



Crystal structure and reactivity of mononuclear cationic palladium(II) and platinum(II) triphos complexes with phenyltin(IV) anions. The formation of polynuclear platinum–triphos ionic and covalent complexes

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Abstract

The ionic complexes $[M(\text{triphos})\text{Cl}]\text{X}$ [$M = \text{Pd}$, $\text{X} = \text{Cl}$ (**1**), SnCl_3 (**1a**), SnPh_2Cl_3 (**1c**); $M = \text{Pt}$, $\text{X} = \text{Cl}$ (**3**), SnCl_3 (**3a**), SnPh_2Cl_3 (**3c**)], $[M(\text{triphos})\text{Cl}]_2\text{X}$ [$\text{X} = \text{SnPh}_2\text{Cl}_4$, $M = \text{Pd}$ (**1b**), Pt (**3b**); $\text{X} = \text{PtCl}_4$, $M = \text{Pt}$ (**3d**)] and $[M(\text{triphos})_2]\text{X}_2$ [$\text{X} = \text{SnPh}_2\text{Cl}_3$, $M = \text{Pd}$ (**2**), Pt (**4**)] where triphos = bis(2-diphenylphosphinoethyl)phenylphosphine, were synthesised and characterised by microanalysis, mass spectrometry, IR, ^{119}Sn Mössbauer, NMR (^{31}P , ^{195}Pt and ^{119}Sn) spectroscopies and conductivity measurements. The X-ray crystal structures of compounds **1b**, **3b** and **3c**, where tetrachlorodiphenylstannate(IV) and trichlorodiphenylstannate(IV) act as counterions stabilising cationic metal complexes, are reported. These compounds contain the cation $[M(\text{triphos})\text{Cl}]^+$ with distorted square-planar geometry at palladium or platinum, triphos acting as a tridentate chelating ligand. The anions $[\text{SnPh}_2\text{Cl}_4]^{2-}$ (**1b**, **3b**) and $[\text{SnPh}_2\text{Cl}_3]^-$ (**3c**) have *trans*-octahedral and distorted trigonal-bipyramidal environments for the metal, respectively. Although the dinegatively charged $[\text{SnPh}_2\text{Cl}_4]^{2-}$ is counteracted by the presence of two singularly positively charged $[M(\text{triphos})\text{Cl}]^+$ species, interanion contacts via hydrogen bonds were found for **1b** and **3b** but were absent for compound **3c**. The crystalline solids $[M(\text{triphos})_2][\text{SnPh}_2\text{Cl}_3]_2$ [$M = \text{Pd}$ (**2**), Pt (**4**)] were formed via a chelate ring-opening reaction of $[M(\text{triphos})\text{Cl}]^+$ induced by triphos. The formation of heterometallic complexes by reaction of AgCl or Au(I) with the complex $[\text{Pt}(\text{triphos})_2][\text{SnPh}_2\text{Cl}_3]_2$ (**4**), followed by ^{31}P NMR in solution, did not take place. The presence of dangling arm phosphine oxide groups, on oxidation of complex **4** with H_2O_2 , was detected. Other ring-opening reactions were observed by ^{31}P NMR and conductivity measurements when solutions containing $\text{PtCl}_2(\text{PhCN})_2$ and triphos in a molar ratio 3:2 were refluxed C_6H_6 . Besides $[\text{Pt}(\text{triphos})\text{Cl}]_2[\text{PtCl}_4]$ (**3d**) and the ionic complex with a dinuclear anion, $[\text{Pt}(\text{triphos})\text{Cl}][\text{Pt}_2(\text{triphos})\text{Cl}_5]$ (**5**), the covalent trinuclear complexes $[\{\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh-P}^1, \text{P}^2\}_2(\text{P}^3, \text{P}^3)\text{PtCl}_2]$ (**6a**, **6b**) were formed as minor products. These latter diastereomeric species become the dominant species upon heating, being thermodynamically controlled complexes. Mixtures of **3d**, **5**, **6a** and **6b** converted to complex $[\text{Pt}(\text{triphos})\text{Cl}]\text{Cl}$ (**3**) by addition of triphos, chelate ring-closure reactions of **6a**, **6b** and the complex anion **5** occurring. With an excess of triphos ($\text{Pt}:\text{triphos} = 3:4$ or higher ratio), broad peaks reflecting fast equilibria between ring-opened and ring-closed products were found. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Palladium; Platinum; Triphosphine complexes; Diphenyltin(IV) anions; X-ray structures; NMR spectroscopy

1. Introduction

The platinum diphosphine complexes are among the most studied in coordination chemistry [1] and their catalytic importance, especially in asymmetric hydro-

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formylation, has been proved [2,3]. The $[\text{Pt}(\text{monophosphine})_3\text{Cl}]^+$ cations have also been known for a long time [4–7]. Due to their catalytic relevance in carbonylation reactions, a series of $[\text{Pt}(\text{chiral diphosphine})-(\text{monophosphine})\text{Cl}]^+$ ionic complexes [8] have been characterised. However, relatively little is known about the platinum complexes containing terdentate phosphorus ligands [9,10].

Complexes containing both mono- and diphosphines [11] are relevant not only in catalysis [12] but also in the synthesis of biologically important derivatives [2]. In fact, bis(ditertiaryphosphine) complexes of the type $[\text{M}(\text{dppe})_2]^+$ ($\text{M} = \text{Au}, \text{Ag}, \text{Cu}$) have attracted much interest over the past decade as some of these complexes have been shown to display antitumour activities comparable to cisplatin [13,14]. Moderate cytotoxicity was also found for $[\text{Pd}(\text{diphosphine})(\text{phosphinoarsine})]^{2+}$ and $[\text{Pd}(\text{diphosphine})\text{Cl}_2]$ complexes as well as for the products of their reaction with thiolate ligands [15,16]. The polydentate phosphines are chelating systems or pendants [17–19] for many types of metals and their properties can be altered to favour different kinds of reactions. The reactions of $[\text{Pt}(\text{diphosphine})\text{Cl}_2]$ with mono and bidentate phosphines in the presence of tin(II) produce cationic complexes, with a Pt–Sn bond and SnCl_3^- as counterion [11,20]. The interaction of the linear triphosphine [triphos = $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$] with SnPh_2Cl_2 [21] leads to the formation of a five-coordinate complex, SnPh_2Cl_2 -(triphos), where the phosphine seems to act as a monodentate ligand. On the other hand, a chelate ring-opening of $[\text{Pd}(\text{triphos})\text{Br}]\text{Br}$ can be induced by oxidising agents giving the square-planar Pd(II) complex $[\text{Pd}(\text{triphos-O})_2][\text{PdBr}_4]$ or the unusual square-pyramidal five-coordinate Pd(II) complex, $[\text{Pd}(\text{triphos-O})_2\text{Br}]\text{Br}$ [22] containing dangling arm phosphine oxide groups. The combination of square-planar Pd(II) or Pt(II) and linear Au(I) centres with triphos in a single complex has been investigated, affording novel bimetallic complexes by a chelate-ring opening reaction, a process which was possible to reverse via Au(I) abstraction from $\text{PtAu}(\text{triphos})\text{Cl}_3$ [23]. However, no more examples of chelate-ring opening or closure reactions concerning M(II)–triphos systems ($\text{M} = \text{Pd}, \text{Pt}$) have been described yet. Likewise, as far as we know, no crystal structures of compounds containing $[\text{SnPh}_2\text{Cl}_4]^{2-}$ or $[\text{SnPh}_2\text{Cl}_3]^-$ anions stabilising cationic metal complexes have been reported [24–29]. In this paper we study the modifications that $[\text{M}(\text{triphos})\text{Cl}]\text{Cl}$ ($\text{M} = \text{Pd}, \text{Pt}$) complexes can undergo on the chloride counterion or the chelate rings. In order to achieve this, the interactions of $[\text{M}(\text{triphos})\text{Cl}]\text{Cl}$ complexes with SnCl_2 , SnPh_2Cl_2 and the triphos ligand in different ratios are reported. Unusual sequences for the reaction with SnPh_2Cl_2 allowed crystals of $[\text{M}(\text{triphos})\text{Cl}][\text{SnPh}_2\text{Cl}_4]$ ($\text{M} = \text{Pd}, \text{Pt}$) and $[\text{Pt}(\text{triphos})\text{Cl}]$ -

$[\text{SnPh}_2\text{Cl}_3]$ which were suitable for X-ray diffraction to be obtained. Using 3:2 platinum:triphos ratios the formation of a Pt covalent trinuclear complex and a dinuclear anionic complex, which undergo a ring-closure reaction to give $[\text{Pt}(\text{triphos})\text{Cl}]\text{Cl}$, was detected by ^{31}P NMR and conductivity measurements.

2. Experimental

2.1. General procedures

Solvents were dried by conventional methods, distilled and kept under argon. Other reagents were of the highest commercial grade available and were used as received. Solvent evaporations were always carried out under vacuum using a rotary evaporator and a vacuum line. Microanalyses (C, H) were performed at the Universities of Santiago de Compostela and Janus Pannonius.

2.2. Instrumentation

Fast atom bombardment (FAB) spectra were obtained on a KRATOS MS 50 spectrometer using 3-nitrobenzyl alcohol as the matrix and electron spray mass spectra were obtained on a Micromass VG-QUATTRO spectrometer by injecting 0.5×10^{-4} M solutions at a flow rate of $15 \mu\text{l min}^{-1}$ and using $\text{CH}_3\text{CN}/\text{H}_2\text{O}/\text{HCOOH}$ (1%) as the mobile phase. Infrared spectra were recorded at ambient temperature as KBr pellets ($4000\text{--}500 \text{ cm}^{-1}$) and Nujol mulls ($500\text{--}100 \text{ cm}^{-1}$) on a Mattson Cygnus 100 spectrophotometer. The bands are reported as: vs very strong, s strong, m medium and sh shoulder. The ^{119}Sn Mössbauer spectra were recorded in constant acceleration mode on an Elscint MVT4 Promeda counting instrument, with a $\text{Ca}^{119\text{m}}\text{SnO}_3$ source from Amersham as described previously [30]. The probe was maintained at a temperature between 90 and 100 K, and the source was kept at room temperature. The digital data were treated with an iterative program and least square deconvoluted as a linear combination of Lorentzian functions [31]. $^{31}\text{P}\{^1\text{H}\}$ spectra were recorded on Bruker AMX500 and Varian Inova 400 spectrometers at 202.46 MHz and 161.9 MHz, respectively. ^{195}Pt and ^{119}Sn NMR spectra were recorded on a Bruker AMX500 spectrometer at 107.52 and 186.5 MHz, respectively. Chemical shifts are reported relative to external standard 85% H_3PO_4 (^{31}P), 1 M Na_2PtCl_6 (^{195}Pt) and SnMe_4 (^{119}Sn); δ is the chemical shift in ppm; s singlet, d doublet, t triplet, dt doublet of triplet, m multiplet, bs broad signal; J is the coupling constant in Hz. Conductivities were obtained at 25°C from 10^{-3} M solutions in CH_3CN or DMF on a WTW model LF-3 instrument. Conductivities were also obtained from CH_2Cl_2 solutions on a Radelkis (0K-102/1) instrument.

2.3. Preparation of complexes

2.3.1. Synthesis of [Pd(triphos)Cl]Cl (**1**)

A suspension of PdCl₂ (0.1771 g, 0.9970 mmol) and NaCl (0.1165 g, 1.9910 mmol) in H₂O (25 ml) was heated in a water bath until a clear solution formed. This was allowed to cool to ambient temperature and triphos (0.6000 g, 1.1220 mmol) in CH₂Cl₂ (30 ml) was added dropwise. The resultant solution was stirred for 1 h at room temperature (r.t.) and solvent was removed in vacuo to leave a white solid. The solid was filtered off, washed with water, dried in vacuo and recrystallised from CH₂Cl₂-*n*-hexane, to give colourless prisms. Yield: 67%, m.p. > 250°C. *Anal.* Found: C, 57.01; H, 4.90. Calc. for C₃₄H₃₃P₃PdCl₂: C, 57.31; H, 4.67%. ³¹P{¹H} NMR (CDCl₃): δ 109.3 (t) [P^B], δ 44.2 (d) [P^A] (²J(³¹P^B-P^A) = 9.4 Hz). IR (cm⁻¹): 318 vs [ν(Pd-Cl)]. MS (FAB): *m/z* (rel. intensity) 675 (100%, [M⁺ - Cl⁻]). *A* (Ω⁻¹ cm² mol⁻¹, DMF): 91.5.

2.3.2. Synthesis of [Pd(triphos)Cl][SnCl₃] (**1a**)

SnCl₂ (0.0533 g, 0.2807 mmol) was dissolved in a 1:1 mixture of MeOH:CH₂Cl₂ (8 ml) and added dropwise to a solution of [Pd(triphos)Cl]Cl (0.2000 g, 0.2807 mmol) in CH₂Cl₂ (25 ml). The final solution was stirred for 18 h and then solvents were removed in vacuo until only a small volume remained. The complex was precipitated with Et₂O, filtered off, recrystallised from CH₂Cl₂-Et₂O and dried in vacuo. Yield 82%, m.p. (dec.) > 200°C. *Anal.* Found: C, 44.50; H, 3.87. Calc. for C₃₄H₃₃P₃PdSnCl₄: C, 45.22; H, 3.69%. ³¹P{¹H} NMR (CD₂Cl₂): δ 110.8 (s) [P^B], δ 46.3 (s) [P^A]. ¹¹⁹Sn NMR (CD₂Cl₂, -40°C): -62.5 (s). IR (cm⁻¹): 310 vs [ν(Pd-Cl)], 312 vs, 296 vs [ν(Sn-Cl)]. MS (FAB): *m/z* (rel. intensity) 675 (100%, [M⁺ - SnCl₃⁻]). *A* (Ω⁻¹ cm² mol⁻¹, CH₃CN): 126.8.

2.3.3. Synthesis of [Pd(triphos)Cl]₂[SnPh₂Cl₄] (**1b**)

To a solution of SnPh₂Cl₂ (0.1207 g, 0.3512 mmol) in dry acetone (25 ml), a solution of [Pd(triphos)Cl]Cl (0.2500 g, 0.3512 mmol) in dry CH₂Cl₂ (30 ml) was added dropwise. The mixture reaction was stirred for 24 h, filtered off, *n*-hexane was added and solvents were slowly evaporated in air. The resulting crystals were filtered off and dried in vacuo. By recrystallisation in acetone-CH₂Cl₂ suitable crystals for X-ray diffraction were obtained. Yield 40%, m.p. (dec.) > 200°C. *Anal.* Found: C, 54.12; H, 4.36. Calc. for C₈₀H₇₆P₆Pd₂SnCl₆: C, 54.29; H, 4.34%. ³¹P{¹H} NMR (CD₂Cl₂): δ 110.2 (s) [P^B], δ 46.1 (s) [P^A]. ¹¹⁹Sn NMR (CD₂Cl₂, -40°C): -253.2 (s). ¹¹⁹Sn Mössbauer: QS (mm s⁻¹): 3.55; IS (mm s⁻¹): 1.33. IR (cm⁻¹): 311s [ν(Pd-Cl)], 228vs [ν(Sn-Cl)], 283m [ν_{as}(Sn-C)], 240sh [ν_s(Sn-C)]. MS (FAB): *m/z* (rel. intensity) 675 (100%, [M⁺ - SnPh₂Cl₄²⁻]). *A* (Ω⁻¹ cm² mol⁻¹, CH₃CN): 121.8.

2.3.4. Synthesis of [Pd(triphos)Cl][SnPh₂Cl₃] (**1c**)

A solution of [Pd(triphos)Cl]Cl (0.2500 g, 0.3512 mmol) in dry CH₂Cl₂ (30 ml) was added dropwise to a solution of SnPh₂Cl₂ (0.2414 g, 0.7024 mmol) in dry acetone (50 ml). The resultant solution was stirred for 48 h, filtered off and the solid was precipitated with Et₂O. It was filtered off and dried in vacuo. Yield 89%, m.p. > 175°C. *Anal.* Found: C, 51.93; H, 3.91. Calc. for C₄₆H₄₃P₃PdSnCl₄: C, 52.29; H, 4.11%. ³¹P{¹H} NMR (CD₂Cl₂): δ 108.5 (t) [P^B], δ 44.1 (d) [P^A]. ¹¹⁹Sn NMR (CD₂Cl₂, -40°C): -239.7 (s). ¹¹⁹Sn Mössbauer: QS (mm s⁻¹): 2.67; IS (mm s⁻¹): 1.25. IR (cm⁻¹): 312s [ν(Pd-Cl)], 229vs [ν(Sn-Cl)], 282m [ν_{as}(Sn-C)], 225vs [ν_s(Sn-C)]. MS (FAB): *m/z* (rel. intensity) 675 (100%, [M⁺ - SnPh₂Cl₃⁻]). *A* (Ω⁻¹ cm² mol⁻¹, CH₃CN): 131.7.

2.3.5. Synthesis of [Pd(triphos)₂][SnPh₂Cl₃]₂ (**2**)

To a solution of [Pd(triphos)Cl]Cl (0.1500 g, 0.2106 mmol) in dry CH₂Cl₂ (15 ml) a solution of SnPh₂Cl₂ (0.1448 g, 0.4212 mmol) in dry acetone (32 ml) was added dropwise. The mixture reaction was stirred for 4 h and then a solution of triphos (0.1126 g, 0.2106 mmol) in dry CH₂Cl₂ (15 ml) was added slowly. The resulting yellow solution was stirred for 18 h, filtered off and solvents were removed in vacuo. Yield 77%, m.p. 183°C. *Anal.* Found: C, 57.90; H, 5.00. Calc. for C₉₂H₈₆P₆PdSn₂Cl₆: C, 57.10; H, 4.50%. ³¹P{¹H} NMR (CD₂Cl₂): δ 54.4 (bs) [P^E], δ 49.9 (s) [P^D], δ -12.7 (bs) [P^C]. ¹¹⁹Sn NMR (CD₂Cl₂, -40°C): -259.1 (s). IR (cm⁻¹): 250s [ν(Sn-Cl)], 276m [ν_{as}(Sn-C)], 245s [ν_s(Sn-C)]. MS (FAB): *m/z* (rel. intensity) 1174 (7%, [M²⁺ - 2SnPh₂Cl₃⁻]), 587 (13%, [M²⁺ - 2SnPh₂Cl₃⁻/2]). *A* (Ω⁻¹ cm² mol⁻¹, CH₃CN): 194.7.

This complex can also be prepared using a Pd:Sn:triphos in the ratio of 2:2:2.

2.3.6. Synthesis of [Pt(triphos)Cl]Cl (**3**)

Method 1. The compound was prepared as described earlier [22]. A solution of triphos (1.0000 g, 1.8706 mmol) in CH₂Cl₂ (50 ml) was added dropwise to a solution of K₂PtCl₄ (0.7192 g, 1.7326 mmol) in H₂O (35 ml). The final solution was stirred for 1 h and solvents removed in vacuo to leave a white precipitate. The solid was filtered off, washed with water, dried in vacuo and recrystallised from CH₂Cl₂-*n*-hexane, to give colourless prisms. Yield 70%. Method 2. A solution of triphos (0.5340 g, 1.0000 mmol) in benzene (3 ml) was added to the refluxing yellow solution of PtCl₂(PhCN)₂ (0.4720 g, 1.0000 mmol) in benzene (45 ml). After a few minutes a fine white precipitate was formed. The mixture was stirred for 1 h, then cooled to r.t. The solid was filtered off, washed with benzene, and dried under reduced pressure to give [Pt(triphos)Cl]Cl as white powder. Yield 91%, m.p. 200°C. *Anal.* Found: C, 51.18; H, 4.33. Calc. for C₃₄H₃₃P₃PtCl₂: C, 51.01; H, 4.15%.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 83.7 (s) [P^{B} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 3015$ Hz; $^2J(^{31}\text{P}^{\text{B}}-\text{P}^{\text{A}}) = 3.1$ Hz], δ 39.8 (s) [P^{A} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2484$ Hz; $^2J(^{31}\text{P}^{\text{B}}-\text{P}^{\text{A}}) = 3.1$ Hz]. ^{195}Pt NMR (CDCl_3): $-\delta$ 4858.3 (dt) [P^{B} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 3015$ Hz; P^{A} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2484$ Hz]. IR (cm^{-1}): 320vs, 314sh [$\nu(\text{Pt}-\text{Cl})$]. MS (FAB): m/z (rel. intensity) 764 (100%, [$M^+ - \text{Cl}^-$]). A ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, DMF): 82.9.

2.3.7. Synthesis of $[\text{Pt}(\text{triphos})\text{Cl}][\text{SnCl}_3]$ (**3a**)

SnCl_2 (0.0474 g, 0.2498 mmol) was dissolved in a 1:1 mixture of $\text{MeOH}:\text{CH}_2\text{Cl}_2$ (6 ml). This was added dropwise to a solution of $[\text{Pt}(\text{triphos})\text{Cl}]\text{Cl}$ (0.2000 g, 0.2498 mmol) in CH_2Cl_2 (25 ml). The final solution was stirred for 7 h, after which solvents were removed in vacuo. A pale yellow solid was deposited. This was recrystallised from $\text{CH}_2\text{Cl}_2-\text{Et}_2\text{O}$ and dried in vacuo. Yield 60%, m.p. $> 200^\circ\text{C}$. Anal. Found: C, 40.70; H, 3.60. Calc. for $\text{C}_{34}\text{H}_{33}\text{P}_3\text{PtSnCl}_4$: C, 41.24; H, 3.36%. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 86.3 (s) [P^{B} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 3035$ Hz], δ 42.3 (d) [P^{A} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2477$ Hz]. ^{195}Pt NMR (CDCl_3): $-\delta$ 4858 (dt) [P^{B} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 3038$ Hz; P^{A} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2482$ Hz]. ^{119}Sn NMR (CD_2Cl_2 , -40°C): $-\delta$ 60.8 (s). IR (cm^{-1}): 312vs [$\nu(\text{Pt}-\text{Cl})$], 315s, 294vs [$\nu(\text{Sn}-\text{Cl})$]. MS (FAB): m/z (rel. intensity) 764 (100%, [$M^+ - \text{SnCl}_3^-$]). A ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, CH_3CN): 126.8.

2.3.8. Synthesis of $[\text{Pt}(\text{triphos})\text{Cl}]_2[\text{SnPh}_2\text{Cl}_4]$ (**3b**)

To a solution of SnPh_2Cl_2 (0.1073 g, 0.3122 mmol) in dry acetone (25 ml), a solution of **1** (0.2500 g, 0.3122 mmol) in EtOH (30 ml) was added dropwise. The mixture reaction was stirred for 24 h, filtered off and solvents were slowly evaporated in air. The resulting crystals were filtered off and dried in vacuo. By recrystallisation in acetone– EtOH crystals suitable for X-ray diffraction were obtained. Yield 69%, m.p. $> 200^\circ\text{C}$. Anal. Found: C, 49.40; H, 4.06. Calc. for $\text{C}_{80}\text{H}_{76}\text{P}_6\text{Pt}_2\text{SnCl}_6$: C, 49.41; H, 3.94%. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 83.3 (s) [P^{B} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 3045$ Hz], δ 39.6 (s) [P^{A} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2468$ Hz]. ^{195}Pt NMR (CDCl_3): $-\delta$ 4856 (dt) [P^{B} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 3053$ Hz; P^{A} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2469$ Hz]. ^{119}Sn NMR (CD_2Cl_2): $-\delta$ 177.4 (s). ^{119}Sn Mössbauer: QS (mm s^{-1}): 3.61; IS (mm s^{-1}): 1.30. IR (cm^{-1}): 326vs [$\nu(\text{Pt}-\text{Cl})$], 227vs [$\nu(\text{Sn}-\text{Cl})$], 279m [$\nu_{\text{as}}(\text{Sn}-\text{C})$], 240sh [$\nu_{\text{s}}(\text{Sn}-\text{C})$]. MS (FAB): m/z (rel. intensity) 764 (92%, [$M^+ - \text{SnPh}_2\text{Cl}_4^-$]). A ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, CH_3CN): 164.1.

2.3.9. Synthesis of $[\text{Pt}(\text{triphos})\text{Cl}][\text{SnPh}_2\text{Cl}_3]$ (**3c**)

To a solution of SnPh_2Cl_2 (0.0859 g, 0.2497 mmol) in dry acetone (25 ml), a solution of **1** (0.2000 g, 0.2497 mmol) in dry CH_2Cl_2 (25 ml) was added dropwise. The reaction mixture was stirred for 24 h and after that another solution of SnPh_2Cl_2 (0.0859 g, 0.2497 mmol) in dry acetone (25 ml) was slowly added. The solution was stirred for 24 h, filtered off and solvents were

evaporated in air. The resulting systoles were filtered off, washed with Et_2O and dried in vacuo. Crystals suitable for X-ray diffraction were obtained by recrystallisation in CH_2Cl_2 –acetone. Yield 88%, m.p. 150°C . Anal. Found: C, 48.49; H, 3.85. Calc. for $\text{C}_{46}\text{H}_{43}\text{P}_3\text{PtSnCl}_4$: C, 48.28; H, 3.79%. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 83.2 (s) [P^{B} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 3047$ Hz], δ 39.6 (s) [P^{A} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2467$ Hz]. ^{195}Pt NMR ($\text{CDCl}_3 + \text{DMSO}-d_6$): $-\delta$ 4859 (dt) [P^{B} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 3034$ Hz; P^{A} , $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2470$ Hz]. ^{119}Sn Mössbauer: QS (mm s^{-1}): 2.96; IS (mm s^{-1}): 1.23. IR (cm^{-1}): 330s, 319m [$\nu(\text{Pt}-\text{Cl})$], 237sh [$\nu(\text{Sn}-\text{Cl})$], 282m [$\nu_{\text{as}}(\text{Sn}-\text{C})$], 227vs [$\nu_{\text{s}}(\text{Sn}-\text{C})$]. MS (FAB): m/z (rel. intensity) 764 (91%, [$M^+ - \text{SnPh}_2\text{Cl}_3^-$]). A ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, CH_3CN): 123.0.

2.3.10. Preparation of $[\text{Pt}(\text{triphos})\text{Cl}]_2[\text{PtCl}_4]$ (**3d**)

See Table 4.

2.3.11. Synthesis of $[\text{Pt}(\text{triphos})_2][\text{SnPh}_2\text{Cl}_3]_2$ (**4**)

A solution of **3** (0.2376 g, 0.2967 mmol) in dry CHCl_3 (32 ml) was added dropwise to a solution of SnPh_2Cl_2 (0.1020 g, 0.2967 mmol) in dry acetone (20 ml). The mixture reaction was stirred for 6 h and then a solution of triphos (0.1586 g, 0.2967 mmol) in CHCl_3 (18 ml) was slowly added. The resulting yellow solution was stirred for 24 h, filtered off and the solvents were evaporated in air and a yellow crystalline solid formed. The solid was recrystallised from CH_2Cl_2 –acetone– EtOH . White crystals were obtained, filtered off, washed with Et_2O and dried in vacuo. Yield 52%, m.p. 122°C . Anal. Found: C, 54.00; H, 4.10. Calc. for $\text{C}_{92}\text{H}_{86}\text{P}_6\text{PtSn}_2\text{Cl}_6$: C, 54.60; H, 4.29%. $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CDCl}_3 + \text{DMSO}-d_6$): δ 38.4 (s) [$\text{P}^{\text{D,E}}$, $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2352$ Hz]. ^{195}Pt NMR (CD_2Cl_2): $-\delta$ 5098 (m). ^{119}Sn NMR (CD_2Cl_2): $-\delta$ 256.0. ^{119}Sn Mössbauer: QS (mm s^{-1}): 2.81; IS (mm s^{-1}): 1.23. IR (cm^{-1}): 250s [$\nu(\text{Sn}-\text{Cl})$], 279m [$\nu_{\text{as}}(\text{Sn}-\text{C})$], 245m [$\nu_{\text{s}}(\text{Sn}-\text{C})$]. MS (FAB): m/z (rel. intensity) 1263 (9%, [$M^{2+} - 2\text{SnPh}_2\text{Cl}_3^-$]); MS (ES) 632 (100%, [$M^{2+} - 2\text{SnPh}_2\text{Cl}_3^-/2$]). A ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, CH_3CN): 200.5.

The same compound was obtained when the ratio Pt:Sn:triphos was 1:2:1. In this case recrystallisation was not necessary.

2.3.12. Preparation of $[\text{Pt}(\text{triphos})\text{Cl}][\text{Pt}_2(\text{triphos})\text{Cl}_5]$ (**5**)

See Table 4.

2.3.13. Preparation of $[\text{Pt}_3(\text{triphos})_2\text{Cl}_6]$ (**6a**, **6b**)

See Table 4.

2.4. Reactions

2.4.1. Titration of complex **3** with AgCl

To a solution of **3** (0.0150 g, 0.0187 mmol) in CDCl_3 (0.5 ml), AgCl (0.0027 g, 0.0187 mmol) was added as a

solid. The mixture reaction was stirred for 12 h and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded.

2.4.2. Titration of complex **3c** with Au(I)

Solutions of Au(I) were prepared by treating Au with HCl and HNO_3 in an oil bath (120°C) and reduction from Au(III) to Au(I) with 2,2-thiodiethanol (thiodiglycol) as was indicated in the literature [23,32,33]. A solution of Au(I) (0.0100 g of Au, 0.0508 mmol), prepared as described previously, in MeOH (1 ml), was added dropwise to a solution of complex **3c** (0.0581 g, 0.0508 mmol) in CDCl_3 (1 ml). After 12 h a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded. This procedure was repeated after additions of two and three molar equivalents of Au(I).

2.4.3. Titration of complex **4** with Au(I)

Solutions of Au(I) were prepared as above. A solution of Au(I) (0.0039 g of Au, 0.0198 mmol), prepared as described previously, in MeOH (0.3 ml), was added dropwise to a solution of complex **4** (0.0200 g, 0.0099 mmol) in CDCl_3 (0.6 ml). After 12 h the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded.

2.4.4. Titration of complex **4** with AgCl

To a solution of complex **4** (0.0200 g, 0.0099 mmol) in CDCl_3 (0.6 ml) AgCl (0.0028 g, 0.0198 mmol) was added as a solid. The reaction mixture was stirred for 12 h and a white solid was obtained. DMSO- d_6 (0.5 ml) was added and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the resulting solution was recorded.

2.4.5. Oxidation of complex **4** with H_2O_2 and reaction with SnPh_2Cl_2

To a solution of complex **4** (0.0200 g, 0.0099 mmol) in CDCl_3 (0.6 ml) H_2O_2 (100 μl , 6%) was added. Immediately a white precipitate was obtained. The solid

was dissolved in DMSO- d_6 (0.5 ml) and after 12 h the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded. To the clear solution SnPh_2Cl_2 (0.0068 g, 0.0198 mmol) in CD_2Cl_2 (0.4 ml) was added and after 12 h the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded.

2.5. X-ray diffraction studies

Colourless prismatic crystals of **1b**, **3b** and **3c** were mounted on glass fibres and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement on the diffraction data from 25 reflections in the ranges $8.76^\circ < \theta < 17.92^\circ$ (**1b**), $8.96^\circ < \theta < 17.95^\circ$ (**3b**) and $10.74^\circ < \theta < 18.00^\circ$ (**3c**) in an Enraf–Nonius Mach3 automatic diffractometer [34]. Data were collected at 293 K using Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) and the ω scan technique and corrected for Lorentz and polarisation effects [35]. A semi-empirical absorption correction (ψ scan) was made [36] for **1b** and an empirical absorption correction was made [37] for **3b** and **3c**.

The structures were solved by direct methods [38], which revealed the positions of all non-hydrogen atoms, and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [39]. The C35 and C36 atoms for **1b** were found to be disordered over two sites (C351 and C352, C361 and C362, each with an occupancy of approximately 0.5). All the hydrogen atoms except those of the disordered C atoms (**1b**) were located in their calculated positions (C–H 0.93–0.97 \AA) and refined using a riding model. For **3c** relatively large positive peaks were found in the final difference Fourier map, but these were all error peaks located near the Sn and Pt atoms. Atomic scattering factors were obtained with the use of international tables for X-ray crystallography [40]. Molecular graphics were produced with the use of drawing programs such as PLATON [36] (**1b**) and ZORTEP [41] (**1b**, **3b**, **3c**).

3. Results and discussion

Fig. 1 shows the complexes studied. Complexes **1** and **3** were prepared using a variation [42] of a literature method [43]. In accordance with Scheme 1, compounds **1** and **3** can also be obtained in a very good yield (91%, **3**) by direct interaction of $\text{MCl}_2(\text{PhCN})_2$ with triphos in refluxing benzene for 2 h. Complexes **1a** and **3a** were afforded by addition of SnCl_2 to solutions of $[\text{M}(\text{triphos})\text{Cl}]\text{Cl}$ in a 1:1 molar ratio.

Crystals of compounds **1b**, **3b** and **3c** suitable for X-ray diffraction were prepared as showed in Eq. (1) (**1b**, **3b**) and Eq. (2) (**3c**) respectively, using the solvents and conditions described in Section 2.

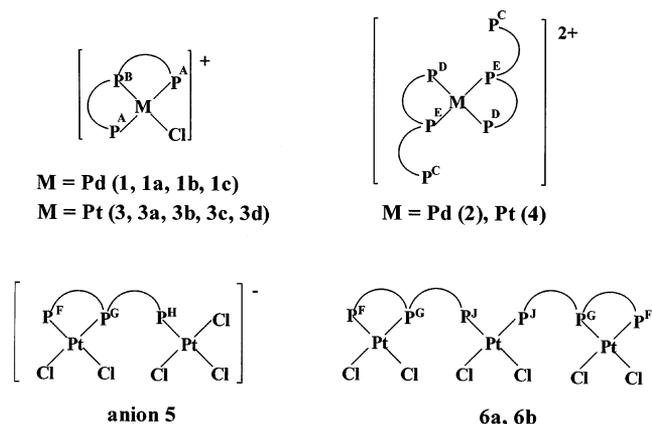
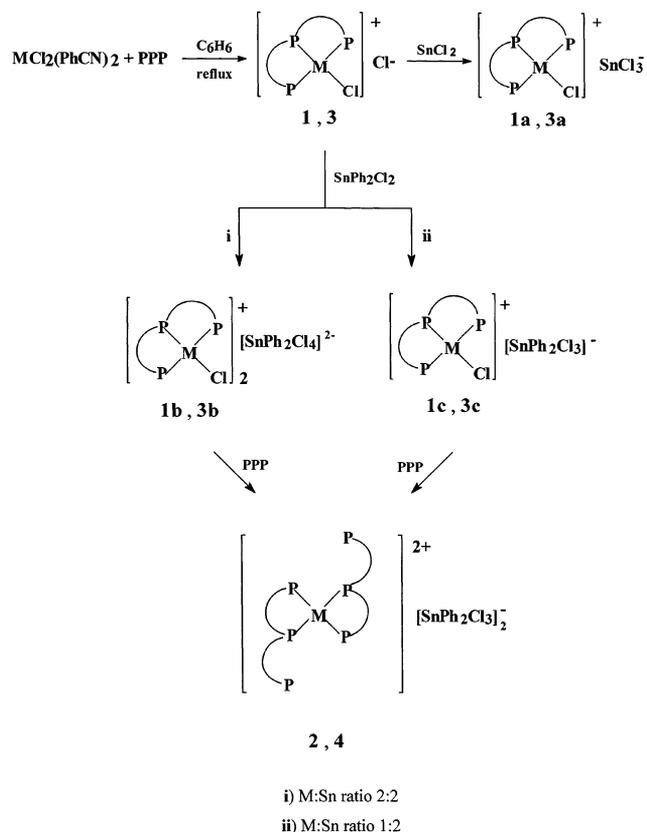
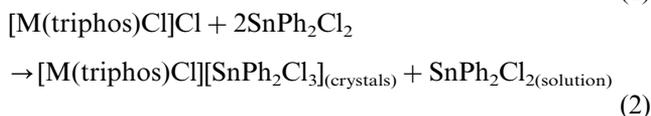
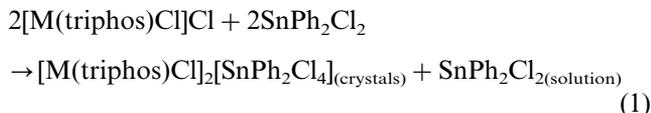


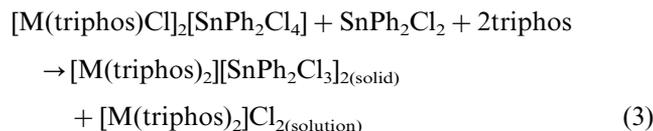
Fig. 1. Marking of the phosphorus atoms in ionic and covalent complexes.



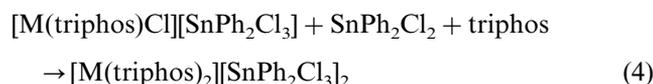
Scheme 1. The formation of ionic palladium and platinum complexes at M:triphos = (1:1 = 2:2) and 1:2 ratios.



In both cases (2:2 and 1:2 ratios), some diphenyltin(IV) chloride remained in solution. Solutions containing $[\text{M}(\text{triphos})\text{Cl}]_2[\text{SnPh}_2\text{Cl}_4]$ and SnPh_2Cl_2 (Eq. (1)) under stirring reacted with two molar equivalents of triphos (M:Sn:triphos = 2:2:2), giving rise to crystalline solids characterised as $[\text{Pd}(\text{triphos})_2][\text{SnPh}_2\text{Cl}_3]_2$ (2) and $[\text{Pt}(\text{triphos})_2][\text{SnPh}_2\text{Cl}_3]_2$ (4) (Eq. (3)).



The reaction under stirring of one molar equivalent of triphos with solutions containing $[\text{M}(\text{triphos})\text{Cl}][\text{SnPh}_2\text{Cl}_3]$ and SnPh_2Cl_2 (Eq. (2)) (Pt:Sn:triphos = 1:2:1) led to the complexes 2 (M = Pd) and 4 (M = Pt) as the only products (Eq. (4)).

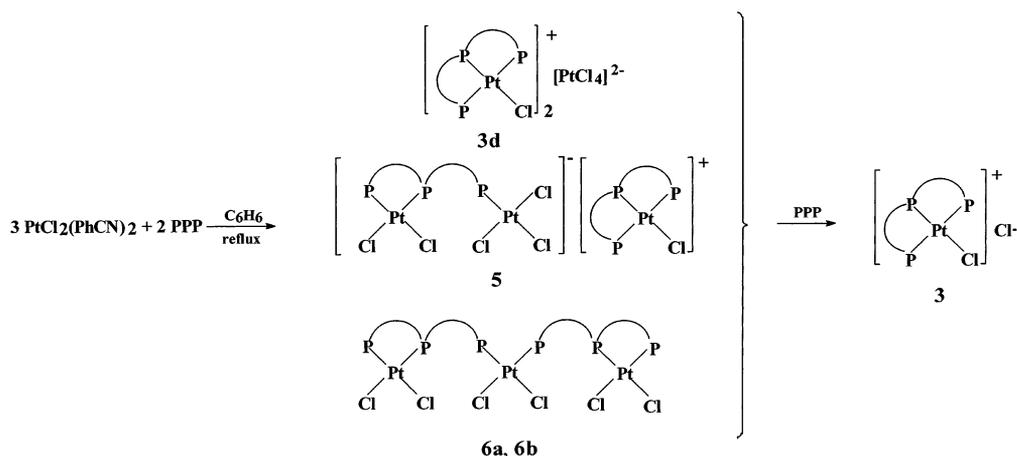


Other Pt:Sn:triphos ratios, 2:2:3, 1:2:3 or 1:3:1, did not give rise to new compounds.

Using $\text{PtCl}_2(\text{PhCN})_2$ and triphos in a 3:2 ratio (Scheme 2) the dominant product formed was the kinetically controlled ionic complex $[\text{Pt}(\text{triphos})\text{Cl}]_2[\text{PtCl}_4]$ (3d) which can be converted into the ionic complex $[\text{Pt}(\text{triphos})\text{Cl}][\text{Pt}_2(\text{triphos})\text{Cl}_5]$ (5) and the neutral $\text{Pt}_3(\text{triphos})_2\text{Cl}_6$ (6a, 6b) thermodynamically controlled complexes.

3.1. X-ray structures

A molecular drawing of compounds 1b and 3b is shown in Fig. 2. Table 1 summarises the crystal parameters, data collection and refinement for compounds 1b, 3b, and 3c. Selected bond distances and angles for complexes 1b, 3b and 3c are listed in Table 2.



Scheme 2. The formation of ionic and covalent platinum complexes at Pt:triphos = 3:2 ratio and their transformation into 3 upon addition of extra triphos.

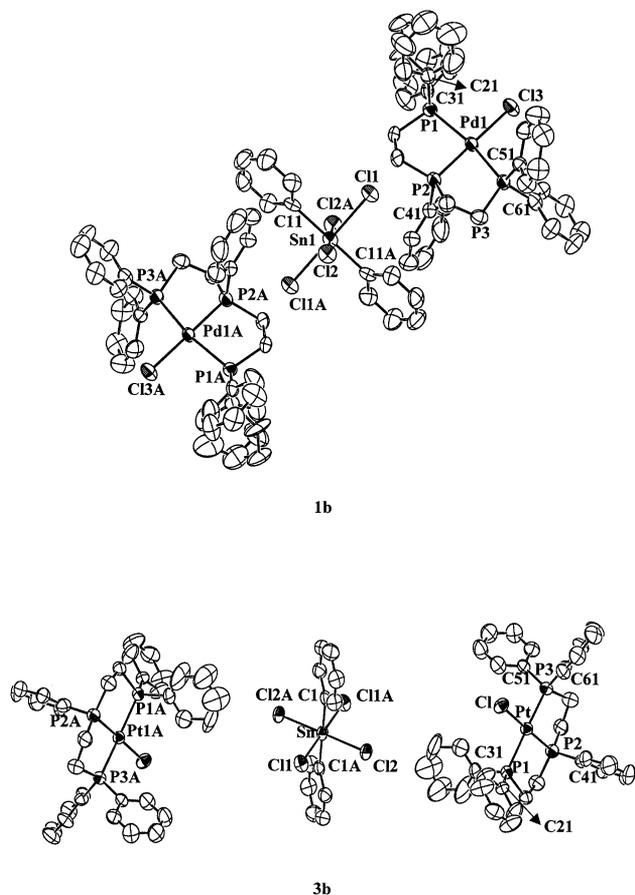


Fig. 2. ORTEP view and numbering scheme of $[M(\text{triphos})\text{Cl}]_2\text{-}[\text{SnPh}_2\text{Cl}_4]$ ($M = \text{Pd}$ (**1b**), Pt (**3b**)).

Crystals of **1b** ($M = \text{Pd}$) and **3b** ($M = \text{Pt}$) consist of two monocations $[M(\text{triphos})\text{Cl}]^+$ which are symmetrically located in relation to one dianion, $[\text{SnPh}_2\text{Cl}_4]^{2-}$, the tin atom being the centre of symmetry. Fig. 3 illustrates the structure of $[\text{Pt}(\text{triphos})\text{Cl}][\text{SnPh}_2\text{Cl}_3]$ (**3c**) which consists of one monocation $[\text{Pt}(\text{triphos})\text{Cl}]^+$ and one monoanion $[\text{SnPh}_2\text{Cl}_3]^-$. The triphosphine in the monocations is bonded to the metal in a double chelate fashion through the three P atoms, acting as a tridentate ligand. One chloride completes the distorted square-planar environment at the palladium or platinum. The $M\text{-P}$ bond distances for the compounds (**1b**, 2.323(2) [P(1)], 2.218(2) [P(2)], 2.321(2) [P(3)] Å; **3b**, 2.315(3) [P(1)], 2.210(3) [P(2)], 2.309(3) [P(3)] Å; **3c**, 2.301(1) [P(1)], 2.212(1) [P(2)], 2.299(1) [P(3)] Å) were very similar to those reported for complexes **1** [44] and **3** [23]. As occurred for **1** and **3** the $M\text{-P}(2)$ bond distances in all cases were shorter than the $M\text{-P}$ terminal bond due to the double chelate effect of triphos. $M\text{-Cl}$ bond lengths 2.358(2) (**1b**), 2.364(2) (**3b**) and 2.353(1) Å (**3c**) were in the expected range. The $P\text{-M-Cl}$ angles, 96.18(8), 97.02(8), 176.58(9)° for **1b**, 95.25(9), 95.84(9), 176.56(10)° for **3b**, 93.64(4), 94.33(4), 174.34(4)° for **3c**, and the $P\text{-M-P}$ angles, 83.64(8),

83.71(8), 164.08(8)° for **1b**, 84.61(9), 84.87(9), 165.57(9)° for **3b**, 85.07(4), 86.25(4), 169.00(4)° for **3c**, were indicative of the distorted square-planar environment at the metal centre.

The phenyl ring planes of the cation (I–V) as well as the best coordination plane at the metal C, are defined in Table 2. The M atom departs from C by 0.059 (**1b**), 0.061 (**3b**) and 0.128 Å (**3c**) compared to the mean values of 0.127 (**1b**), 0.130 (**3b**) and 0.016 Å (**3c**) for atoms defining the plane. The less crowded environment of P(2) led to a phenyl plane III almost perpendicular to the coordination plane C in complexes **1b** and **3b**. However, the presence of a different counterion ($[\text{SnPh}_2\text{Cl}_3]^-$) in **3c** resulted in a lower III–C dihedral angle of 68.46°.

The dianion $[\text{SnPh}_2\text{Cl}_4]^{2-}$ of compounds **1b** and **3b** showed a *trans*-octahedral geometry with the phenyl rings in coplanarity. The Sn–C and Sn–Cl distances of 2.144(9) and 2.564(2), 2.584(2) Å (**1b**), 2.143(11) and 2.569(3), 2.581(2) Å (**3b**), respectively, were in the expected range although the Sn–Cl bonds are longer than those found for $[\text{C}_{10}\text{H}_9\text{ONH}]_2[\text{SnPh}_2\text{Cl}_4]$ where this dianion stabilises two 8-methoxyquinolinium cations [29]. The angles C–Sn–C [180.00(1)°, C–Sn–Cl [89.90(2), 90.10(2)° (**1b**)] and [89.80(3), 90.20(3)° (**3b**)] and *trans* Cl–Sn–Cl [180.00(0)°] are also in accordance with a *trans*-octahedral arrangement. Table 2 defines the phenyl ring planes VI and VII as well as the equatorial coordination plane at the tin atom C'. The dihedral angles VI–C' of 88.78 (**1b**), 88.39° (**3b**), where Sn does not depart from C', are in agreement with a dianion which deviates slightly from a standard octahedron [29].

The anion $[\text{SnPh}_2\text{Cl}_3]^-$ present in compound **3c** has a slightly distorted trigonal-bipyramidal structure with phenyl rings in equatorial positions (C–Sn–C angle 132.90(2)°). The Sn–C bond lengths of 2.129(5) and 2.130(4) Å and the Sn–Cl bond distances of 2.347(1), 2.526(1) and 2.540(1) Å were slightly shorter than those found for $[\text{SnPh}_2\text{Cl}_4]^{2-}$. The angles C–Sn–Cl [87.65(6)–132.90(2)°] and Cl–Sn–Cl [87.33(6), 87.65(6), 174.98(6)°] were consistent with the trigonal-bipyramidal environment at the tin atom. The orientation of the phenyl ring planes labelled VI and VII with respect to the coordination plane C' (Table 2) was similar, giving the dihedral angles VI–C' 51.54° and C'–VII 58.20°.

All interionic $\text{H}\cdots\text{Cl}$ contacts for **1b** and **3b** (cation–anion, cation–cation and anion–anion) agree with the $\text{H}\cdots\text{A}$ distances and angular criteria for weak H-bonds. No anion–anion interactions were found for complex **3c**. This absence of $\text{H}\cdots\text{Cl}$ interactions between $[\text{SnPh}_2\text{Cl}_3]^-$ anions can be attributed to their arrangement in opposite senses in the unit cell and their separation by the two cations. The only $\text{H}\cdots\text{Cl}$ intermolecular interaction found is due to C–H of the phenyl ring plane III of one cation and the chloro bound to

platinum in the other cation. The $\text{SnPh}_2\text{Cl}_3^-$ ions take part in $\text{H}\cdots\text{Cl}$ anion–cation interactions through the C–H bonds of the phenyl substituents on the terminal phosphorus of the cations.

The only $\text{H}\cdots\text{Cl}$ intraionic interactions for **1b** [2.709(8), 2.726(8), 2.804(4) Å with calculated C–H \cdots Cl angles of 151.89, 152.61, 139.09°, respectively] and for **3b** [2.733(8), 2.723(5), 2.799(8) Å with calculated C–H \cdots Cl angles 149.43, 152.40, 140.44°, respectively] corresponded to intracationic contacts. However, for **3c** both intracationic and intra-anionic contacts were observed. These interactions were 2.814(7), 2.796(2) Å (c–c), and 2.706(7), 2.798(6) Å (a–a) with C–H \cdots Cl angles of 147.36, 144.81° (c–c), and 117.54, 115.52° (a–a), respectively.

3.2. Mass spectra

FAB MS spectra for **1**, **1a**, **1b**, **1c** and **3**, **3a**, **3b**, **3c** showed one base peak corresponding to the $[\text{Pd}(\text{triphos})\text{Cl}]^+$ (675) and $[\text{Pt}(\text{triphos})\text{Cl}]^+$ (764) cations, respectively, following the tendency of fragmentation

found for palladium and platinum dichloro complexes [45]. The most abundant peak at $m/z = 632$ found in the electron spray mass spectrum (ESMS) [46,47] of **4** was consistent with the presence in solution of $[\text{Pt}(\text{triphos})_2]^{2+}$. The FAB spectra were also consistent with the presence of the $[\text{M}(\text{triphos})_2]^{2+}$ cation in both complexes **2** and **4**.

3.3. ^{119}Sn Mössbauer spectra

The QS and IS parameters were in agreement with coordination numbers around tin: six in complexes with the anion $[\text{SnPh}_2\text{Cl}_4]^{2-}$ (**1b**, **3b**) and five in complexes with the anion $[\text{SnPh}_2\text{Cl}_3]^-$ (**1c**, **3c**, **4**). These results were also in accordance with the results found by X-ray diffraction and infrared spectra.

3.4. NMR spectra

3.4.1. Palladium– and platinum–triphos complexes

Fig. 1 shows the marking of the phosphorus atoms in the ionic and covalent complexes studied. The $^{31}\text{P}\{^1\text{H}\}$

Table 1
Crystallographic data for compounds **1b**, **3b** and **3c**

	1b	3b	3c
Empirical formula	$\text{C}_{80}\text{H}_{76}\text{Cl}_6\text{P}_6\text{Pd}_2\text{Sn}$	$\text{C}_{80}\text{H}_{76}\text{Cl}_6\text{P}_6\text{Pt}_2\text{Sn}$	$\text{C}_{46}\text{H}_{43}\text{Cl}_4\text{P}_3\text{PtSn}$
Formula weight	1764.42	1944.79	1144.29
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal size (mm)	0.35 × 0.10 × 0.10	0.35 × 0.15 × 0.10	0.35 × 0.25 × 0.25
Colour, habit	colourless, prisms	colourless, prisms	colourless, prisms
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions			
<i>a</i> (Å)	9.904(2)	9.911(2)	11.425(3)
<i>b</i> (Å)	19.727(2)	19.821(5)	12.723(2)
<i>c</i> (Å)	20.158(2)	20.140(7)	16.679(2)
<i>α</i> (°)	90.00	90.00(—)	70.11(1)
<i>β</i> (°)	100.52(3)	100.64(2)	83.74(2)
<i>γ</i> (°)	90.00	90.00(—)	84.11(2)
Volume (Å ³)	3872.0(3)	3889.0(2)	2260.6(7)
<i>Z</i>	2	2	2
Calculated density (Mg m ⁻³)	1.516	1.661	1.681
Absorption coefficient (mm ⁻¹)	1.153	4.280	4.017
<i>F</i> (000)	1780	1908	1120
<i>θ</i> range for data collection (°)	2.30–26.34	2.15–26.29	2.36–26.37
Index ranges	–12 ≤ <i>h</i> ≤ 0 0 ≤ <i>k</i> ≤ 24 –24 ≤ <i>l</i> ≤ 25	0 ≤ <i>h</i> ≤ 12 –24 ≤ <i>k</i> ≤ 0 –25 ≤ <i>l</i> ≤ 24	–14 ≤ <i>h</i> ≤ 14 –14 ≤ <i>k</i> ≤ 15 0 ≤ <i>l</i> ≤ 20
Reflections collected	8330	8869	9524
Independent reflections	7865 [<i>R</i> _{int} = 0.0868]	7883 [<i>R</i> _{int} = 0.1145]	9195 [<i>R</i> _{int} = 0.0227]
Absorption correction	semi-empirical	empirical	empirical
Max. and min. transmission	0.957 and 0.927	1.000 and 0.403	1.000 and 0.599
Data/restraints/parameters	7865/0/450	7883/431	9194/668
Goodness-of-fit on <i>F</i> ²	0.930	0.987	1.005
Final <i>R</i> indices ^a	<i>R</i> ₁ = 0.0570, <i>wR</i> ₂ = 0.1008	<i>R</i> ₁ = 0.0452, <i>wR</i> ₂ = 0.0797	<i>R</i> ₁ = 0.0288, <i>wR</i> ₂ = 0.0714
Largest difference peak and hole (e Å ⁻³)	0.640 and –0.954	0.799 and –2.042	2.024 and –0.975

^a [*I* > 2σ(*I*)].

Table 2
Selected distances (Å) and angles (°) for compounds **1b**, **3b** and **3c**

	1b	3b	3c
	[Pd(triphos)Cl] ₂ [SnPh ₂ Cl ₄]	[Pt(triphos)Cl] ₂ [SnPh ₂ Cl ₄]	[Pt(triphos)Cl][SnPh ₂ Cl ₃]
<i>Bond distances</i>			
P–M	2.218(2)	2.210(3)	2.212(1)
	2.321(2)	2.309(3)	2.299(1)
	2.323(2)	2.315(3)	2.301(1)
M–Cl	2.358(2)	2.364(2)	2.353(1)
Sn–C	2.144(9)	2.143(1)	2.129(5)
			2.130(4)
Sn–Cl	2.564(2)	2.569(3)	2.347(1)
	2.584(2)	2.581(2)	2.526(1)
<i>Bond angles</i>			
P–M–P	83.64(8)	84.61(9)	85.07(4)
	83.71(8)	84.87(9)	86.25(4)
	164.08(8)	165.57(9)	169.00(4)
P–M–Cl	96.18(8)	95.25(9)	93.64(4)
	97.02(8)	95.84(9)	94.33(4)
	176.58(9)	176.56(1)	174.34(4)
C–Sn–C	180.00(1)	180.00(1)	132.90(2)
C–Sn–Cl	89.90(2)	89.80(3)	87.65(6)
	90.10(2)	90.20(3)	89.50(1)
			90.55(1)
			91.81(1)
			92.14(1)
			108.95(1)
			118.16(1)
			132.90(2)
Cl–Sn–Cl	180.00(0)	180.00(0)	87.33(6)
			87.65(6)
			174.98(6)
I–II ^a	71.19	80.40	84.36
III–C	88.57	88.57	68.46
IV–V	64.86	65.67	68.75
VI–C'	88.78	88.39	51.54
C'–VII			58.20

^a Angles between planes defined as: I (C21–C26)P1 (**1b**, **3b**), (C31–C36)P1 (**3c**); II (C31–C36)P1 (**1b**, **3b**), (C41–C46)P1 (**3c**); III (C41–C46)P2 (**1b**, **3b**), (C51–C56)P2 (**3c**); IV (C51–C56)P3 (**1b**, **3b**), (C61–C66)P3 (**3c**); V (C61–C66)P3 (**1b**, **3b**), (C71–C76)P3 (**3c**); VI (C11–C16)Sn (**1b**, **3b**, **3c**); VII (C11A–C16A)Sn (**1b**), (C1A–C6A)Sn (**3b**), (C21–C26)Sn (**3c**); C [Pd P(1) P(2) P(3) Cl(3)] (**1b**), [Pt P(1) P(2) P(3) Cl] (**3b**, **3c**); C' [Sn Cl(1) Cl(2) Cl(1A) Cl(2A)] (**1b**, **3b**), [Sn C(11) C(21) Cl(2)] (**3c**).

data of palladium and platinum complexes with triphos are shown in Table 3. The ³¹P peak for **1** (Table 3) at 109.3 ppm can be assigned to the central phosphorus (P^B) and that at 44.2 ppm to the terminal phosphorus (P^A), on the basis of multiplicity, integration (1:2) and in comparison with complex **3**, the two compounds being isostructural. The robust square-planar structure of **3** possesses two equivalent phosphorus donor PPh₂ groups, P^A, *trans* to each other (39.8 ppm, ¹J(³¹P–¹⁹⁵Pt) = 2484 Hz) and a 'middle' phosphorus (P^B) coupled to those in *cis* positions (83.7 ppm, ¹J(³¹P–¹⁹⁵Pt) = 3015 Hz) (Table 3, Fig. 1). The addition of one equivalent of SnCl₂ to **1** and **3** resulted in the same complex cations with SnCl₃[−] as the counterion (**1a**, **3a**; Scheme 1). Likewise the addition of one and two equivalents of SnPh₂Cl₂ to **1** and **3** gave rise to the compounds which retain the palladium or platinum square-planar cations and with SnPh₂Cl₄^{2−} (**1b**, **3b**) or

SnPh₂Cl₃[−] (**1c**, **3c**) as the counterions. The PP couplings of 3.1 Hz for **3** were lower than those found for **1** of 9.4 Hz.

The peaks of the ligand underwent large downfield shifts (Δδ) upon complexation, as was found before for related chelating ligands [48,49]. For the central phosphorus P^B of complexes **1a–1c** and **3a–3c** Δδ values were very large compared to those of the terminal phosphorus P^A. This is due to the participation of P^B in the two fused five-membered chelate rings.

The reaction carried out at the ratio Pt:triphos = 3:2 yielded a mixture of ionic and trinuclear covalent complexes (Scheme 2). The ³¹P NMR spectrum of **3d** was practically identical with that of **3**. A novel dinuclear ionic species **5** has also been characterised by ³¹P NMR. Its formation could easily be rationalised by phosphino–chloro ligand exchange between the complex cation and tetrachloroplatinate(II) anion of **3d**, result-

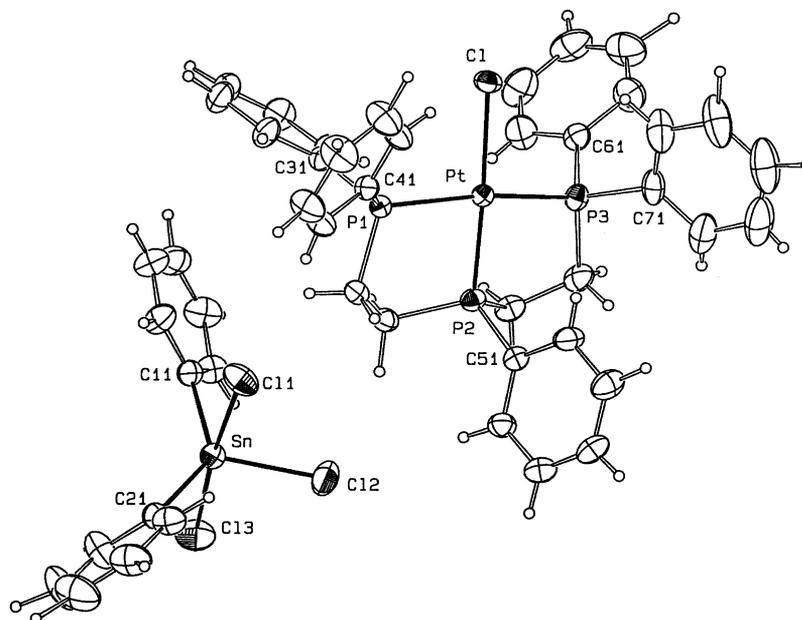


Fig. 3. ORTEP view and numbering scheme of $[\text{Pt}(\text{triphos})\text{Cl}][\text{SnPh}_2\text{Cl}_3]$ (**3c**).

Table 3

^{31}P NMR data of complexes **1–6** and titrations

	Phosphorus ^h	δ (ppm)	$\Delta\delta$ (ppm) ^j	$^1J(^{31}\text{P}-^{195}\text{Pt})$ (Hz)	$^2J(^{31}\text{P}-^{31}\text{P})$ (Hz)
1 ^{a,b}	$\text{P}^{\text{A}}, \text{P}^{\text{B}}$	44.2, 109.3	58.7, 127.5		9.4, 9.4
2 ^c	$\text{P}^{\text{C}}, \text{P}^{\text{D}}, \text{P}^{\text{E}}$	−12.7, 49.9, 54.4	1.8, 64.4, 72.6		
3 ^{a,b}	$\text{P}^{\text{A}}, \text{P}^{\text{B}}$	39.8, 83.7	54.3, 101.9	2484, 3015	3.1, 3.1
3c ^a	$\text{P}^{\text{A}}, \text{P}^{\text{B}}$	39.6, 83.2	54.1, 101.4	2451, 3080	
4 ^d	$\text{P}^{\text{D}}, \text{P}^{\text{E}}$	38.4		2352	
4 ^e	$\text{P}^{\text{C}}, \text{P}^{\text{D}}, \text{P}^{\text{E}}$	−15.4, 34.2, 41.5	−0.9, 48.7, 59.7	2324, 2793	
5 ^{f,g}	$\text{P}^{\text{F}}, \text{P}^{\text{G}}, \text{P}^{\text{H}}$	12.0, 50.6, 44.9	26.5, 68.8, 59.4	3689, 3557, 3630	56, (56, 2.5), 2.5
6a ^g	$\text{P}^{\text{F}}, \text{P}^{\text{G}}, \text{P}^{\text{J}}$	6.2, 52.9, 45.8	20.7, 71.1, 60.3	3643, ~3560, 3690	57, (57, <2), <2
6b ^g	$\text{P}^{\text{F}}, \text{P}^{\text{G}}, \text{P}^{\text{J}}$	7.9, 52.3, 45.6	22.4, 70.5, 60.1	3691, ~3560, 3688	57, (57, <2), <2
3 +1AgCl ^a	$\text{P}^{\text{A}}, \text{P}^{\text{B}}$	42.3, 86.3			
3c +1Au(I) ^k	$\text{P}^{\text{A}}, \text{P}^{\text{B}}$	39.5, 83.4; 30.0, 41.3, 47.2		2451, 3080	61.3
3c +2Au(I) ^k	$\text{P}^{\text{A}}, \text{P}^{\text{B}}$	39.5, 83.7; 29.8, 41.4, 47.5		2452, 3079	62.0
3c +3Au(I) ^k	$\text{P}^{\text{A}}, \text{P}^{\text{B}}$	39.5, 83.9; 29.8, 41.5, 47.4		2451, 3075	
4 +2AgCl ^d	$\text{P}^{\text{A}}, \text{P}^{\text{B}}$	44.5, 90.5; 10.7, 13.4		2471, 3072	
4 +2Au(I) ^{k,l}	$\text{P}^{\text{A}}, \text{P}^{\text{B}}$	39.5, 83.4; 25.3, 27.6, 29.7		2451, 3079	
4 +H ₂ O ₂ ^d		33.0, 48.0, 51.5		2344	
4 +H ₂ O ₂ +SnPh ₂ Cl ₂ ^m		31.3, 46.0, 49.5		2331, 2347	

^a Spectra measured in CDCl₃ at room temperature (r.t.).

^b ^{31}P NMR spectra of **1a–1c** were practically identical with that of **1** and the spectra of **3a**, **3b** and **3d** were very similar to those of **3** and **3c**.

^c Spectra measured in CD₂Cl₂ at r.t.

^d Spectrum measured in CDCl₃+DMSO-d₆ at r.t.

^e Spectrum measured in CD₂Cl₂ at 193 K.

^f NMR data of the complex anion.

^g Spectra measured in DMSO-d₆ at r.t.

^h For the marking of the phosphorus atoms of triphos see Fig. 1.

ⁱ Signal of double intensity (based on integration).

^j $\Delta\delta$ coordination chemical shift.

^k Titration recorded in CDCl₃+MeOH at r.t.

^l $^3J(^{31}\text{P}-^{31}\text{P}) = 48.1$ Hz.

^m Titration recorded in CDCl₃+DMSO-d₆+CD₂Cl₂ at r.t.

Table 4
Conductivity measurements carried out with Pt–triphos (PPP) systems

Run	Method of preparation	Molar conductivity Λ ($\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$)	Conductivity κ (μS)	Composition of the complex mixture (on the basis of ^{31}P NMR) (%)		
				3	5	6a+6b
1	PtCl ₂ (PhCN) ₂ +PPP, benzene reflux, 2 h	8.60	34.5 ^a	100 ^c	0	0
2	Run 1, preparation; addition of 1 equiv. SnCl ₂	9.85	39.5 ^a	100 ^d	0	0
3	3PtCl ₂ (PhCN) ₂ +2PPP, benzene reflux during addition of PPP; immediate filtration of the product	3.37	13.5 ^b	22 ^e	71	3+4
4	3PtCl ₂ (PhCN) ₂ +2PPP, benzene reflux during addition of PPP; filtration of the product after 24 h stirring at r.t.	3.04	12.2 ^b	25 ^e	63	5+7
5	3PtCl ₂ (PhCN) ₂ +2PPP, benzene reflux for 1 h after addition of PPP; filtration of the product after 24 h stirring at r.t.	2.34	9.4 ^b	6 ^e	76	8+10
6	Run 5, preparation; benzene reflux, 7 days	0.87	3.5 ^b	5 ^e	54	18+23

^a Conditions: 0.0500 mmol Pt in 11 ml CH₂Cl₂.

^b The addition of 0.0160 mmol PPP resulted in the same conductivity ($\kappa = 34.8 + 0.4 \mu\text{S}$).

^c Counterion Cl⁻ (**3**).

^d Counterion SnCl₃⁻ (**3a**).

^e Counterion [PtCl₄]²⁻ (**3d**).

ing in a [Pt₂(triphos)Cl₅]⁻ anion of unprecedented structure.

Two species with very similar NMR characteristics have been observed upon heating or conducting the reaction for longer reaction times at room temperature. The formation of two diastereomers can be explained as follows. Although the ligand used is achiral, upon ‘asymmetric’ coordination it becomes chiral, since the two PPh₂ groups are bound to two platinum atoms with different chemical environments. Consequently, in the case of a two phosphorus stereogenic centre, this type of coordination resulted in two non-ionic trinuclear diastereomers, **6a** and **6b** (Scheme 2). The *cis* geometry for the ‘middle’ platinum has been unequivocally determined for both **6a** and **6b**. Surprisingly, the corresponding *trans* isomer was not detected even in trace amounts. All of the $^1J(^{31}\text{P}-^{195}\text{Pt})$ constants of diagnostic value were between 3600 and 3700 Hz for phosphorus *trans* to the chloro ligand. It has been clearly demonstrated that the kinetically controlled ionic product **3d** could be transformed into the thermodynamically controlled products **5** and **6a**, **6b** (Tables 3 and 4). Heating at 70°C for a week resulted in the predominant formation of these species. It is worth noting that the mixture of the species isolated as white solid (run 6, Table 4) was transformed to a mixture of **6a** and **6b** upon standing in the solid state for a year at room temperature. All of the Pt:triphos = 3:2 mixtures of covalent and ionic species (runs 3–6) transformed into **3** upon addition of 0.33 equivalents of triphos in a very clean facile reaction (Scheme 2), giving rise to the chelate ring-closure of **5** (complex anion) and **6a**, **6b** (neutral diastereomers).

Even at higher Pt:triphos ratios (Pt:triphos = 3:4 or higher) complex **3**, exhibiting two sharp 1:4:1 patterns, predominates when tin(II) chloride is also added in twofold excess. An additional minor broad peak with detectable platinum satellites was obtained in both DMSO-d₆ and CDCl₃ at 44.0 ppm ($^1J(^{31}\text{P}-^{195}\text{Pt}) = 2550 \text{ Hz}$) and 44.8 ppm ($^1J(^{31}\text{P}-^{195}\text{Pt}) \approx 2500 \text{ Hz}$), respectively. However, an extremely broad peak of double integration value (without any detectable satellites) appeared at around 19 ppm in both cases. In the absence of tin(II) chloride, a similar situation has been obtained ($\delta\text{P} = 37.8 \text{ ppm}$; $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2342 \text{ Hz}$). The appearance of broad peaks can be explained by the formation of PtP₄ species. The less broad peaks can be assigned to the central phosphorus of triphos coordinated to platinum and the extremely broad peaks refer to the terminal phosphorus donors in fast exchange between ring-opened and ring-closed forms [22] of triphos. Although the broad peak became sharper upon heating, a signal near to coalescence was not achieved because of the low solubility of the Pt–triphos system.

Complexes **2** and **4** (Eqs. (3) and (4)) were obtained as solids via a chelate ring-opening reaction of [M-(triphos)Cl]⁺ cations induced by ligand in the presence of SnPh₂Cl₂. The ^{31}P NMR spectrum of **2** was in agreement with the formation of PdP₄ complexes showing peaks at 54.4, 49.9 and -12.7 ppm assigned to P^E, P^D and P^C, respectively (Scheme 1, Fig. 1). A broad signal between 20 and -10 ppm suggested the exchange processes mentioned above. However, the ^{31}P NMR spectrum of complex **4** in CDCl₃ + DMSO-d₆ at room temperature showed the only peak at 38.4 ppm, with a coupling constant of 2352 Hz indicative of P

trans to P. Considering the ESMS data, this complex contained the cation $[\text{Pt}(\text{triphos})_2]^{2+}$. The presence of dangling P atoms was confirmed when the ^{31}P NMR spectrum of **4** was recorded at low temperatures in CD_2Cl_2 (see Fig. 4). At 193 K a splitting (D and E peaks) of the only signal at 38.4 ppm was detected (34.2 and 41.5 ppm) with $^1J(^{31}\text{P}-^{195}\text{Pt})$ values of 2324 and 2793 Hz typical of P *trans* to each other; these were assigned to P^{D} *trans* to P^{D} and P^{E} *trans* to P^{E} , respectively (Fig. 1, Scheme 1). The dangling phosphorus appeared as a broad peak C in the region of free triphos (peaks L and M). The ^{31}P spectrum of **4** at 193 K allowed the proposal of a structure which explains the ring-opening cation reactions of **3b** or **3c** described in Scheme 1 with the formation of the $[\text{Pt}(\text{triphos})_2]^{2+}$ cations.

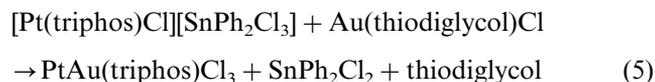
The ^{195}Pt NMR spectra of compounds **3b** and **3c** were, as expected, a doublet of triplets (-4856 and -4859 ppm, respectively) with $^1J(^{31}\text{P}-^{195}\text{Pt})$ values of 3053, 2469 (**3b**) and 3034, 2470 Hz (**3c**) characteristic of P *trans* to Cl and P *trans* to P, respectively [50–52]. The ^{195}Pt spectrum of **4** showed a multiplet at -5098 ppm from which coupling constant values were not available.

The ^{119}Sn spectra for compounds **1a** and **3a** with trichlorostannato counterion showed a singlet around -61.0 ppm. The ^{119}Sn chemical shifts for **1c**, **2**, **3b** and **4** were -239.7 , -259.1 , -177.4 and -256.0 ppm, respectively, in the expected range for coordination numbers six (**3b**) and five (**1c**, **2**, **4**) around tin. Although in the solid state the six coordinate $[\text{SnPh}_2\text{Cl}_4]^{2-}$ anion has been characterised for compound **1b**, in solution this species does not seem to have sufficient Lewis acidity to allow expansion of the tin coordination from five to six and the ^{119}Sn NMR spectrum showed a signal at -253.2 ppm consistent with dissociation into $[\text{SnPh}_2\text{Cl}_3]^-$

and Cl^- [53]. This contrasts with dissociation in the opposite sense proposed by Ouyang et al. for $[\text{SnPh}_2\text{Cl}_3]^-$ in $[\text{C}_{10}\text{H}_9\text{ON.H.NOH}_2\text{C}_{10}][\text{SnPh}_2\text{Cl}_3]$ suggesting its conversion into $[\text{SnPh}_2\text{Cl}_4]^{2-}$ and SnPh_2Cl_2 [29].

3.4.2. Reactivity of $[\text{Pt}(\text{triphos})\text{Cl}]^+$ (**3**, **3c**) and $[\text{Pt}(\text{triphos})_2]^{2+}$ (**4**)

The addition of AgCl to solutions of complex **3** in CDCl_3 followed by ^{31}P NMR showed the absence of any interaction of $\text{Ag}(\text{I})$ with compound **3** (Table 3). However, when one equivalent of $\text{Au}(\text{I})$ was added to complex **3c** a chelate-ring opening reaction occurred with the formation of the neutral heterobimetallic [23] complex $\text{PtAu}(\text{triphos})\text{Cl}_3$ (Eq. (5)).



The ^{31}P NMR data (Table 3) showed that besides the signals due to the complex **3c** (even when two or three equivalents of $\text{Au}(\text{I})$ were added) there were three signals corresponding to the complex $\text{PtAu}(\text{triphos})\text{Cl}_3$ ($\delta = 30.0$ (AuPPh_2), 41.3 (PtPPh_2) and 47.2 (PtPPh) ppm). This contrasts with the chloro ligand and counterion substitution by nitrate ions when AgNO_3 was added, where the formation of complexes of the type $[\text{M}(\text{triphos})(\text{ONO}_2)]\text{NO}_3$ ($\text{M} = \text{Pd}, \text{Pt}$) excludes a chelate ring-opening reaction [54]. The reaction induced by gold(I) resulted in a chiral central phosphorus for the heterobimetallic complex showing a coupling constant with the terminal phosphorus bound to platinum in the remaining chelate ring of ca. 60 Hz, which is similar to that found in complexes **6a**, **6b**.

The addition of excess $\text{Au}(\text{I})$ or AgCl to complex **4** did not produce the formation of any heterometallic

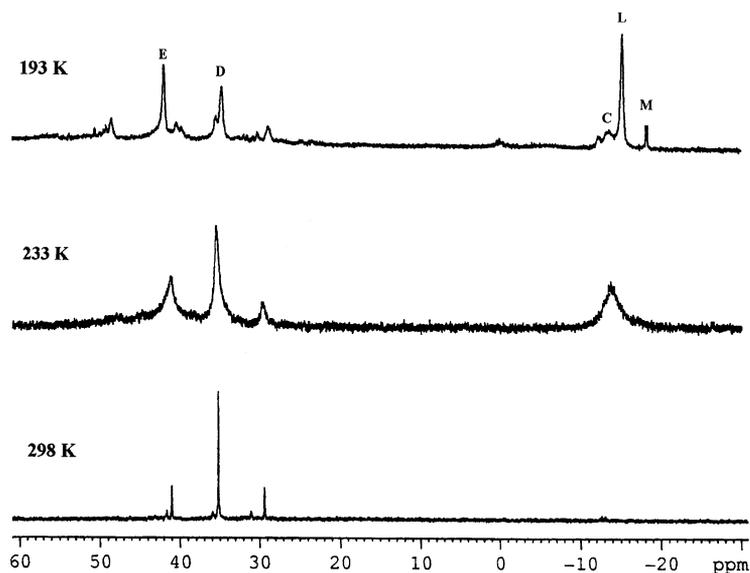


Fig. 4. ^{31}P NMR- $\{^1\text{H}\}$ NMR spectra of $[\text{Pt}(\text{triphos})_2][\text{SnPh}_2\text{Cl}_3]_2$ (**4**) at different temperatures.

complex of the type $[\text{Pt}(\text{triphos})_2(\text{M}'\text{Cl})_2][\text{SnPh}_2\text{Cl}_3]_2$ ($\text{M}' = \text{Au}, \text{Ag}$). In both cases the presence of signals assigned to the complex **3c** with other signals due to homonuclear complexes [55] with metal to ligand ratios of 3:1 [$\delta = 13.4$ ppm (bs) (AgPPh_2 , AgPPh); 27.6 ppm (d) (AuPPh_2); 29.7 ppm (t) (AuPPh)] and 1:1 [$\delta = 10.7$ ppm (bs) (AgPPh_2 , AgPPh) and 25.3 ppm (bs) (AuPPh_2 , AuPPh)] were detected. This demonstrates that the addition of two equivalents of $\text{Au}(\text{thiodiglycol})\text{Cl}$ or AgCl to complex **4** was able to produce a chelate ring-closure reaction by ligand abstraction.

However, the addition of H_2O_2 to **4** led to the oxidation of dangling phosphorus and the resulting phosphine oxide groups seemed to undergo facile reaction with SnPh_2Cl_2 .

3.5. Conductivity measurements

The molar conductivities for complexes **1a**, **1b**, **1c**, **3a**, **3b**, **3c**, **2** and **4** were obtained in 10^{-3} M CH_3CN solutions. The values were in agreement with the presence of 1:1 (**1a**, **1c**, **3a**, **3c**) and 1:2 (**2**, **4**) electrolytes. The low value of conductivity for complex **1b** (an expected 2:1 electrolyte), $[\text{Pd}(\text{triphos})\text{Cl}]_2[\text{SnPh}_2\text{Cl}_4]$, showed a very restricted mobility in solution in comparison with the analogous Pt complex **3b**. This could be a consequence of dissociation processes in solution (detected by ^{119}Sn NMR) leading to the formation of **1c**.

For complexes **3**, **3a**, **3d**, **5** and **6a**, **6b** prepared in solution (Table 4) starting from $\text{PtCl}_2(\text{PhCN})_2$, the composition and identification of the different mixtures (runs 1–6) were followed by ^{31}P NMR and conductivity measurements, respectively. The conductivity data were in agreement with the NMR results. The addition of SnCl_2 to **3** resulted in an increase in conductivity, which is rather surprising since the ionic mobility of the trichlorostannate ion was expected to be lower than that of the chloride counterion. Although there is no indication for the presence of five-coordinate covalent species containing two chloro ligands, it is probably involved in an equilibrium with the ionic complex **3**. The equilibrium must be shifted toward **3a** by complete dissociation of the covalent species resulting in the formation of the trichlorostannate counterion.

The conductivity values obtained for the reactions of $\text{PtCl}_2(\text{PhCN})_2$ and triphos in a ratio of 3:2 (runs 3–6) were in keeping with the composition of the mixtures (**3d**, **5** and **6a**, **6b**) determined by NMR. The highest conductivity obtained with these mixtures was much lower than that obtained with **3**, the decrease being proportional to the increase in the composition of covalent complexes. This must be due to the substantially lower mobility of the tetrachloroplatinate(II) counterion than of the chloride.

Upon addition of triphos to the mixtures, starting with a Pt:triphos ratio of 3:2 and increasing to a 3:3 ratio (Scheme 2), the conductivity resulted in the same value as found for complex **3**, indicating that a ring-closure reaction was carried out.

4. Supplementary material

Supplementary data for compounds **1b**, **3b** and **3c** have been deposited with the Cambridge Crystallographic Data Centre with deposition numbers CCDC 149833 (**1b**), CCDC 149834 (**3b**) and CCDC 149835 (**3c**). Copies of this information may be obtained free of charge 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).

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