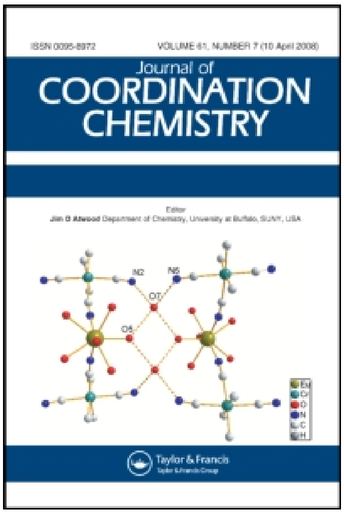

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Studies of the reactions of platinum halo complexes with tin(II) halides

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Studies of the reactions of platinum halo complexes with tin(II) halides

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The reaction of a dichloromethane solution of a mixture of *cis,trans*-[$PtCl_2(SMe_2)_2$] with a tetrahydrofuran solution of $SnBr_2$ resulted in oxidation of platinum(II) with halogen exchange producing *cis,trans*-[$PtBr_4(SMe_2)_2$]. Reaction of a mixture of *cis,trans*-[$PtCl_2(SEt_2)_2$], potassium tetrachloroplatinate(II) or potassium hexachloroplatinate(IV) with $SnBr_2$ in hydrochloric acid solution resulted in formation of predominantly anionic five-coordinate trichlorostannyl platinum(II) complexes. Reaction of potassium tetrabromoplatinate(II) with $SnCl_2$ in hydrobromic acid in the presence of tetraphenylphosphonium bromide affords *cis*-[PPh_4]$_2$[$PtBr_2(SnBr_3)_2$]. The insertion of $SnCl_2$ into Pt–Cl bond of platinum(II) complexes *cis*-[$PtCl_2(L_2)$] {$L_2 = (PPh_3)_2$; $(PMe_3)_2$; $\{P(OMe)_3\}_2$; dppm (*bis*(diphenylphosphino)methane); dppa (*bis*(diphenylphosphino)amine); and dppe (1,2-*bis*(diphenylphosphino)ethane)} is described.

Keywords: Chelate; Coordinate; Insertion; Platinum; Tin

1. Introduction

The trichlorostannyl complexes of platinum are of particular interest due to their ability to function as various homogeneous catalysts [1]. There are two known methods for preparation of the trichlorostannyl platinum complexes. The first involves insertion of $SnCl_2$ into a Pt–Cl bond and the second is the oxidative addition of $SnCl_4$ to platinum(II) complexes [2–4]. The equilibrium reactions of platinum(II) complexes with $SnCl_2$ are complicated in solution by the existence of *cis,trans*-[$PtCl_2(SnCl_3)_2$]$^{2-}$, [$Pt(SnCl_3)_5$]$^{3-}$ or other cluster complexes [1, 5]. The role of tin(II) chloride has been the subject of many studies but not yet led to a clear understanding of its co-catalyst role [6]. The complexes [$Pt(SnBr_3)_5$]$^{3-}$ and [$PtBr_2(SnBr_3)_2$]$^{2-}$ have also been prepared by the insertion of $SnBr_2$ into Pt–Br bonds. The complexes [$Pt(SnCl_3)_5$]$^{3-}$ and [$PtCl_2(SnCl_3)_2$]$^{2-}$ are stable in acetone but [$Pt(SnBr_3)_5$]$^{3-}$ and [$PtBr_2(SnBr_3)_2$]$^{2-}$ undergo loss of $SnBr_2$ in solution [7].

Much attention has been directed to the insertion of $SnCl_2$ into Pt–Cl bonds and there are a few examples of Pt–Sn complexes containing a mixture of halides.

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For example, the reaction of *cis*-[$PtCl_2(PPh_3)_2$] with SnI_2 in $CDCl_3$ results in formation of *cis,trans*-[$PtI_2(PPh_3)_2$] and there is no evidence of $SnCl_2$ or SnI_2 insertion products such as [$PtI(SnICl_2)(PPh_3)_2$] or [$PtCl(SnClI_2)(PPh_3)_2$] [8]. Moreover, the reaction of [$PtCl_2$(bdpp)] (bdpp = 2,4-*bis*(diphenylphosphino)pentane) with SnI_2 results in formation of [PtI_2(bdpp)], [$PtI(SnCl_3)$(bdpp)] and perhaps [$PtI(SnCl_2I)$(bdpp)] in a small amount, whereas the reaction of [PtI_2(bdpp)] with $SnCl_2$ gives [$PtI(SnCl_3)$(bdpp)] and I_2. Therefore, there is no evidence for the insertion of $SnCl_2$ or SnI_2 into Pt–I bonds [8]. Binary system of [$PtCl_2$(bdpp)] and SnF_2 has been used as an active enantioselective catalytic system for the asymmetric hydroformylation of styrene which is effective up to 220°C, whereas in the presence of $SnCl_2$ instead of SnF_2, the activity is lost above 150°C. However, there was no signal in the ^{31}P NMR spectrum assigned to formation of [$PtCl(SnF_2Cl)$(bdpp)] [9]. It has been shown that halide scrambling occurs in a mixture of equal amounts of $[Pt(SnCl_3)_5]^{3-}$ and $[Pt(SnBr_3)_5]^{3-}$ resulting in anions of the type $[Pt(SnCl_xBr_y)_5]^{3-}$ ($x + y = 3$) in an equilibrium in solution [10]. The chemical shifts of the $[SnX_3]^-$ species increase in the order of $Cl < Br < I$ [11]. Halogen exchange in trichlorostannyl complexes of iron and molybdenum by $SnBr_2$ or SnI_2 has been used as a convenient route for preparation of corresponding tribromo or triiodostannyl complexes of the above metals, respectively [12].

Due to the importance of these catalytic systems, the reactions of platinum complexes with tin(II) halides have been investigated, reporting the ^{31}P NMR spectra of a related series of compounds of the form [$PtCl(SnCl_3)(L_2)$] or [$Pt(SnCl_3)_2(L_2)$] prepared by the insertion of $SnCl_2$ into Pt–Cl bonds.

2. Experimental

2.1. *General considerations*

All solvents and chemicals for preparation of the complexes were of reagent grade and used without purification. Elemental analyses were performed on a Heraus CHN Rapid system or Perkin Elmer 2400 II elemental analyzer. NMR data were recorded using Bruker Avance DRX 500 or AQS 300 MHz spectrometers. Spectra are referenced to TMS (^1H, ^{13}C), 85% H_3PO_4 (^{31}P), Na_2PtCl_6 in D_2O (^{195}Pt) or $SnMe_4$ (^{119}Sn). The complexes *cis*-[$PtCl_2(PPh_3)_2$] and *cis,trans*-[$PtCl_2(SMe_2)_2$], and *cis,trans*-[$PtCl_2(SEt_2)_2$] were prepared according to the literature [13–15].

2.2. *Preparation of cis,trans-[$PtBr_4(SMe_2)_2$] (1)*

A solution of $SnBr_2$ (62 mg, 0.22 mmol) in THF (1 cm^3) was allowed to diffuse into a dichloromethane solution (2 cm^3) of a mixture of *cis,trans*-[$PtCl_2(SMe_2)_2$] (30 mg, 0.08 mmol) to afford red crystalline solid. Yield: 70%. Anal. Calcd for $C_4H_{12}Br_4S_2Pt$ (%): C, 7.5; H, 1.9; S, 10.0. Found: C, 7.8; H, 1.9; S, 10.0. NMR data in CD_2Cl_2: δ (^1H) (*cis* isomer) 2.84 [s, 24 H, $^3J(PtH) = 32.3$ Hz], (*trans* isomer) 2.77 [s, 24 H, $^3J(PtH) = 31.6$ Hz]; $\delta(^{13}C)$ 26.06, 27.13 (s, 16C, all methyl groups in Pt–SMe_2); $\delta(^{195}Pt)$ −2761, −3108 (s). Crystals suitable for X-ray crystallographic study were grown from CH_2Cl_2/*n*-hexane.

2.3. *Reaction of cis, trans-[PtCl$_2$(SEt$_2$)$_2$] with SnBr$_2$*

To a 5 M HCl solution (4 cm^3) containing a mixture of *cis,trans*-[PtCl$_2$(SEt$_2$)$_2$] (40 mg, 0.09 mmol) was added SnBr$_2$ (90 mg, 0.32 mmol). The solution color changed from yellow to red-orange and a red solid formed rapidly. The product was filtered off and air dried. Yield: 58%. Anal. Calcd for $C_{36}H_{90}Cl_{18}Pt_4S_9Sn_5$ (%): C, 15.3; H, 3.2. Found: C, 14.6; H, 2.9. NMR data in CD_2Cl_2: δ (^{1}H) 1.47 [t, 6H, ^3J(HH) = 7.3 Hz, methyl groups in Pt–SEt$_2$ *trans* to Cl], 1.48 [t, 12H, ^3J(HH) = 7.4 Hz, methyl groups in Pt–SEt$_2$ *cis* to Cl], 3.12 [m, 12H, all methylene groups in Pt–SEt$_2$]; δ (^{13}C) 12.98, 13.01 [s, 6C of methyl groups], 31.78, 32.30 [s, 6C of methylene groups; δ (^{195}Pt) −4390 [s, Pt(SnCl$_3$)$_5^{3-}$, ^1J(^{195}Pt–^{119}Sn) was not observed], −4148 [s, PtCl(SEt$_2$)$_3$]$^+$; δ (^{119}Sn) −123 [s, ^{1}J (^{195}Pt–^{119}Sn) = 15912 Hz, ^2J(^{119}Sn–^{117}Sn) = 6245 Hz].

2.4. *Reaction of [K$_2$PtCl$_6$] with SnBr$_2$*

To a 3 M HCl solution (3 cm^3) containing K$_2$PtCl$_6$ (30 mg, 0.06 mmol) was added SnBr$_2$ (86 mg, 0.31 mmol) and an acetone solution (2 cm^3) of *bis*(triphenylphosphoranylidene) ammonium chloride (106 mg, 0.21 mmol). The solution color changed from yellow to red-orange and a red solid formed rapidly. Yield: 83%. δ (^{119}Sn) in dichloromethane: −124 [s, ^1J(^{195}Pt–^{119}Sn) = 15952 Hz, ^2J(^{119}Sn–^{117}Sn) = 6159 Hz].

The reaction between K$_2$PtCl$_4$, SnBr$_2$ and [NHEt$_3$]Cl was carried out in the same way. Yield: 78%. Anal. Calcd for $C_{18}H_{48}Cl_{15}N_3PtSn_5$ (%): C, 13.3; H, 3.0; N, 2.6. Found: C, 13.3; H, 2.9; N, 2.7. δ (^{119}Sn) in dichloromethane: −125 [s, ^1J(^{195}Pt–^{119}Sn) = 15940 Hz, ^2J(^{119}Sn–^{117}Sn) = 6143 Hz].

2.5. *Preparation of cis-[PPh$_4$]$_2$[PtBr$_2$(SnBr$_3$)$_2$] (5)*

SnCl$_2$ (64 mg, 0.34 mmol) was added to a 6 M HBr solution (10 cm^3) containing K$_2$PtBr$_4$ (40 mg, 0.07 mmol) under argon. The solution changed to dark red. After addition of a solution of tetraphenylphosphonium bromide (85 mg, 0.20 mmol) in ethanol (2 cm^3), a dark red solid formed which was filtered off and air dried. Yield: 85%. NMR data in dichloromethane: δ (^{195}Pt) −4534 [s, ^1J(^{195}Pt–^{119}Sn) = 26841 Hz, ^1J(^{195}Pt–^{117}Sn) = 24623 Hz]; δ (^{119}Sn) −420 [s, ^1J(^{195}Pt–^{119}Sn) = 25760 Hz, ^2J(^{119}Sn–^{117}Sn) was not observed].

2.6. *Preparation of cis, trans-[PtCl(SnCl$_3$)(PPh$_3$)$_2$] (6)*

Following the same procedure as for preparation of **1**, a solution of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (100 mg, 0.13 mmol) in dichloromethane (5 cm^3) was reacted with SnCl$_2$ · 2H$_2$O (143 mg, 0.64 mmol) in THF (2 cm^3) to give an orange solid. Yield: 65%. *Cis*-[PtCl (SnCl$_3$)(PPh$_3$)$_2$]: δ(^{31}P) in CH$_2$Cl$_2$/CDCl$_3$: 27.4 [d, ^1J(Pt–P) = 3020 Hz, ^2J(P–P) = 14.2 Hz, PPh$_3$ *trans* to SnCl$_3$]; 10.7 [d, ^1J(Pt–P) = 3665 Hz, ^2J(P–P) = 14.2 Hz, PPh$_3$ *trans* to Cl], *trans*-[PtCl(SnCl$_3$)(PPh$_3$)$_2$]: 19.4 [s, ^1J(Pt–P) = 2328 Hz].

2.7. *Preparation of trans-[Pt(SnCl$_3$)$_2$(PMe$_3$)$_2$] (7)*

To a suspension of *cis*-[PtCl$_2$(PMe$_3$)$_2$] (40 mg, 0.10 mmol) in dichloroethane (5 cm^3) was added SnCl$_2$ (181 mg, 0.95 mmol) in tetrahydrofuran (1 cm^3). After 15 min, the solution changed to orange, during which time the starting platinum complex had completely dissolved. The resultant solution was stirred for 1 h, reduced in volume to about 1 cm^3 and then filtered into an NMR tube. In a similar way were prepared other tristannyl platinum complexes **8–11**, but in the case of **10** a molar ratio of Pt : Sn/1 : 20 was used.

3. Results and discussion

3.1. *Reaction of cis,trans-[$PtCl_2(SMe_2)_2$] with $SnBr_2$*

The reaction of *cis,trans*-[$PtCl_2(SMe_2)_2$] with $SnBr_2$ affords *cis,trans*-[$PtBr_4(SMe_2)_2$] (**1**), as shown in equation (1). The product, obtained in high purity and yield, was characterized by elemental analysis and multinuclear NMR (^1H, ^{13}C, ^{195}Pt) spectroscopy. The structure of **1** in the solid state was also identified as *trans*-[$PtBr_4(SMe_2)_2$] by matching the X-ray crystallographic unit cell parameters to published values [16].

$$\textit{cis, trans}\text{-}[PtCl_2(SMe_2)_2] \xrightarrow{SnBr_2} \underset{\mathbf{1}}{\textit{cis,trans}\text{-}[PtBr_4(SMe_2)_2]} \qquad (1)$$

NMR data show that this complex exists as a mixture of *cis* and *trans* isomers. For example, ^1H NMR spectrum of **1** in CD_2Cl_2 displays two signals at $\delta = 2.84$ with $^3J(Pt–H) = 32.3$ Hz (major isomer) and $\delta = 2.77$ with $^3J(Pt–H) = 31.6$ Hz (minor isomer) for the protons of SMe_2 groups of the *cis* and *trans* isomers, respectively, consistent with the earlier report for *cis,trans*-[$PtBr_4(SMe_2)_2$] [17]. *trans*-[$PtBr_4(SMe_2)_2$] has been synthesized by the spontaneous deoxygenation of [$Pt_2(Me_2SO)_2Br_4$] in the presence of catalytic amounts of HBr or by the reaction of *trans*-[$PtBr_2(SMe_2)_2$] with bromine [16, 18]. In the ^{13}C NMR spectrum of **1**, two signals at $\delta = 26.06$ and 27.13 were observed due to carbons of SMe_2 of *cis,trans*-[$PtBr_4(SMe_2)_2$]; satellites due to coupling to ^{195}Pt could not be resolved. The ^{195}Pt NMR of **1** reveals signals at $\delta = -2761$ and -3108 ppm, supporting the presence of two geometric isomers in solution. When reaction 1 was carried out under argon, the same result was observed; no dependence on Pt : Sn ratio was observed. These results are in contrast to those for the $SnCl_2$ analogue reaction with *cis,trans*-[$PtCl_2(SMe_2)_2$] in CH_2Cl_2/THF resulting in formation of [$PtCl(SMe_2)_3]_3[Pt(SnCl_3)_5$] [14].

The formation of a platinum(IV) product containing bromide in this case, whereas the platinum(II) precursor does not contain bromide, indicates that $SnBr_2$ acts as a source of bromide as well as an oxidizing agent.

3.2. *Reaction of cis,trans-[$PtCl_2(SEt_2)_2$], [K_2PtCl_6] and [K_2PtCl_4] with $SnBr_2$ in HCl solution*

The reaction of *cis,trans*-[$PtCl_2(SEt_2)_2$] with tin(II) bromide in hydrochloric acid solution affords [$PtCl(SEt_2)_3]_3[Pt(SnCl_3)_5$] (**2**) as the major product in equation (2). The product has been characterized by multinuclear NMR (^1H, ^{13}C, ^{119}Sn, ^{195}Pt) spectroscopy and elemental analysis. A ^{119}Sn NMR spectrum of **2** in dichloromethane shows a signal at $\delta = -123$ ppm with $^1J(^{195}Pt–^{119}Sn) = 15912$ Hz and

$^2J(^{19}\text{Sn}–^{117}\text{Sn}) = 6245$ Hz, consistent with previously reported values for **2** prepared by the reaction of *cis*,*trans*-$[PtCl_2(SEt_2)_2]$ with $SnCl_2$ in HCl solution [2].

$$\textit{cis, trans}\text{-}[PtCl_2(SEt_2)_2] + SnBr_2 \xrightarrow{HCl} \underset{\mathbf{2}}{[PtCl(SEt_2)_3]_3[Pt(SnCl_3)_5]} \tag{2}$$

There was also a signal at $\delta = -122$ ppm with $^1J(^{195}\text{Pt}–^{119}\text{Sn}) = 15971$ Hz. It should be noted that in the mixed halide system, it is not possible to assign each resonance exactly. We assign the signal at $\delta = -122$ to species of the type $[Pt(SnCl_3)_4(SnCl_xBr_y)]^{3-}$ $(x + y = 3)$ resulting from halide scrambling. Therefore, the chemical shift of tin and platinum as well as elemental analysis data do not change remarkably from those of $[Pt(SnCl_3)_5]^{3-}$ (see experimental section). The presence of $[PtBr(SEt_2)_3]^+$ cannot be ignored because it also has elemental analysis data close to those of $[PtCl(SEt_2)_3]^+$. Therefore, additional signals at $\delta = -4308$ and -4512 have been tentatively assigned to $[PtBr(SEt_2)_3]^+$ and $[Pt(SnCl_3)_4(SnCl_xBr_y)]^{3-}$. In the ^{13}C NMR spectrum, there were two additional signals at $\delta = 12.86$ and 13.09 ppm assigned to carbons of the methyl groups of $[PtBr(SEt_2)_3]^+$. The carbons of methylene groups appear at $\delta = 31.71$ and 33.24 ppm. Assignments of the hydrogens of methylene and methyl groups of $[PtBr(SEt_2)_3]^+$ in ^{1}H NMR spectrum could not be done due to overlapping signals.

The anion pentakis(trichlorostannyl)platinum(II) is formed as the major product when K_2PtCl_6 or K_2PtCl_4 reacted with $SnBr_2$ in hydrochloric acid solution in the presence of triethylammonium chloride or *bis*(triphenylphosphoranylidene) ammonium chloride, respectively, as shown in equations (3) and (4). In the case of K_2PtCl_4, there was a signal at $\delta = -124$ ppm with $^1J(^{195}\text{Pt}–^{119}\text{Sn}) = 15971$ Hz in ^{119}Sn NMR spectrum assigned to species of the type $[Pt(SnCl_3)_4(SnCl_xBr_y)]^{3-}$ $(x + y = 3)$.

$$K_2PtCl_6 + SnBr_2 + HCl \xrightarrow{[NEt_3H]Cl} \underset{\mathbf{3}}{[NHEt_3]_3[Pt(SnCl_3)_5]} \tag{3}$$

$$K_2PtCl_4 + SnBr_2 + HCl \xrightarrow{[N(PPh_3)_2]Cl} \underset{\mathbf{4}}{[N(PPh_3)_2]_3[Pt(SnCl_3)_5]} \tag{4}$$

3.3. *Reaction of [K_2PtBr_4] with $SnCl_2$ in HBr solution*

With the reaction of K_2PtBr_4 and $SnCl_2$ in HBr solution in the presence of tetraphenylphosphonium bromide, the dark red complex of *cis*-$[PPh_4]_2[PtBr_2(SnBr_3)_2]$ (**5**) was formed [equation (5)].

$$K_2PtBr_4 + SnCl_2 + HCl \xrightarrow[{[PPh_4]Br}]{HBr} \underset{\mathbf{5}}{\textit{cis}\text{-}[PPh_4]_2[PtBr_2(SnBr_3)_2]} \tag{5}$$

The product was characterized by ^{195}Pt and ^{119}Sn NMR spectroscopy. The ^{195}Pt NMR spectrum of **5** in dichloromethane reveals a singlet at $\delta = -4534$ which is flanked by $^{119/117}$Sn satellites with $^1J(^{195}\text{Pt}–^{119}\text{Sn}) = 26841$ Hz and $^1J(^{195}\text{Pt}–^{117}\text{Sn}) = 24623$ Hz. In addition, the ^{119}Sn NMR spectrum of **5** shows a signal at $\delta = -420$ with $^1J(^{195}\text{Pt}–^{119}\text{Sn}) = 26760$ Hz, which is very close to the reported values for *cis*-$[NMe_4]_2[PtBr_2(SnBr_3)_2]$ with $\delta(^{119}\text{Sn}) = -422$ and $\delta(^{195}\text{Pt}) = -4538$ (in acetone) and $^1J(^{195}\text{Pt}–^{119}\text{Sn}) = 25720$ Hz and $^1J(^{195}\text{Pt}–^{117}\text{Sn}) = 24592$ Hz [7]. *Cis*-$[NMe_4]_2[PtBr_2$

$(SnBr_3)_2]$ has been prepared by reaction of K_2PtBr_4 and $SnBr_2$ in HBr solution in the presence of Me_4NBr [19]. There was a small broad signal at $\delta = -416$ which is very close to the previously reported chemical shift for $SnBr_3^-$ in $CDCl_3$ ($\delta = -399$) [7] assigned to the species in the anionic form of $SnBr_3^-$. The chemical shift of tin in tin(II) compounds is influenced by the counter ion and solvent resulting from the well-known tendency of tin(II) to act as a Lewis acid and coordinate with many substances [14].

It can be seen that $SnCl_2$ in aqueous HBr solution acts as $SnBr_2$ and insertion of $SnBr_2$ into Pt–Br occurs. In addition, $SnBr_2$ in aqueous HCl solution acts as $SnCl_2$ and insertion of $SnCl_2$ into Pt–Cl bonds occurs. In the absence of acid as solvent, halogen exchange reactions occur. We reported another remarkable solvent dependence in the reactions of platinum complexes with $SnCl_2$ which resulted in the formation of four or five-coordinate platinum complexes [2].

3.4. *Reaction of cis-[PtCl$_2$(P)$_2$] with SnCl$_2$*

Cis-$[PtCl_2(PPh_3)_2]$ reacted with 5 equiv. $SnCl_2 \cdot 2H_2O$ in CH_2Cl_2/THF to produce a mixture of *cis,trans*-$[PtCl(SnCl_3)(PPh_3)_2]$, characterized by ^{31}P NMR spectroscopy [equation (6)].

$$\textit{cis}\text{-}[PtCl_2(PPh_3)_2] + SnCl_2 \rightleftarrows \underset{\mathbf{6}}{\textit{cis,trans}\text{-}[PtCl(SnCl_3)(PPh_3)_2]} \tag{6}$$

The ^{31}P NMR spectrum in dichloromethane displays two doublets at $\delta = 27.4$ with $^1J(^{31}P\text{-}^{195}Pt) = 3020$ Hz and $^2J(P\text{–}P) = 14.2$ Hz, and also $\delta = 10.7$ with $^1J(^{31}P\text{-}^{195}Pt) = 3665$ Hz and $^2J(P\text{–}P) = 14.2$ Hz for *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$. In addition, there was a singlet at $\delta = 19.4$ with $^1J(^{31}P\text{-}^{195}Pt) = 2328$ Hz due to *trans*-$[PtCl(SnCl_3)(PPh_3)_2]$. The ^{31}P NMR parameters of *cis,trans*-$[PtCl(SnCl_3)(PPh_3)_2]$ have been reported previously [20–22]. There was also a small singlet at $\delta = 14.1$ assigned to *cis*-$[PtCl_2(PPh_3)_2]$, but $^1J(^{31}P\text{-}^{195}Pt)$ could not be resolved [8].

The use of acetone or other oxygen donor solvents resulted in dissociation of **6**, as shown in equation (7). Interaction between tin(II) halide as a hard Lewis acid according to the Pearson classification and oxygen of acetone as a hard Lewis base may account for these observations [23, 24].

$$\underset{\mathbf{6}}{\textit{cis,trans}\text{-}[PtCl(SnCl_3)(PPh_3)_2]} \xrightarrow{\text{acetone}} \textit{cis}\text{-}[PtCl_2(PPh_3)_2] + SnCl_2 \tag{7}$$

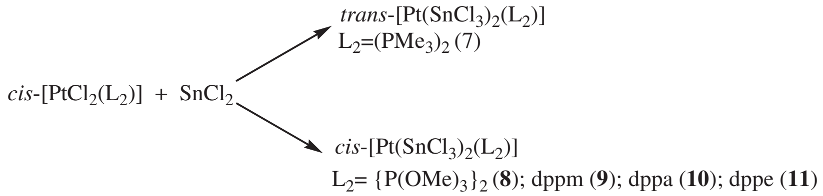
Addition of 1 equivalent of the chelating ligands dppm, dppa or dppe and two equivalents of monodentate ligands PMe_3 or $P(OMe)_3$ to a dichloromethane solution of *cis,trans*-$[PtCl_2(SMe_2)_2]$ gave *cis*-[PtCl$_2$(dppm)], *cis*-[PtCl$_2$(dppa)], *cis*-[PtCl$_2$(dppe)], *cis*-$[PtCl_2(PMe_2)_2]$ and *cis*-$[PtCl_2\{P(OMe)_3\}_2]$, respectively, as white solids in good to high yields having low solubility in organic solvents. The ^{31}P NMR data listed in table 1 are consistent with the literature [25–28].

The reaction of *cis*-$[PtCl_2(L_2)]$ $\{L_2 = (PMe_3)_2; \{P(OMe)_3\}_2;$ dppm; dppa; dppe$\}$ with $SnCl_2 \cdot 2H_2O$ in $C_2H_4Cl_2$/THF was performed by mixing the dichloroethane solution of *cis*-$[PtCl_2(L_2)]$ with an excess of $SnCl_2 \cdot 2H_2O$ in tetrahydrofuran (see experimental section). In each synthetic reaction leading to **7**–**11**, a color change from white to yellow or orange was observed when the platinum complexes were mixed with tin(II) chloride (scheme 1). Addition of a non-polar solvent e.g. diethyl ether, *n*-pentane or *n*-hexane to

Table 1. ^{31}P NMR data for *cis*-$[PtCl_2(L_2)]$ and platinum complexes obtained in the $[PtCl_2(L_2)] + SnCl_2$ systems.

Complex	$\delta(^{31}P)$	$^1J(Pt–P)$	Ref.
cis-$[PtCl_2(PPh_3)_2]$[a]	14.9	3673	8
cis-$[PtCl(SnCl_3)(PPh_3)_2]$[b]	27.4	3020	c
	10.7	3665	c
trans-$[PtCl(SnCl_3)(PPh_3)_2]$[b]	19.4	2328	c
cis-$[PtCl_2(PMe_3)_2]$[d]	−24.0	3478	c
trans-$[Pt(SnCl_3)_2(PMe_3)_2]$[e]	−43.2	1474	c
trans-$[PtCl(SnCl_3)(PMe_3)_2]$[e,f]	−43.5	1454	c
cis-$[PtCl_2\{P(OMe)_3\}_2]$[d]	73.7	5701	c
cis-$[Pt(SnCl_3)_2\{P(OMe)_3\}_2]$[e]	84.3	3058	c
cis-$[PtCl_2(PEt_3)_2]$[g]	9.3	3518	21
trans-$[Pt(SnCl_3)_2(PEt_3)_2]$[h]	8.4	1873	21
cis-$[PtCl_2\{P(OEt)_3\}_2]$[g]	68.1	5697	21
trans-$[Pt(SnCl_3)_2\{P(OEt)_3\}_2]$[g]	104.0	3623	21
cis-$[PtCl(SnCl_3)_2\{P(OEt)_3\}_2]$	85.2	4761	21
	80.2	5431	
cis-$[PtCl_2(dppm)]$[d]	−63.8	3071	c
cis-$[Pt(SnCl_3)_2(dppm)]$[e]	−51.7	2368	c
cis-$[PtCl_2(dppa)]$[i]	−5.2	3130	26
cis-$[Pt(SnCl_3)_2(dppa)]$[e]	6.7	2467	c
cis-$[PtCl_2(dppe)]$[j]	43.8	3600	27
cis-$[Pt(SnCl_3)_2(dppe)]$[b]	53.4	2596	c

[a] In $CDCl_3$; [b] in $CH_2Cl_2/CDCl_3$; [c] this work; [d] in $C_2H_4Cl_2/CDCl_3$; [e] in $C_2H_4Cl_2 \cdot THF/CDCl_3$; [f] at −30°C. [g] In $CHCl_3$ at −50°C; [h] in CH_2Cl_2 at −50°C; [i] solid state; [j] in DMSO.



Scheme 1. Synthesis of bis(trichlorostannyl) platinum(II) complexes.

these solutions afforded orange solids, but ^{31}P NMR spectra showed the simultaneous presence of several complexes in solution due to equilibria characteristic of these reactions. Thus, satisfactory elemental analysis data and yields of reactions could not be obtained.

The ^{31}P NMR spectrum for reaction of *cis*-$[PtCl_2(PMe_3)_2]$ with $SnCl_2$ in $C_2H_4Cl_2$/THF at room temperature displayed a central resonance at $\delta = -43.2$ ppm flanked by two satellites with $^1J(^{31}P\text{-}^{195}Pt) = 1474$ Hz, assigned to $[Pt(SnCl_3)_2(PMe_3)_2]$ (**7**) (figure 1). Alkyl phosphines of $[Pt(SnCl_3)_2(L)_2]$ have a preference for *trans* geometry [29]. Also, it has been shown that *trans-bis*(phosphine) complexes of platinum(II) containing two $SnCl_3$ ligands have coupling constants $^1J(^{31}P\text{-}^{195}Pt) < 1900$ Hz [21, 22]. For example, the reported $^1J(^{31}P\text{-}^{195}Pt)$ coupling constant for *trans*-$[Pt(SnCl_3)_2(PR_3)_2]$ (R = Et, Pr) are 1873 and 1844 Hz, respectively [21]. Thus, *trans* stereochemistry for **7** can be suggested. Notably, the $^{119/117}Sn$ satellites in the ^{31}P NMR spectrum at room temperature were not observed, indicating fast Pt–Sn bond breaking takes place on the NMR time scale.

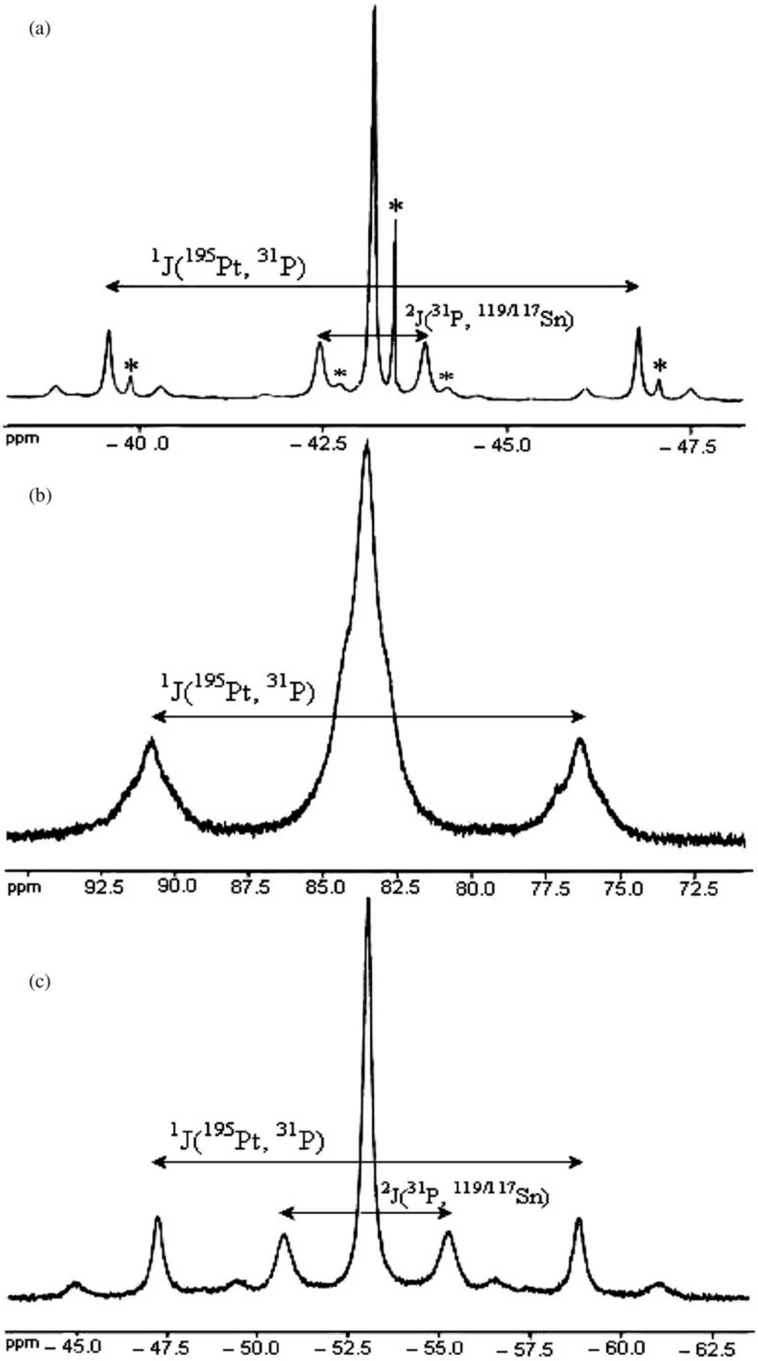


Figure 1. Solution ^{31}P NMR spectra measured in $C_2H_4Cl_2$/THF at −30°C for the reaction of *cis*-[$PtCl_2(L_2)$] with $SnCl_2$; (a) L = PMe_3, *shows *trans*-[$PtCl(SnCl_3)(PMe_3)_2$]; (b) L = $P(OMe)_3$; (C) L_2 = dppm.

When the temperature was decreased to −30°C, the signals were flanked by tin satellites with $^1J(^{31}\text{P-}^{195}\text{Pt}) = 1459$ Hz with average of ^{119}Sn and ^{117}Sn couplings of $^2J(^{31}\text{P-}^{119/117}\text{Sn}) = 290$ Hz (figure 1). A signal at $\delta = -43.5$ ppm with $^1J(^{31}\text{P-}^{195}\text{Pt}) = 1454$ Hz with average ^{119}Sn and ^{117}Sn couplings of $^2J(^{31}\text{P-}^{119/117}\text{Sn}) = 295$ Hz was assigned to *trans*-[PtCl(SnCl$_3$)(PMe$_3$)$_2$] by analogy [21]. When trimethylphosphite was used, the ^{31}P NMR spectrum contains a signal at $\delta = 84.3$ with platinum satellites $^1J(^{31}\text{P-}^{195}\text{Pt}) = 3058$ Hz. After cooling the solution to −30°C, all resonances became broad and tin satellites could not be observed (figure 1); there was a broad singlet at $\delta = 83.6$ ppm with $^1J(^{31}\text{P-}^{195}\text{Pt}) = 2914$ Hz. We could not follow the reaction at lower temperatures due to the freezing point of dichloroethane. In the case of **9**, the ^{31}P NMR spectrum displayed a central resonance at $\delta = -51.7$ accompanied by platinum satellites with $^1J(^{31}\text{P-}^{195}\text{Pt}) = 2368$ Hz. The ^{31}P NMR spectrum of **9** at −30°C showed a signal at $\delta = -53.0$ with $^1J(^{31}\text{P-}^{195}\text{Pt}) = 2339$ Hz and $^2J(^{31}\text{P-}^{119/117}\text{Sn}) = 898$ Hz (figure 1). Other platinum(II) complexes *cis*-[PtCl$_2$(L$_2$)] reacted with SnCl$_2$ to afford *cis*-[Pt(SnCl$_3$)$_2$(L$_2$)]. The ^{31}P NMR data are listed in table 1. The low solubility of **10** and **11** precludes following the ^{31}P NMR at low temperatures. NMR data in table 1 shows that coordination of SnCl_3^- to dichloroplatinum(II) as *cis*-[Pt(SnCl$_3$)$_2$(P$_2$)] or *cis*-[PtCl(SnCl$_3$)(P$_2$)] causes a marked deshielding on the ^{31}P resonance and a marked decrease of the platinum-phosphorus coupling constant, indicating greater π-back bonding in $\text{SnCl}_3{}^-$ relative to Cl$^-$. The differences observed between monodentate or bidentate phosphine or phosphite complexes discussed in this article reflect the differences in equilibrium reactions between chloride and trichlorostannyl complexes.

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