, $wR_2 = 0.0769$ [a]
R indices (all data)	$R_1 = 0.1658$, $wR_2 = 0.1887$ [b]	$R_1 = 0.0549$, $wR_2 = 0.0830$ [b]	$R_1 = 0.0692$, $wR_2 = 0.0827$ [b]
Largest difference peak and hole	0.553 and −0.487 e Å^{-3}	0.836 and −0.706 e Å^{-3}	1.032 and −1.087 e Å^{-3}

[a] $S = [w(F_o)^2 - (F_c)^2)^2/(n-p)]^{1/2}$ where n = number of reflections and p = total number of parameters.
[b] $R_1 = |F_o - F_c|/|F_o|$, $wR_2 = [w((F_o)^2 - (F_c)^2)^2/w(F_o)^2]^{1/2}$.

transmetallation process. Analysis by FAB$^+$-MS of this complex exhibits a signal corresponding to the molecular ion at $m/z = 692$ with the appropriate isotope distribution [17]. An additional peak corresponding to the loss of the fragment *ph*PS is observed at $m/z = 399$. The ^{1}H-NMR spectrum of this complex only exhibits the signals due to the presence of the aromatic rings in the molecule. The ^{31}P-NMR is more informative as one peak is observed at 42.42 ppm this signal being due to the presence of the *cis* isomer. The same sample was left to stand for 24 h. to allow the process to reach equilibrium, after this time the ^{31}P-NMR experiment was carried out and two peaks were observed, one at 42.42 ppm and the other at 53.62 ppm in a 1.5:1 ratio, the first and more intense signal being due to the presence of the *cis* isomer and the other peak at higher field due to the known *trans* isomer[2] [18]. Crystals of **4** suitable for X-ray diffraction analysis were obtained from a CH$_2$Cl$_2$/MeOH double layer system as yellow orange prisms and show the compound [Pd(Ph$_2$PC$_6$H$_4$-2-S)$_2$] (**4**) to be in a *cis* conformation. The crystal structure (Fig. 2) of this complex shows the Pd center in a distorted square planar environment (P(1)–Pd(1)–S(2), 171.66(4)°; P(2)–Pd(1)–S(1), 172.23(4)°), this distortion being due to the *cis* arrangement of both *ph*PS$^-$ ligands around the metal. In all other respects the bonds distances and angles are similar to those found for the *trans* isomer [18]. According to these observation we believe that this compound could have been produced by a route similar to that depicted in Scheme 2.

Since formation of **4** from the tin(IV) complexes is irrespective of the R group we decided to carry out further experiments with only the metalloligand containing R = Ph (**1**). Thus, by reacting [Pt(Cl)$_2$(NCC$_6$H$_5$)$_2$] with complex (**1**) the same behaviour was observed as that for the palladium analogue. As in the case of palladium the more valuable information was obtained from the ^{31}P-NMR spectrum showing a single signal due to the presence of the *cis* isomer at $\delta = -42.94$ ppm

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[2] It is noteworthy that the *trans* isomer of **4** was obtained by a dealkylation reaction (Menschutkin Reaction) using amines of the phosphino-thioether complex *trans*-[Pd(Ph$_2$PC$_6$H$_4$-2-SMe)$_2$](BF$_4$)$_2$ [18].

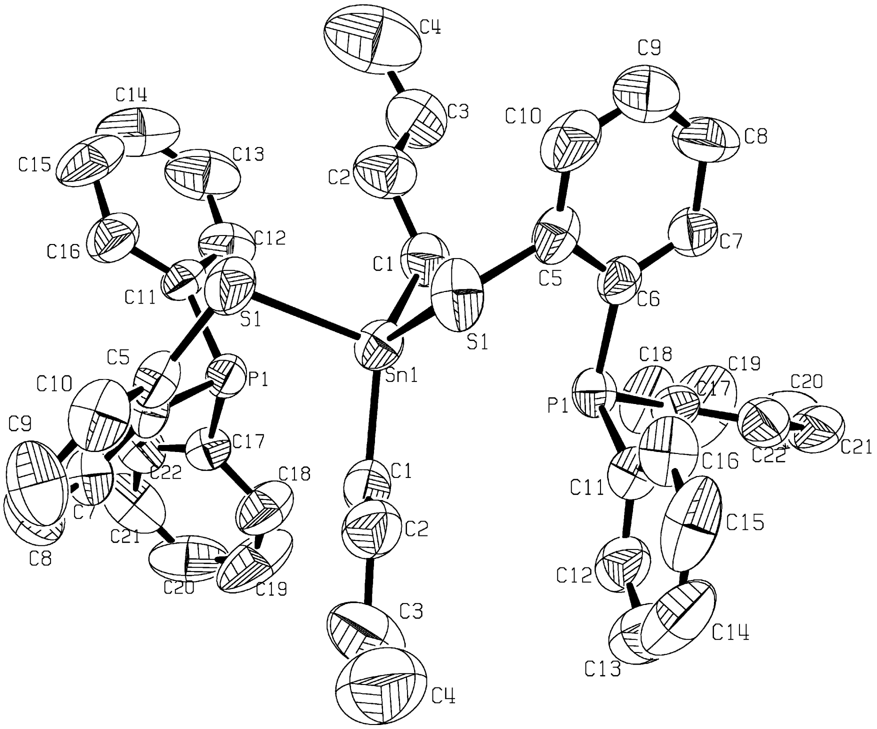

Fig. 1. An ORTEP representation of the structure of [Sn(^{n}Bu)$_2$(Ph$_2$PC$_6$H$_4$-2-S)$_2$] (**2**) at 50% of probability showing the atom labeling scheme. Selected bond lengths (Å): Sn(1)–C(1) 2.141(10), Sn(1)–S(1) 2.473(3). Bond angles (°): C(1)–Sn(1)–C(1)#1 132.8(6), C(1)–Sn(1)–S(2)#1 106.7(3), C(1)#1–Sn(1)–S(1)#1 105.3(3), C(1)–Sn(1)–S(1) 105.3(3), C(1)#1–Sn(1)–S(1) 106.7(3), S(1)#1–Sn(1)–S(1) 92.90(13).

($J_{P-Pt} = 2680$ Hz). Crystals of **5** suitable for X-ray diffraction analysis were obtained from a double layer system CH$_2$Cl$_2$/MeOH as yellow prisms, thus the identity of the complex and its conformation was unequivocally determined to be *cis*-[Pt(Ph$_2$PC$_6$H$_4$-2-S)$_2$] (Fig. 3). The crystal structure shows the Pt center

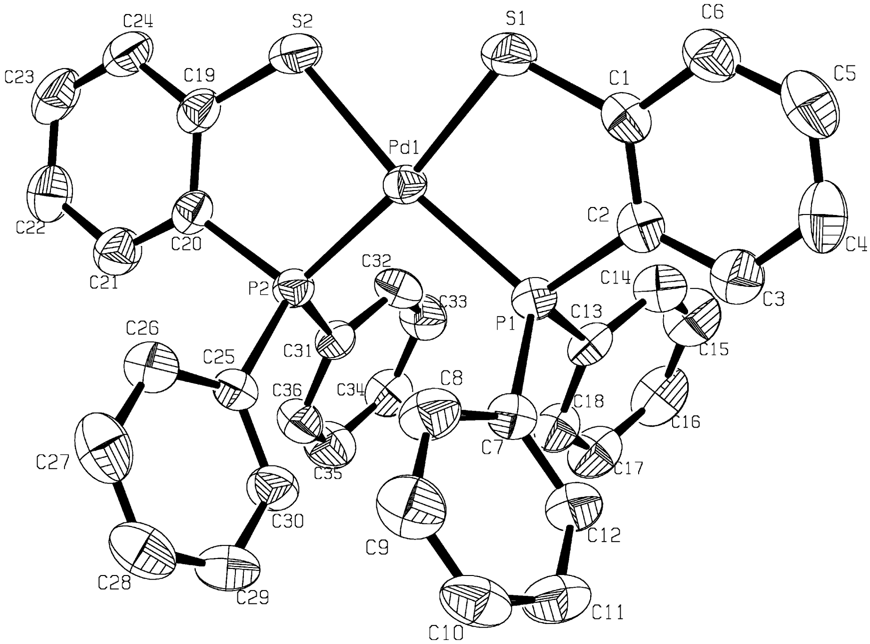

Fig. 2. An ORTEP representation of the structure of *cis*-[Pd(Ph$_2$PC$_6$H$_4$-2-S)$_2$] (**4**) at 50% of probability showing the atom labeling scheme. Selected bond lengths (Å): Pd(1)–P(2) 2.2772(10), Pd(1)–P(1) 2.2828(10), Pd(1)–S(2) 2.3177(10), Pd(1)–S(1) 2.3188(11). Bond angles (°): P(2)–Pd(1)–P(1) 100.54(4), P(2)–Pd(1)–S(2) 87.07(4), P(1)–Pd(1)–S(2) 171.66(4), P(2)–Pd(1)–S(1) 172.23(4), P(1)–Pd(1)–S(1) 87.22(4), S(2)–Pd(1)–S(1) 85.20(4).

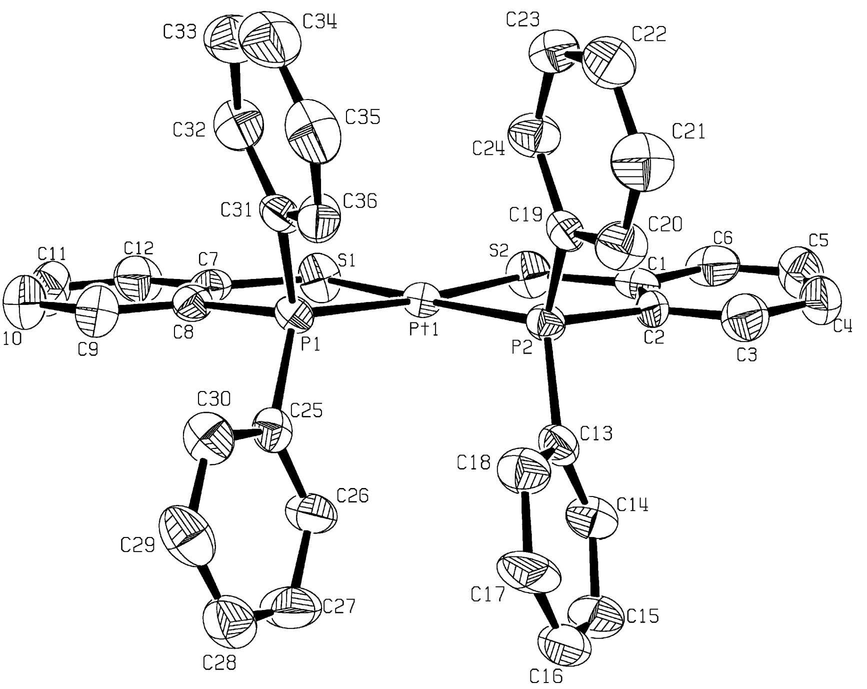

Fig. 3. An ORTEP representation of the structure of *cis*-[Pt($Ph_2PC_6H_4$-2-S)$_2$] (**5**) at 50% of probability showing the atom labeling scheme. Selected bond lengths (Å): Pt(1)–P(2) 2.265(2), Pt(1)–P(1) 2.265(2), Pt(1)–S(1) 2.325(2), Pt(1)–S(2) 2.327(2). Bond angles (°): P(2)–Pt(1)–P(1) 100.05(7), P(2)–Pt(1)–S(1) 172.28(7), P(1)–Pt(1)–S(1) 87.65(7), P(2)–Pt(1)–S(2) 87.60(8), P(1)–Pt(1)–S(2) 171.73(8), S(1)–Pt(1)–S(2) 84.75(8).

to be located in a slightly distorted square planar environment (P(2)–Pt(1)–S(1), 172.28(7)°; P(1)–Pt(1)–S(2), 171.73(8)°), once again the distortion being due to the steric hindrance caused by the *cis* arrangement of the *ph*PS$^-$ ligands around the metal center.

A similar procedure was applied for nickel, however in this case the starting material employed was $NiCl_2 \cdot 6H_2O$, analysis of the green microcrystalline powder obtained by FAB$^+$-MS, elemental analysis and multinuclear NMR revealed the compound to have a similar formulation –[Ni($Ph_2PC_6H_4$-2-S)$_2$]– to that of the palladium and platinum analogues, ^{31}P-NMR analysis of this sample shows a spectrum where a single signal at $\delta = 42.69$ ppm can be clearly distinguished due to the presence of the *cis* isomer. As is the case for the palladium complex, the ^{31}P-NMR spectra of this sample after 24 h standing shows two signals one and the more intense corresponding to the presence of the *trans* isomer ($\delta = 56.45$ ppm)[3] [19] and another of minor intensity ($\delta = 42.69$ ppm) due to the presence of the *cis* isomer (1:16 *cis*/*trans* ratio). Crystals of **6** suitable for X-ray diffraction analysis were obtained in a similar manner to those of complexes **4** and **5**. The crystal structure obtained shows the Ni center to be in a slightly distorted square planar geometry, with the *ph*PS$^-$ ligands being coordinated to the metal center in a *trans* fashion. In this case the isomerization process observed for palladium resulted to be more pronounced, this is probably due to the fact that the structural preference energy for the nickel is smaller in comparison to that of Pd and Pt, therefore the isomerization process occurs faster, thus leading to the behaviour observed in the ^{31}P-NMR. In addition, since Ni(II) is considerable smaller in comparison to Palladium(II) or Platinum(II), it would be more difficult to allocated both *ph*PS$^-$ ligands in a *cis* conformation due to steric hindrance. It is also possible that being the affinity of Ni(II) for the phosphorus center lower in comparison to that of Pd(II) and Pt(II) the hemilability process in this particular case may cause the isomerization process to be more favored leading to the *trans* isomer, this in fact may also justify the different *cis*/*trans* ratios observed in the cases of Ni (1:16 *cis*:*trans* ratio) and Pd (1.5:1 *cis*:*trans* ratio) where a clear trend can be observed to the point where no *trans* isomer is observed for the case of platinum.

To reinforce our hypothesis that the transmetallation route it is indeed stereoselective, we carried out reactions of the starting materials [M(Cl)$_2$(NCC_6H_5)$_2$] M = Pd, Pt or $NiCl_2 \cdot 6H_2O$ with the *ph*PSH proligand in the presence of NEt_3 as base under the same reaction conditions, analyses by ^{31}P-NMR indicate that irrespec-

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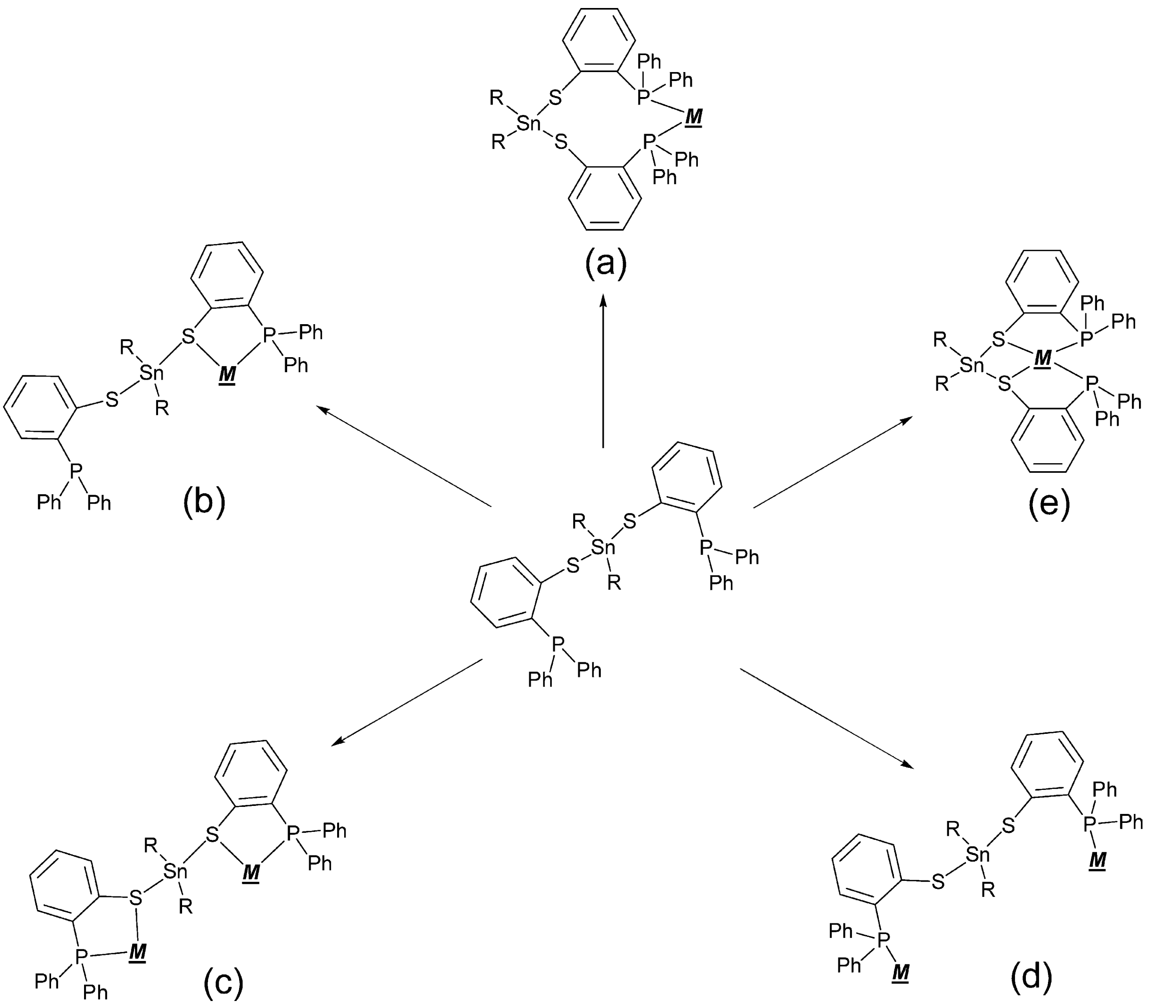
[3] Analogously to complex **4** complex **6** was also synthesized for the first time by an *S*-dealkylation process of *trans*-[Ni($Ph_2PC_6H_4$-2-SMe)$_2$](BF_4)$_2$ [19].



Scheme 1. Possible coordination modes of the metalloligands $[Sn(R)_2(Ph_2PC_6H_4\text{-}2\text{-}S)_2]$.

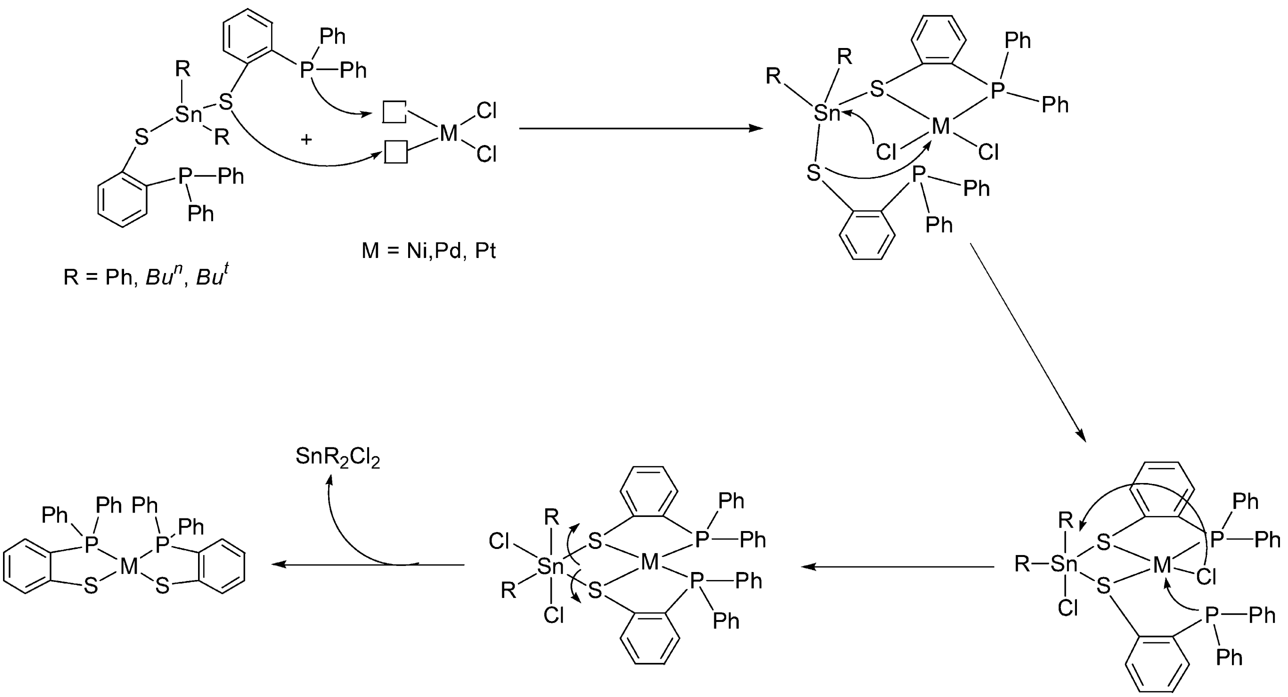
tively of the metal (Ni, Pd or Pt) the product obtained it is always that in *trans* configuration (*trans*-$[M(Ph_2PC_6H_4\text{-}2\text{-}S)_2]$ M = Ni, Pd, Pt), thus probing that the route *via* transmetallation forces the bis-chelated products to a *cis* configuration (kinetic product) which in time isomerizes to the *trans* (thermodynamic product) configured products. It is very likely that this isomerization process occurs through an unbinding–binding process thus illustrating too the hemilabile properties of the ligand *ph*PS^-.

In summary, we have shown that by using the tin(IV) metalloligands of the type $[Sn(R)_2(Ph_2PC_6H_4\text{-}2\text{-}S)_2]$ we can stereoselectively synthesize through transmetallation reactions the *cis* isomers of the complexes $[M(Ph_2PC_6H_4\text{-}2\text{-}S)_2]$ M = Ni, Pd, Pt (Scheme 3).

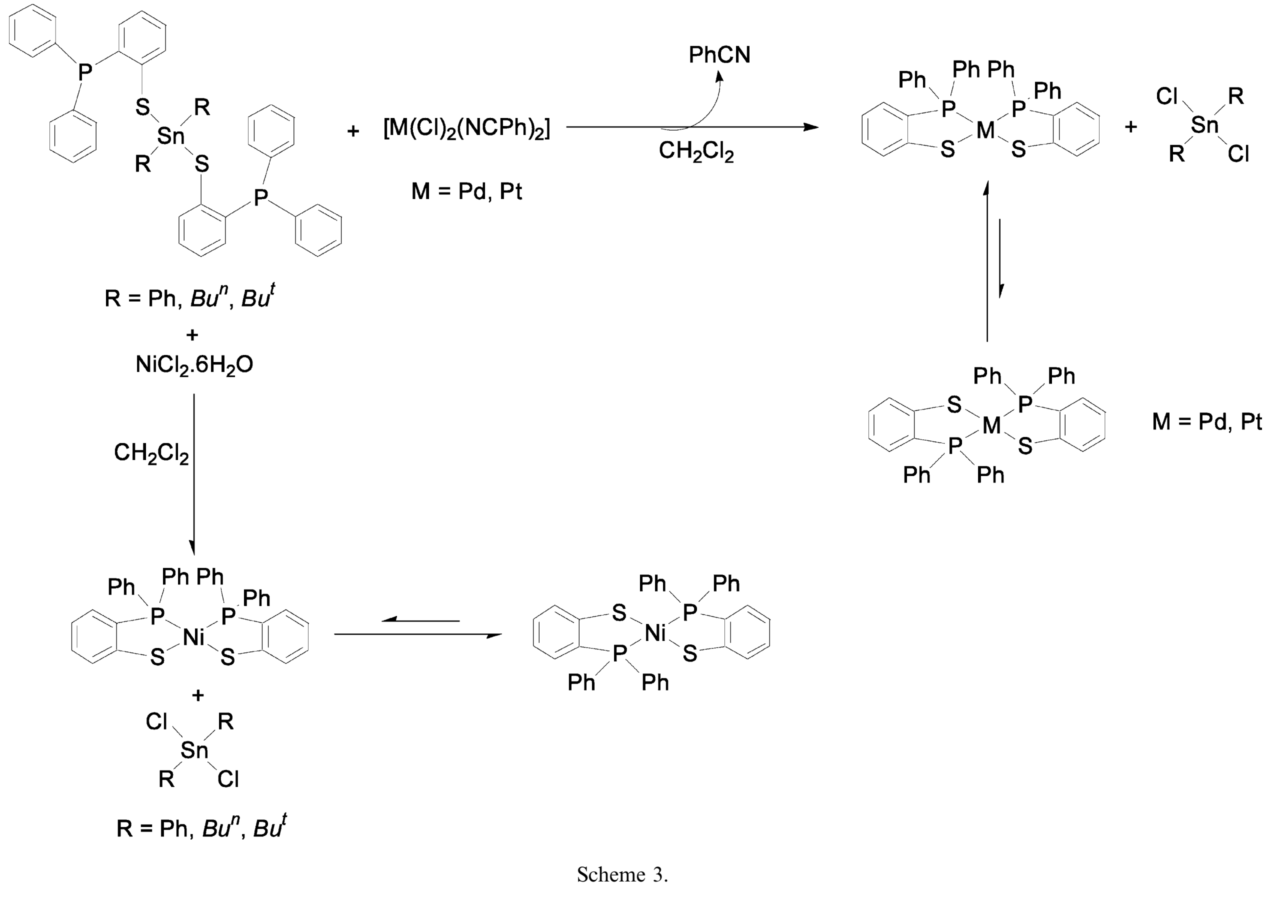
The crystal structure obtained in the case of nickel does not result in the same conformation (*cis*) as that observed for Pd and Pt, however this is probably due more to the inherent properties of the metal center more than due to the synthetic route. Moreover, preliminary results with starting materials of the Group 9 (Vaska's type complexes) indicate that the transmetallation process is driven by the amount of chloride present in the starting materials. Thus, efforts aimed to evaluate this hypothesis by varying the amount of chlorides in the starting materials are currently under investigation in our group.

4. Supplementary material

Supplementary data for complex **2**, **4** and **5** 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 number CCDC 207947–207949.



Scheme 2. A proposal of the probable steps involved in the formation of the complexes *cis*-[M(Ph$_2$PC$_6$H$_4$-2-S)$_2$] M = Ni, Pd and Pt.



Scheme 3.

Acknowledgements

D. C.-G. and V. G.-B. would like to thank CONACYT and DGAPA for financial support. We would like to thank Chem. Eng. Luis Velasco Ibarra and M.Sc. Francisco Javier Perez Flores and QFB. Ma del Rocío Patiño for their invaluable help in the running of the FAB$^+$-Mass and IR Spectra. The support of this research by CONACYT (J41206-Q) is gratefully acknowledged.

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