

Insertion reactions of SnCl_2 into Pt–Cl bonds in pentahalophenylplatinate(II) complexes

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Abstract

Several pentahalophenylplatinate complexes with Pt–Sn metal–metal bonds have been synthesized by facile insertion of SnCl_2 into Pt–Cl bonds of the starting platinum substrates. The complexes have been characterized spectroscopically and, in the case of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ and $(\text{NBu}_4)_2[\text{trans-Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$, the structures have been analyzed by X-ray diffraction. The reactivity of these derivatives towards neutral ligands has been explored. The electronic spectra of some selected derivatives have also been examined.

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1. Introduction

There are a variety of synthetic methods available for the formation of transition metal–tin bonds [1]. One of them, the insertion reaction of SnCl_2 , is a well-documented process that can take place easily at metal–metal bonds in binuclear transition metal complexes ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{W}, \text{Ru}$) [2], and also at M–halogen bonds ($\text{M} = \text{Mn}, \text{Re}, \text{Pt}$) [3]. The process takes place under very mild conditions and has led to a wide variety of complexes of different stoichiometries and structures. For instance, by reaction of $[\text{PtCl}_4]^{2-}$ with SnCl_2 , depending on the molar ratio, several derivatives $[\text{PtCl}_n(\text{SnCl}_3)_{4-n}]^{2-}$ are obtained; even $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ can be isolated by using an excess of SnCl_2 [4], although the lability of the M–Sn bonds very often leads to mixtures of different species in equilibrium [1]. Previous studies have

shown that several polytrichlorostannate platinum derivatives are stable [5] and in some of these complexes the SnCl_3 ligand plays different roles in catalytic processes [6].

Here, we report the results of the reactions of several anionic organometallic substrates of platinum with SnCl_2 , in which SnCl_2 has been inserted into Pt–Cl bonds rendering derivatives with Pt–Sn bonds. The Pt–Sn bonds are donor–acceptor in nature, with donor character on the Sn atom due to its lone electron pair. The crystal structures of two of these derivatives, $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ (**1**) and $(\text{NBu}_4)_2[\text{trans-Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ (**6**), have been established by X-ray diffraction. The ‘ SnCl_3 ’ moiety is a weakly coordinating anionic ligand [7] and can be readily displaced by other groups. We have tested the reactivity of these Pt–Sn derivatives towards neutral phosphine ligands, resulting in the replacement of the trichlorostannyl group by the phosphines. Finally, the electronic and luminescent properties of some selected Pt–Sn derivatives have been studied.

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2. Experimental

2.1. Materials

Literature methods were used for the preparation of the following starting materials: $(\text{NBu}_4)_2[\text{trans-PtCl}_2(\text{C}_6\text{F}_5)_2]$ [8], $(\text{NBu}_4)_2[\text{trans-PtCl}_2(\text{C}_6\text{Cl}_5)_2]$ [9] and $(\text{NBu}_4)[\text{trans-PtCl}_2(\text{C}_6\text{X}_5)\text{PPh}_3]$ (X = F, Cl) [10], $(\text{NBu}_4)_2[\text{PtCl}(\text{C}_6\text{F}_5)_3]$ [11], $(\text{NBu}_4)_2[\text{trans-Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{C}_6\text{Cl}_5)_2]$ [10]. All solvents and chemicals were of analytical reagent grade and were used without further purification. *Physical measurements.* C, H and N analyses were carried out on a Perkin–Elmer 240 microanalyzer. IR spectra were recorded (4000–200 cm^{-1}) on a Perkin–Elmer 883 spectrophotometer as Nujol mulls between polyethylene sheets. ^{19}F , ^{31}P and ^{119}Sn NMR spectra were recorded at room temperature on a Varian Unity 300 spectrometer. Mass spectra were recorded on a VG AutoSpec spectrometer. Conductivities were measured with a Philips PW9501 conductimeter on approximately 5×10^{-4} M acetone solutions. Emission and excitation spectra were obtained on a Perkin–Elmer Luminescence Spectrometer LS 50B.

2.2. Syntheses

2.2.1. Preparation of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ (1)

$(\text{NBu}_4)[\text{trans-PtCl}_2(\text{C}_6\text{F}_5)_2]$ (0.250 g, 0.23 mmol) was dissolved in dichloromethane (20 ml) and 0.087 g (0.46 mmol) of anhydrous SnCl_2 was added. After 1 h of reaction, the solution was evaporated to dryness. Upon addition of ca. 5 ml of isopropyl alcohol and vigorous stirring the oily residue was transformed into a yellow solid, which was filtered, washed with isopropyl alcohol and *n*-hexane and air dried. Yield: 85%. *Anal.* Calc. for $\text{C}_{44}\text{H}_{72}\text{Cl}_6\text{F}_{10}\text{N}_2\text{PtSn}_2$: C, 36.09; H, 4.96; N, 1.91. Found: C, 36.12; H, 5.08; N, 1.79%. Molar conductivity: 184 $\text{S cm}^2 \text{mol}^{-1}$. IR (cm^{-1}): C_6F_5 1634 (w), 1607 (w), 1057 (s), 957 (s), 775 (s, X-sensitive [18]); $\nu(\text{Sn-Cl})$ 324 (vs, br); NBu_4 889 (m, br). NMR (20 °C, ppm): ^{19}F ($\text{D}_6\text{-acetone}$) δ -112.6 (d, 4 F_o , $^3J_{\text{Pt-F}_o}$ = 301 Hz, $^4J_{\text{Sn-F}_o}$ = 96 Hz), -166.4 (t, 2 F_p), -167.8 (multiplet, 4 F_m); ^{119}Sn (CD_2Cl_2) δ -133.6 (not well resolved quintet, $^1J_{\text{Pt-Sn}}$ = 28280 Hz). MS FAB(-): molecular peak not observed, m/z 753 $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{SnCl}_3)]$ (25%), 565 $[\text{Pt}(\text{C}_6\text{F}_5)_2\text{Cl}]$ (100%).

2.2.2. Preparation of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{Cl}_5)_2]$ (2)

Following the same procedure, 0.25 g (0.20 mmol) of $(\text{NBu}_4)[\text{trans-PtCl}_2(\text{C}_6\text{Cl}_5)_2]$ was reacted with 0.076 g (0.40 mmol) of anhydrous SnCl_2 to give a yellow solid. Yield: 80%. *Anal.* Calc. for $\text{C}_{44}\text{H}_{72}\text{Cl}_{16}\text{N}_2\text{PtSn}_2$: C, 32.45; H, 4.46; N, 1.72. Found: C, 32.47; H, 4.52; N, 1.73%. Molar conductivity: 175 $\text{S cm}^2 \text{mol}^{-1}$. IR

(cm^{-1}): C_6Cl_5 1322 (s), 1303 (m), 1293 (s), 1228 (m), 812 (m, X-sensitive [18]), 673 (s), 609 (s); $\nu(\text{Sn-Cl})$ 328 (vs, br); NBu_4 882 (m, br). MS FAB(-): molecular peak not observed, m/z 919 $[\text{Pt}(\text{C}_6\text{Cl}_5)_2(\text{SnCl}_3)]$ (32%), 670 $[\text{Pt}(\text{C}_6\text{Cl}_5)(\text{SnCl}_3)]$ (100%).

2.2.3. Preparation of $(\text{NBu}_4)_2[\text{Pt}(\text{SnCl}_3)(\text{C}_6\text{F}_5)_3]$ (3)

To a solution of $(\text{NBu}_4)_2[\text{PtCl}(\text{C}_6\text{F}_5)_3]$ (0.15 g, 0.12 mmol) in 15 mL of CH_2Cl_2 was added SnCl_2 (0.023 g, 0.12 mmol). After 2 h of reaction, the solution was evaporated to dryness and isopropyl alcohol was added to the oily residue to give a pale yellow solid which was filtered off, washed with isopropyl alcohol and *n*-hexane and air dried. Yield: 84%. *Anal.* Calc. for $\text{C}_{50}\text{H}_{72}\text{Cl}_3\text{F}_{15}\text{N}_2\text{PtSn}$: C, 42.70; H, 5.12; N, 1.99. Found: C, 42.53; H, 4.98; N, 1.92%. Molar conductivity: 188 $\text{S cm}^2 \text{mol}^{-1}$. IR (cm^{-1}): C_6F_5 1633 (w), 1606 (w), 1055 (vs), 956 (vs); X-sensitive [18] 798 (s), 782 (m), 771 (s); $\nu(\text{Sn-Cl})$ 326 (vs), 299 (vs); NBu_4 886 (m). NMR (20 °C, CDCl_3) ^{19}F δ -111.9 (d, 4 F_o , $^3J_{\text{Pt-F}_o}$ = 361 Hz), -114.2 (d, 2 F_o , $^3J_{\text{Pt-F}_o}$ = 549 Hz), -167.1 (t, 2 F_p), -167.1 (t, 1 F_p), -167.3 to -167.4 (multiplet, 6 F_m). MS FAB(-): molecular peak not observed, m/z 696 $[\text{Pt}(\text{C}_6\text{F}_5)_3]$ (49%), 565 $[\text{Pt}(\text{C}_6\text{F}_5)_2\text{Cl}]$ (100%).

2.2.4. Preparation of $(\text{NBu}_4)[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)(\text{PPh}_3)]$ (4)

$(\text{NBu}_4)[\text{trans-PtCl}_2(\text{C}_6\text{F}_5)(\text{PPh}_3)]$ (0.100 g, 0.106 mmol) was dissolved in dichloromethane (20 ml) and 0.040 g (0.21 mmol) of anhydrous SnCl_2 was added. The suspension was reacted for 1 h and filtered through celite. The solution was evaporated to dryness and 10 ml of isopropyl alcohol was added to the oily residue, resulting in a pale yellow solid which was filtered, washed with isopropyl alcohol and *n*-hexane and air dried. Yield: 82%. *Anal.* Calc. for $\text{C}_{40}\text{H}_{51}\text{Cl}_3\text{F}_5\text{NPPtSn}$: C, 36.48; H, 3.90; N, 1.06. Found: C, 36.74; H, 3.94; N, 1.04%. Molar conductivity: 102 $\text{S cm}^2 \text{mol}^{-1}$. IR (cm^{-1}): C_6F_5 1638 (w), 1609 (w), 1058 (s), 958 (vs), 792 (s, X-sensitive [18]); $\nu(\text{Sn-Cl})$ 354 (vs, br), 332 (vs); PPh_3 1100 (s), 748 (s), 739 (s), 704 (s), 692 (s), 533 (vs), 514 (s), 494 (s); NBu_4 888 (m, br). NMR (20 °C, CDCl_3) ^{19}F δ -117.9 (d, 2 F_o , $^3J_{\text{Pt-F}_o}$ = 409 Hz), -164.4 (t, 1 F_p), -167.2 (multiplet, 2 F_m). ^{31}P δ 11.2 (s, $^1J_{\text{Pt-P}}$ = 1795 Hz). MS FAB(-): molecular peak not observed, m/z 906 $[\text{Pt}(\text{SnCl}_3)_2\text{PPh}_3]$ (5%), 695 $[\text{Pt}(\text{SnCl}_3)(\text{C}_6\text{F}_5)(\text{PPh}_2)]$ (100%).

2.2.5. Preparation of $(\text{NBu}_4)[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{Cl}_5)(\text{PPh}_3)]$ (5)

Following a similar procedure, 0.100 g (0.098 mmol) of $(\text{NBu}_4)[\text{trans-PtCl}_2(\text{C}_6\text{Cl}_5)(\text{PPh}_3)]$ was reacted with 0.037 g (0.20 mmol) of SnCl_2 . Yield: 80%. *Anal.* Calc. for $\text{C}_{40}\text{H}_{51}\text{Cl}_8\text{NPPtSn}$: C, 34.32; H, 3.67; N, 1.00. Found: C, 34.22; H, 3.74; N, 0.96%. Molar conductivity: 101 $\text{S cm}^2 \text{mol}^{-1}$. IR (cm^{-1}): C_6Cl_5 1325 (vs), 1294 (s),

1058 (s), 958 (vs), 836 (w, X-sensitive [18]), 674 (s), 625 (m); $\nu(\text{Sn}-\text{Cl})$ 335 (vs), 325 (vs); PPh_3 1104 (s), 746 (s), 693 (s), 534 (vs), 511 (s), 493 (s); NBu_4 887 (m, br). NMR (20 °C): ^{31}P (CDCl_3) δ 11.4 (s, $^1J_{\text{Pt}-\text{P}} = 1004$ Hz, $^2J_{\text{Sn}-\text{P}} = 91$ Hz, $^2J_{\text{Sn}-\text{P}} = 95$ Hz); ^{119}Sn (CD_2Cl_2) δ 15.1 (d, $^1J_{\text{Pt}-\text{Sn}} = 27050$ Hz, $^2J_{\text{P}-\text{Sn}} = 225$ Hz). MS FAB(-): m/z 1157 molecular peak (38%), 967 [$\text{Pt}(\text{SnCl}_3)\text{Cl}(\text{C}_6\text{Cl}_5)$ PPh_3] (64%), 705 [$\text{Pt}(\text{SnCl}_3)\text{Cl}(\text{C}_6\text{Cl}_5)$] (25%).

2.2.6. Preparation of $(\text{NBu}_4)_2[\text{trans-Pt}_2(\mu\text{-Cl})_2(\text{C}_6\text{F}_5)_2(\text{SnCl}_3)_2]$ (6)

0.15 g (0.10 mmol) of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{C}_6\text{F}_5)_2(\text{SnCl}_3)_2]$ was reacted with PtCl_2 (0.027 g, 0.10 mmol) in 15 mL of refluxing acetone for 10 h, the initial suspension giving rise to a brown-green solution. The mixture was filtered off in order to eliminate the small quantity of solids in suspension and the filtrate was evaporated to dryness. Upon addition of diethyl ether to the oily residue, a light brown solid was obtained, which was filtered off and air dried. Yield: 86%. Anal. Calc. for $\text{C}_{44}\text{H}_{72}\text{Cl}_8\text{F}_{10}\text{N}_2\text{Pt}_2\text{Sn}_2$: C, 30.51; H, 4.16; N, 1.62. Found: C, 30.63; H, 4.30; N, 1.64%. Molar conductivity: $217 \text{ S cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): C_6F_5 1638 (w), 1608 (w), 1057 (vs), 961 (vs), 809 (s, X-sensitive [18]); $\nu(\text{Sn}-\text{Cl})$ 354 (s), 338 (vs); NBu_4 876 (m). NMR (20 °C, CDCl_3) ^{19}F δ -118.4 (dd, $2F_o$, $^3J_{\text{Pt}-F_o} = 341$ Hz), -160.7 (td, $1F_p$), -164.1 to -165.0 (multiplet, $2F_m$). MS FAB(-): molecular peak not observed, m/z 623 [$\text{Pt}(\text{SnCl}_3)_2\text{Cl}(\text{C}_6\text{F}_5)$] (15%), 565 [$\text{Pt}(\text{C}_6\text{F}_5)_2\text{Cl}$] (100%).

2.2.7. Preparation of $(\text{NBu}_4)_2[\text{trans-Pt}_2(\mu\text{-Cl})_2(\text{C}_6\text{Cl}_5)_2(\text{SnCl}_3)_2]$ (7)

(a) Under the same conditions described above $(\text{NBu}_4)_2[\text{trans-Pt}(\text{C}_6\text{Cl}_5)_2(\text{SnCl}_3)_2]$ (0.15 g, 0.092 mmol) was reacted with PtCl_2 (0.024 g, 0.097 mmol) to render a brown-yellow solid. Yield: 74%. Anal. Calc. for $\text{C}_{44}\text{H}_{72}\text{Cl}_{18}\text{N}_2\text{Pt}_2\text{Sn}_2$: C, 27.86; H, 3.80; N, 1.48. Found: C, 28.13; H, 3.69; N, 1.68%. Molar conductivity: $220 \text{ S cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): C_6Cl_5 1322 (s), 1295 (s), 1262 (s), 1224 (m), 800 (w, X-sensitive [18]), 676 (s), 637 (m); $\nu(\text{Sn}-\text{Cl})$ 349 (s), 326 (vs); NBu_4 882 (m, br). MS FAB(-): molecular peak not observed, m/z 728 [$\text{PtCl}(\text{C}_6\text{Cl}_5)_2$] (62%), 704 [$\text{Pt}(\text{SnCl}_3)\text{Cl}(\text{C}_6\text{Cl}_5)$] (53%), 515 [$\text{PtCl}_2(\text{C}_6\text{Cl}_5)$] (100%). (b) 0.15 g (0.099 mmol) of $(\text{NBu}_4)_2[\text{trans-Pt}(\mu\text{-Cl})_2\text{Cl}_2(\text{C}_6\text{Cl}_5)_2]$ was dissolved in 25 mL of acetone and SnCl_2 (0.0375 g, 0.198 mmol) was added. After reacting at room temperature for 2 h, the suspension was filtered off and the filtrate evaporated to dryness. The residue was treated with isopropyl alcohol to render a solid which was filtered, washed with isopropyl alcohol and air dried. Yield: 60%.

2.2.8. Reaction of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ with PPh_3 (1:1)

0.100 g (0.068 mmol) of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ was dissolved in 20 mL of acetone and

0.018 g (0.068 mmol) of PPh_3 was added. The mixture was reacted at room temperature for 2 h and evaporated to dryness. The residue was treated with isopropyl alcohol to render a white solid, $(\text{NBu}_4)[\text{trans-Pt}(\text{SnCl}_3)(\text{C}_6\text{F}_5)_2\text{PPh}_3]$ (8), which was filtered, washed with isopropyl alcohol and *n*-hexane and air dried. Yield: 71%. Anal. Calc. for $\text{C}_{46}\text{H}_{51}\text{Cl}_3\text{F}_{10}\text{NPPtSn}$: C, 43.88; H, 4.08; N, 1.11. Found: C, 44.16; H, 4.12; N, 1.08%. Molar conductivity: $113 \text{ S cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): C_6F_5 1632 (w), 1603 (w), 1057 (s), 957 (vs), 777 (m, X-sensitive [18]); $\nu(\text{Sn}-\text{Cl})$ 325 (s); PPh_3 1099 (s), 736 (s), 698 (s), 527 (s), 515 (s), 498 (m); NBu_4 890 (m). NMR (20 °C, CDCl_3) ^{19}F δ -115.5 (d, $4F_o$, $^3J_{\text{Pt}-F_o} = 242$ Hz), -163.9 (t, $2F_p$), -164.7 to -164.9 (multiplet, $4 F_m$). ^{31}P δ 14.7 (s, $^1J_{\text{Pt}-\text{P}} = 1178$ Hz). MS FAB(-): m/z 1021 molecular peak (20%), 412 [$\text{Pt}(\text{SnCl}_3)$] (38%).

2.2.9. Reaction of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ with L ($L = \text{PPh}_3, \text{PEtPh}_2, \text{PET}_2\text{Ph}, \text{PET}_3$) (1:2)

$L = \text{PPh}_3$. $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ (0.100 g, 0.068 mmol) was dissolved in 20 mL of acetone along with 0.036 g (0.14 mmol) of PPh_3 . The mixture was reacted for 15 h at room temperature and evaporated to dryness. A few milliliters of isopropyl alcohol was added to the residue and, after a vigorous stirring, a white solid was formed, $[\text{trans-Pt}(\text{C}_6\text{F}_5)_2(\text{PPh}_3)_2]$, which was filtered, washed with *n*-hexane and air dried. Yield: 72%. Anal. Calc. for $\text{C}_{48}\text{H}_{30}\text{F}_{10}\text{P}_2\text{Pt}$: C, 52.71; H, 2.87. Found: C, 52.35; H, 2.82%.

$L = \text{PEtPh}_2$. 0.100 g (0.068 mmol) of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ and 42 μL (0.21 mmol) of PEtPh_2 gave 0.047 g of $[\text{trans-Pt}(\text{C}_6\text{F}_5)_2(\text{PEtPh}_2)_2]$ (72% yield). Anal. Calc. for $\text{C}_{40}\text{H}_{30}\text{F}_{10}\text{P}_2\text{Pt}$: C, 50.17; H, 3.16. Found: C, 49.74; H, 3.07%.

$L = \text{PET}_2\text{Ph}$. 0.100 g (0.068 mmol) of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ and 36 μL (0.21 mmol) of PET_2Ph gave 0.040 g of $[\text{trans-Pt}(\text{C}_6\text{F}_5)_2(\text{PET}_2\text{Ph})_2]$ (68% yield). Anal. Calc. for $\text{C}_{32}\text{H}_{30}\text{F}_{10}\text{P}_2\text{Pt}$: C, 44.61; H, 3.91. Found: C, 44.64; H, 4.01%.

$L = \text{PET}_3$. 0.100 g (0.068 mmol) of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ and 30.3 μL (0.246 mmol) of PET_3 in 30 mL of acetone were refluxed for 30 h. After evaporating to dryness, the residue was treated with diethyl ether to give 0.034 g of $[\text{trans-Pt}(\text{C}_6\text{F}_5)_2(\text{PET}_3)_2]$ (65% yield), which was filtered and air dried. Anal. Calc. for $\text{C}_{32}\text{H}_{30}\text{F}_{10}\text{P}_2\text{Pt}$: C, 35.66; H, 3.55. Found: C, 35.20; H, 3.58%.

2.2.10. Reaction of $(\text{NBu}_4)_2[\text{trans-Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{C}_6\text{X}_5)_2]$ with PPh_3 (1:2)

$X = \text{F}$. $(\text{NBu}_4)_2[\text{trans-Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ (0.100 g, 0.058 mmol) was dissolved in 30 mL of dichloromethane and reacted with 0.030 g (0.12 mmol) of PPh_3 . The solution turned deep orange and after 3 h of stirring at room temperature was evaporated to

dryness. Isopropyl alcohol was added to the residue to give a yellow solid, $(\text{NBu}_4)[\text{PtCl}(\text{SnCl}_3)(\text{C}_6\text{F}_5)\text{PPh}_3]$ (**9**), which was filtered, washed with *n*-hexane and air dried. Yield: 60%. *Anal.* Calc. for $\text{C}_{40}\text{H}_{51}\text{Cl}_4\text{F}_5\text{NPtSn}$: C, 42.61; H, 4.56. Found: C, 42.47; H, 4.58%. Molar conductivity: $112 \text{ S cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): C_6F_5 1634 (w), 1609 (w), 1059 (s), 954 (vs), 807 (m, X-sensitive [18]); $\nu(\text{Sn}-\text{Cl})$ 312 (s, br); PPh_3 1099 (s), 744 (s), 710 (s), 691 (vs), 526 (vs), 517 (vs), 502 (s); NBu_4 889 (w). NMR (20 °C, CDCl_3) ^{19}F δ -118.4 (d, $2F_o$, $^3J_{\text{Pt}-F_o} = 399 \text{ Hz}$), -164.8 (t, $1F_p$), -165.4 (multiplet, $2F_m$). ^{31}P δ 22.5 (s, $^1J_{\text{Pt}-\text{P}} = 1168 \text{ Hz}$). MS FAB(-): *m/z* 886 molecular peak (45%), 719 $[\text{Pt}(\text{SnCl}_3)\text{Cl}(\text{PPh}_3)]$ (35%).

$X = \text{Cl}$. Similarly, 0.100 g (0.053 mmol) of $(\text{NBu}_4)_2[\text{trans-Pt}_2(\mu-\text{Cl})_2(\text{SnCl}_3)_2(\text{C}_6\text{Cl}_5)_2]$ was reacted with PPh_3 (0.028 g, 0.11 mmol) to give a yellow solid identified as $(\text{NBu}_4)[\text{PtCl}(\text{SnCl}_3)(\text{C}_6\text{Cl}_5)\text{PPh}_3]$ (**10**). Yield: 70%. *Anal.* Calc. for $\text{C}_{40}\text{H}_{51}\text{Cl}_9\text{NPtSn}$: C, 38.71; H, 4.26; N, 1.16. Found: C, 38.50; H, 4.25; N, 1.11%. Molar conductivity: $99 \text{ S cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): C_6Cl_5 1335 (s), 1323 (s), 1263 (m), 835 (m, X-sensitive [18]), 675 (s), 611 (m); $\nu(\text{Sn}-\text{Cl})$ 324 (s, br); PPh_3 1095 (s), 695 (s), 520 (s), 499 (s), 441 (m); NBu_4 888 (m). NMR (20 °C, CDCl_3) ^{31}P δ 19.8 (s, $^1J_{\text{Pt}-\text{P}} = 1243 \text{ Hz}$, $^2J_{\text{Sn}-\text{P}} = 355 \text{ Hz}$). MS FAB(-): *m/z* 969 molecular peak (22%), 719 $[\text{Pt}(\text{SnCl}_3)\text{Cl}(\text{PPh}_3)]$ (75%).

2.3. Crystal structure of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ (**1**)

Crystal data and other parameters are listed in Table 1 for complexes **1** and **6**. Suitable crystals of complex **1** were obtained by slow diffusion of a solution of SnCl_2 in diethylether into a solution of $(\text{NBu}_4)_2[\text{trans-PtCl}_2(\text{C}_6\text{F}_5)_2]$ in methanol at room temperature. A pale-yellow crystal was fixed with epoxy on top of a glass fiber and mounted on the goniometer head of an automated four circle diffractometer (Siemens STOE/AED2). Data were collected at 293 K by the $\omega/2\theta$ method. Three check reflections measured at regular intervals showed no loss of intensity through the course of data collection. An empirical absorption correction based on psi scans (19 reflections) was applied. The structure was solved by direct methods. The asymmetric unit contains only half the molecule, with the platinum atom lying on an inversion center. All non-hydrogen atoms of the anion of complex **1** were located in succeeding difference Fourier syntheses and refined with anisotropic thermal parameters. Three of the four butyl branches of the NBu_4^+ cation were modeled with disorder over two positions (occupancies 0.65 and 0.35), and the fourth butyl group had one of its atoms also disordered (C7 and C7'). The disordered atoms were refined with isotropic thermal parameters. No hydrogen atoms were

Table 1

Crystal data and structure refinement parameters for $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ (**1**) and $(\text{NBu}_4)_2[(\text{SnCl}_3)(\text{C}_6\text{F}_5)\text{Pt}(\mu-\text{Cl})_2\text{Pt}(\text{C}_6\text{F}_5)(\text{SnCl}_3)]$ (**6**)

	1	6
Empirical formula	$\text{C}_{44}\text{H}_{72}\text{Cl}_6\text{F}_{10}\text{N}_2\text{Pt}_2\text{Sn}_2$	$\text{C}_{44}\text{H}_{72}\text{Cl}_8\text{F}_{10}\text{N}_2\text{Pt}_2\text{Sn}_2$
Formula weight	1464.21	1730.2
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
<i>a</i> (Å)	14.153(1)	11.570(2)
<i>b</i> (Å)	11.750(1)	17.172(2)
<i>c</i> (Å)	18.131(2)	16.229(2)
α (°)	90	90
β (°)	91.25(1)	94.891(9)
γ (°)	90	90
Volume (Å ³)	3014.4(5)	3212.6(8)
Z, density(calculated) (Mgm^{-3})	2, 1.613	2, 1.789
Absorption coefficient (mm^{-1})	3.463	5.500
<i>F</i> (0 0 0)	1440	1664
Crystal size (mm)	$0.61 \times 0.57 \times 0.57$	$0.24 \times 0.22 \times 0.18$
θ range for data collection (°)	1.81 to 24.98.	2.08 to 23.50
Index ranges	<i>h</i> (0, 16); <i>k</i> (0, 13); <i>l</i> (-21, 21)	<i>h</i> (0, 12); <i>k</i> (0, 19); <i>l</i> (-18, 18)
Reflections collected/unique	5794/5284 [$R_{\text{int}} = 0.0256$]	5023/4743 [$R_{\text{int}} = 0.0336$]
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	4487/0/267	3975/0/307
Goodness-of-fit on F^2	1.002	1.014
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0607$, $wR_2 = 0.1222$	$R_1 = 0.0547$, $wR_2 = 0.0743$
<i>R</i> indices (all data)	$R_1 = 0.1367$, $wR_2 = 0.1608$	$R_1 = 0.1363$, $wR_2 = 0.0963$
Largest difference peak and hole (e/Å^{-3})	0.615 and -0.652	0.503 and -0.459

$$R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2}; \text{goodness-of-fit} = [w(F_o^2 - F_c^2) / (N_{\text{obs}} - N_{\text{param}})]^{1/2}; w = [\sigma^2(F_o) + (g_1P)^2 + g_2P]^{-1}; P = [\max(F_o^2; 0) + 2F_c^2] / 3.$$

added to the model. This disorder is expected since the specific volume for non-hydrogen atoms is unusually large (23.2 \AA^3), so the atoms have enough space to generate either static and/or dynamic disorder. The final difference density map showed no peaks above 1 e \AA^{-3} .

2.4. Crystal structure of $(\text{NBu}_4)_2[(\text{SnCl}_3)(\text{C}_6\text{F}_5)\text{Pt}(\mu\text{-Cl})_2\text{Pt}(\text{C}_6\text{F}_5)(\text{SnCl}_3)]$ (**6**)

Crystals of complex **6** were grown by slow diffusion of hexane into a dichloromethane solution of the compound at room temperature. A colorless prismatic crystal was fixed with epoxy on top of a glass fiber and transferred to the goniometer head of an automated four circle diffractometer (Siemens P4). Cell constants were calculated from 45 well centered reflections with 2θ angles ranging from 15° to 25° . Data were collected at room temperature by the $\omega/2\theta$ method. Three check reflections measured at regular intervals showed no significant loss of intensity through the course of data collection. An empirical absorption correction based on psi scans (17 reflections) was applied. The structure was solved by the Patterson method. All non-hydrogen atoms were located in succeeding difference Fourier syntheses and refined with anisotropic thermal parameters. Hydrogen atoms were added at calculated positions and assigned isotropic displacement parameters equal to 1.2 or 1.5 times the U_{iso} value of their respective parent carbon atoms. The final difference density map showed no peaks above 1 e \AA^{-3} . All calculations were carried out using the program SHELXL-97 [12].

3. Results and discussion

3.1. Synthesis of complexes **1–7**

We have reacted several anionic platinum substrates having different numbers of Pt–Cl bonds with SnCl_2 . In all cases, insertion of SnCl_2 into all Pt–Cl bonds has taken place. When the complexes $(\text{NBu}_4)_2[\text{trans-PtCl}_2(\text{C}_6\text{X}_5)_2]$ ($\text{X} = \text{F}, \text{Cl}$) are reacted with anhydrous SnCl_2 (molar ratio 1:2), the derivatives $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{X}_5)_2]$ ($\text{X} = \text{F}$ **1**, Cl **2**) are formed. Complex $(\text{NBu}_4)_2[\text{PtCl}(\text{C}_6\text{F}_5)_3]$ reacts with SnCl_2 in 1:1 molar ratio to yield $(\text{NBu}_4)_2[\text{PtSnCl}_3(\text{C}_6\text{F}_5)_3]$ (**3**). Similarly, $(\text{NBu}_4)[\text{trans-PtCl}_2(\text{C}_6\text{X}_5)(\text{PPh}_3)]$ can react with SnCl_2 to form $(\text{NBu}_4)[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{X}_5)(\text{PPh}_3)]$ ($\text{X} = \text{F}$ **4**, Cl **5**). All of these reactions proceed under mild conditions, in dichloromethane or acetone at room temperature. The insertion is almost immediate with good yield. The conductivity values for all of these complexes in acetone solution correspond to 2:1 (**1–3**) or 1:1 (**4, 5**) electrolytes, which implies that the Pt–Sn bonds formed are strong enough to be stable in solution. This fact has also been demonstrated by using NMR spectroscopy.

The ^{119}Sn RMN spectra of complexes **1** and **5** show Pt–Sn coupling, indicating that the Pt–Sn bond is inert. There are other precedents of the use of ^{119}Sn NMR to reveal the presence of Pt–Sn bonds in solution as is the case of the complex $[\text{PtCl}(\text{SnCl}_3)(\text{bdpp})]$ ($\text{bdpp} = (2S,4S)\text{-2,4-bis(diphenylphosphino)pentane}$) [13].

Binuclear $(\text{NBu}_4)_2[\text{Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{C}_6\text{X}_5)_2]$ ($\text{X} = \text{F}$ **6**, Cl **7**) can be obtained by reaction of $(\text{NBu}_4)_2[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{C}_6\text{X}_5)_2]$ with two equivalents of SnCl_2 , resulting in the insertion of this group into the terminal Pt–Cl bonds. This procedure, as for the other derivatives, is a very facile reaction. In no case did we observe insertion of SnCl_2 into the Pt–Cl_{bridging} bonds. Another synthetic approach for complex **7** consists of the reaction of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{Cl}_5)_2]$ (**2**) with PtCl_2 in refluxing acetone for at least 10 h. This kind of reaction is not common but several examples are known in the literature [8].

3.2. Crystal structure of complex **1**

The structure of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ (**1**) has been established by X-ray diffraction and is shown in Fig. 1. Selected bond distances and angles are given in Table 2. The molecule contains a platinum center in a rhombically distorted square-planar environment with the ligands in *trans* positions (the platinum atom lies on an inversion center). Thus, the three metal atoms maintain a linear disposition with Pt–Sn distances of $2.5249(8) \text{ \AA}$. This distance is notably shorter than the sum of their covalent radii (2.71 \AA) [14], in the middle of the range of $2.487\text{--}2.634 \text{ \AA}$ observed for such interactions [15]. The geometry around the Sn center is distorted tetrahedral, with Cl–Sn–Cl angles in the range $96.4(1)\text{--}98.4(2)^\circ$ and Pt–Sn–Cl angles in the range $119.4(1)\text{--}121.2(1)^\circ$. The Pt–C and Sn–Cl distances are within the expected ranges. In this complex, the Sn–F

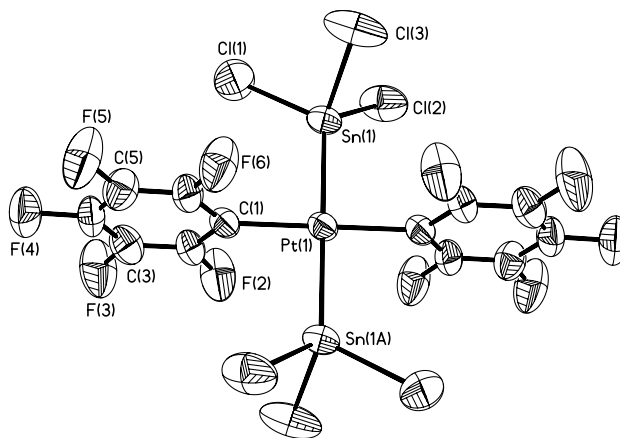


Fig. 1. Structure of the anion of $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ (**1**). Ellipsoids are shown at 30% probability level.

Table 2

Selected bond lengths (Å) and angles (°) for (NBu₄)₂[*trans*-Pt(SnCl₃)₂(C₆F₅)₂] (**1**) and (NBu₄)₂[(SnCl₃)(C₆F₅)Pt(μ-Cl)₂Pt(C₆F₅)(SnCl₃)] (**6**)

1		6	
<i>Bond lengths</i> (Å)			
Pt(1)–C(1)	2.071(11)	Pt(1)–C(1)	1.996(12)
Pt(1)–Sn(1)	2.5249(8)	Pt(1)–Cl(1)	2.395(3)
Sn(1)–Cl(3)	2.346(4)	Pt(1)–Sn(1)	2.4745(11)
Sn(1)–Cl(2)	2.348(3)	Sn(1)–Cl(4)	2.323(4)
Sn(1)–Cl(1)	2.357(4)	Sn(1)–Cl(2)	2.339(4)
		Sn(1)–Cl(3)	2.326(4)
<i>Bond angles</i> (°)			
C(1)–Pt(1)–Sn(1)	89.8(3)	C(1)–Pt(1)–Cl(1)	177.5(4)
C(1)–Pt(1)–Sn(1)#1	90.2(3)	C(1)–Pt(1)–Sn(1)	89.3(3)
Cl(2)–Sn(1)–Cl(1)	98.4(2)	C(1)–Pt(1)–Cl(1)#1	91.7(3)
Cl(3)–Sn(1)–Cl(2)	96.39(14)	Cl(1)–Pt(1)–Cl(1)#1	85.80(10)
Cl(3)–Sn(1)–Cl(1)	96.5(2)	Cl(1)–Pt(1)–Sn(1)	93.17(8)
Cl(1)–Sn(1)–Pt(1)	119.49(11)	Cl(1)#1–Pt(1)–Sn(1)	176.78(9)
Cl(3)–Sn(1)–Pt(1)	119.39(10)	Cl(4)–Sn(1)–Cl(3)	99.5(2)
Cl(2)–Sn(1)–Pt(1)	121.21(10)	Cl(4)–Sn(1)–Cl(2)	99.8(2)
		Cl(3)–Sn(1)–Cl(2)	99.2(2)
		Cl(4)–Sn(1)–Pt(1)	116.43(12)
		Cl(3)–Sn(1)–Pt(1)	121.22(12)
		Cl(2)–Sn(1)–Pt(1)	116.82(10)
		Pt(1)–Cl(1)–Pt(1)#1	94.20(10)

Symmetry transformations used to generate equivalent atoms: #1 –x, –y, –z.

distances are long enough to exclude any type of interaction between the Sn atom and the *ortho*-fluorine atom of the C₆F₅ ligand, an effect observed in other complexes of platinum with pentahalophenyl groups [16]. In (NBu₄)₂{Sn[Pt(μ-Cl)(C₆F₅)₂]₃} [17], a complex having longer Pt–Sn bonds [2.703(3) and 2.742(3) Å], the Sn–F contacts range from 2.889(14) to 3.193(14) Å. The planes of the C₆F₅ rings are almost perpendicular to the coordination plane of the platinum (96.3)°.

3.3. Crystal structure of complex **6**

Fig. 2 shows the structure of the anionic complex **6**. Table 2 lists the most important bond distances and angles. Due to symmetry, only half of the molecule is independent. The Pt atom lies in the center of a square-planar environment formed by C(1), Cl(1), Cl(1a) and Sn(1). The Pt–Sn distance of 2.475(1) Å is slightly shorter than in complex **1**, while the Pt–C and Pt–Cl distances are comparable: 1.996(12) and 2.395(3) Å, respectively. The environment of the Sn atom is distorted tetrahedral, with Cl–Sn–Cl and Pt–Sn–Cl angles ranging from 96.41(14)° to 121.22(10)°. The angle between the C₆F₅ ring and the coordination plane of the platinum is 78.4(5)°.

3.4. Reactivity of derivatives with Pt–Sn bonds with neutral ligands

The lability of the Pt–Sn bonds is observed by reaction of different derivatives with neutral ligands. We

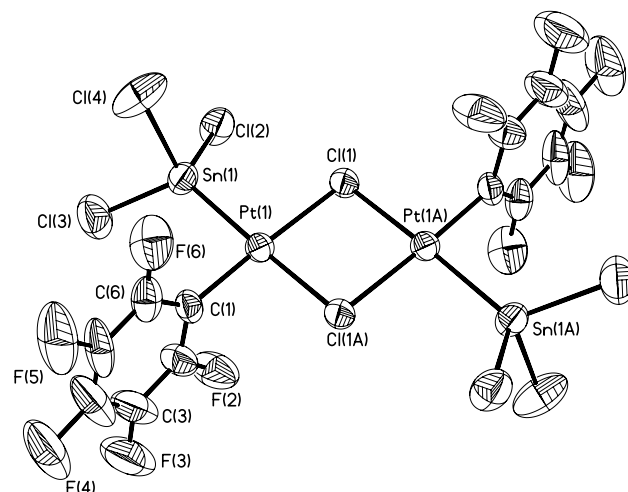
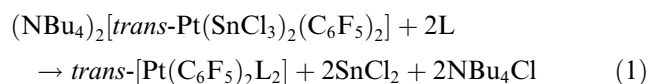


Fig. 2. Structure of the anion of (NBu₄)₂[(SnCl₃)(C₆F₅)Pt(μ-Cl)₂Pt(C₆F₅)(SnCl₃)] (**6**).

have reacted (NBu₄)₂[*trans*-Pt(SnCl₃)₂(C₆F₅)₂] (**1**) with phosphine ligands, such as PPh₃, PPh₂Et, PPhEt₂ and PEt₃. When the reactions are carried out in a 1:2 molar ratio and in refluxing acetone, in all cases the neutral derivatives *trans*-[Pt(C₆F₅)₂L₂] (L = PPh₃, PPh₂Et, PPhEt₂, PEt₃), are obtained in good yield (Eq. (1)), showing that it is possible to replace both SnCl₃ by L groups due to the stability of the neutral complexes and to the lability of the Pt–Sn bonds. These complexes had been obtained previously by other methods.



L = PPh₃, PPh₂Et, PPhEt₂, PEt₃

When the reaction is carried out in a 1:1 molar ratio, we expected to obtain the complexes in which replacement of only one SnCl₃ group by a ligand L had occurred. However, only for PPh₃ a clean product is formed, namely (NBu₄)[*trans*-Pt(SnCl₃)(C₆F₅)₂](PPh₃) (**8**). In the other cases, mixtures of both starting material and disubstituted complex could be identified on the basis of their IR spectra. The complex (NBu₄)₂[*trans*-Pt(SnCl₃)₂(C₆Cl₅)₂] (**2**) can also undergo reaction with neutral phosphine ligands, but regardless of the molar ratio, in all cases the result is a mixture of compounds that we did not attempt to separate, but which were identified by IR as the mono- and disubstituted products and also unreacted starting material.

The diplatinum derivatives (NBu₄)₂[*trans*-Pt₂(μ-Cl)₂(SnCl₃)₂(C₆X₅)₂] react with PPh₃ in 1:2 molar ratio by cleavage of the Cl bridges and coordination of the phosphine to the platinum, giving (NBu₄)[PtCl(SnCl₃)(C₆X₅)(PPh₃)] (X = F **9**, Cl **10**), in which the four ligands around Pt are different.

3.5. Spectroscopic studies

All the new products were identified and characterized on the basis of their elemental analyses, IR, NMR and mass spectra (see Section 2). The IR spectra of all the complexes show the typical absorptions of the groups which are present. The SnCl_3 moiety gives an absorption in the range $300\text{--}400\text{ cm}^{-1}$ that corresponds to the $\nu(\text{Sn--Cl})$ vibration. This is very strong, broad and in some cases is a double band. The absorptions corresponding to the X-sensitive mode of the C_6F_5 or C_6Cl_5 groups in square-planar complexes can give information on the number and disposition of these groups, since it is related to the skeletal symmetry of the molecule [18]. Thus, complexes having a single C_6X_5 show a unique absorption, while complex **3**, with three C_6F_5 groups, shows three bands. We have identified complexes with two C_6F_5 groups bonded to the platinum as the *trans* isomers due to the presence of only one strong absorption in the X-sensitive region, since *cis* complexes will show two absorptions of the same intensity [19].

Additional information was inferred from NMR spectroscopy. The ^{19}F NMR spectra of complexes that contain C_6F_5 ligands show separate resonances (2:2:1) for the three types of fluorine present: *ortho*-, *meta*- and *para*-fluorine. The signal for the *ortho*-fluorine consists of a doublet, because of coupling with *meta*-fluorine (generally, coupling with *para*-fluorine is not clearly observed). This signal also shows coupling with ^{195}Pt . The *para*-fluorine is seen as a triplet, because of coupling to *meta*-fluorine; and *meta*-fluorine is seen as a multiplet because of coupling with both *ortho*- and *para*-fluorine. Complex **3** shows two different sets of signals, which agrees with the two types of C_6F_5 present in the complex (one *trans* to the SnCl_3 group and two *trans* to each other). For complex **1**, besides the satellites due to coupling with ^{195}Pt , another set of satellites resulting from coupling with ^{117}Sn and ^{119}Sn appear in the spectrum. This demonstrates again that the Pt–Sn bond persists in solution. Complex **6** shows a more complicated pattern in the *ortho* region, with four signals centered

at -118.4 ppm, which are probably due to the inequivalence of the two *ortho*-fluorine atoms. The ^{31}P NMR shows a singlet and Pt–P coupling can also be observed. Only in the case of complexes **5** and **10** can coupling with Sn also be observed. The ^{119}Sn RMN spectra of complex **1** show an apparent singlet (in fact it is a not well resolved quintet with $^4J(^{19}\text{F}, \text{Sn}) = 70$ Hz) with platinum satellites. For complex **5**, the ^{119}Sn NMR shows a doublet, due to coupling Sn–P and platinum satellites are present as well.

Mass spectra have been recorded for all of the complexes **1–10**. The molecular peaks could be identified in the cases of complexes **5**, **8**, **9** and **10**, showing a correct isotopic distribution.

3.6. Electronic and luminescence spectroscopic properties

While the optical properties of many platinum(II) complexes have been thoroughly investigated [20], it is quite surprising that comparable photophysical studies on trichlorostannyl platinum(II) derivatives are scarce in the literature. Vogler et al. have examined the properties of $(\text{NBu}_4)_3[\text{Pt}(\text{SnCl}_3)_5]$ concluding that the absorption and emission spectra are dominated by bands which could be assigned to intraligand sp transitions [21]. However, the photophysical properties of series of $\text{M}_2[\text{cis-PtX}_2(\text{SnX}_3)_2]$ ($\text{M} = \text{NBu}_4^+$, $\text{PhCH}_2\text{PPh}_3^+$, $\text{CH}_3\text{PPh}_3^+$, Pr_4N^+ ; $\text{X} = \text{Cl}, \text{Br}$) [22] and $(\text{PhCH}_2\text{PPh}_2)_2[\text{PtBr}_3(\text{SnBr}_3)]$ complexes were found by Nelson and co-workers to be similar to those found in $[\text{PtX}_4]^{2-}$ systems [23] and attributed to d–d transitions.

In order to gain further insight, we have examined the electronic spectra of some selected complexes. For the mononuclear compounds **1**, **4** and **5** and for the binuclear derivative **7** their UV–Vis absorptions in CH_2Cl_2 ($\sim 2 \times 10^{-5}$ M) and frozen (77 K) emission data are listed in Table 3. For comparison, the corresponding data for the chloride precursors are also included. The absorption spectrum of complex $(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ (**1**) exhibits one intense band at 235 nm with a shoulder at 269 nm and a second less intense

Table 3
Emission and excitation spectral data in CH_2Cl_2 10^{-3} M solutions

Compound	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$ ($\epsilon \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{em}}^{\text{max}}/\text{nm}$ (77 K)	$\lambda_{\text{exc}}^{\text{max}}/\text{nm}$ (77 K)
$(\text{NBu}_4)_2[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)_2]$ (1)	235(22.28), 269sh(7.67), 310(0.9)	515, 588, 594sh ^a	325, 399
$(\text{NBu}_4)[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)(\text{PPh}_3)]$ (4)	235(23.2), 265(7.1), 324(0.9)	584	356
$(\text{NBu}_4)[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{Cl}_5)(\text{PPh}_3)]$ (5)	234(57.7), 279(20.2), 307(17.4), 322(16.5)	574, 615 ^b	429, 460, 475sh
$(\text{NBu}_4)_2[\text{Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{C}_6\text{Cl}_5)_2]$ (7)	234(69.9), 275(33.09), 320(3.3)	690	390
$(\text{NBu}_4)_2[\text{trans-PtCl}_2(\text{C}_6\text{F}_5)_2]$	260(3.5), 333(0.47)	580($\lambda_{\text{exc}}^{\text{max}}$ 345 nm) ^c	284, 298, 344
$(\text{NBu}_4)[\text{trans-PtCl}_2(\text{C}_6\text{Cl}_5)(\text{PPh}_3)]$	233(48.68), 263(25.02)	510 ^d	330, 345, 380, 399
$(\text{NBu}_4)_2[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{C}_6\text{Cl}_5)_2]$	240(35), 260(21), 310(4.1), 411(0.53)	626	354, 463

^a At room temperature in CH_2Cl_2 , a very weak emission is detected at 600 nm (λ_{exc} 445 nm).

^b At room temperature, a weak emission is detected with maxima at 519 and 588 nm.

^c A weak high energy emission occurs (369, 425 nm) by exciting at 300 nm.

^d At room temperature, two bands are observed at 377 and 519 nm (upon excitation at λ_{exc} 333 nm).

one at 310 nm ($900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The related chloride precursor $(\text{NBu}_4)_2[\text{trans-PtCl}_2(\text{C}_6\text{F}_5)_2]$ shows also two bands at 260 nm ($3500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and at 333 ($470 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). For both complexes the high energy bands, which are dipole-allowed as evidenced by their high extinction coefficients, are tentatively assigned to C_6F_5 -localized transitions. However, in the case of complex **1** overlap with $\text{Pt}(5d) \rightarrow d\pi \text{ SnCl}_3^-$ transitions could also be also possible. In fact, it has been previously noted that the SnCl_3^- group is a π -acceptor ligand; the empty Sn $d\pi$ orbitals serve as acceptors of Pt(II) electron density in metal-to-ligand charge transfer transitions and such transitions are observed in the $37000\text{--}45000 \text{ cm}^{-1}$ UV region for complex $(\text{NPr}_4)_2[\text{cis-PtCl}_2(\text{SnCl}_3)_2]$ [22]. The low energy absorptions, which exhibit very low molar absorptivities (typical of Laporte forbidden transitions), could be tentatively ascribed to ligand field d–d transitions. The observed blue-shift on going from the chloro complex to the corresponding SnCl_3^- derivative **1** is consistent with the fact that SnCl_3^- is a slightly better σ -donor than Cl^- . The electronic spectrum of the monomeric *bis*(trichlorostannyl)triphenylphosphine derivative $(\text{NBu}_4)[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{Cl}_5)(\text{PPh}_3)]$ **5** with maxima at 234, 279, 307 and 322 nm (see Fig. 3) differs considerably from that of its precursor $(\text{NBu}_4)[\text{trans-Pt}(\text{C}_6\text{Cl}_5)\text{Cl}_2(\text{PPh}_3)]$ (maxima 233 and 263 nm, see Table 3) in exhibiting two additional low energy absorptions at 307 nm ($\epsilon \approx 17400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 322 nm ($\epsilon \approx 16500 \text{ dm}^3 \text{ mol}^{-1} \text{ L}^{-1}$) suggesting significant participation of the SnCl_3^- orbitals in these latter electronic transitions. These intense low energy (>300 nm) bands

are tentatively ascribed to intraligand (IL) transitions of the SnCl_3^- ligand. Assignment to $\text{Pt(II)} \rightarrow (d\pi) \text{ SnCl}_3^-$ MLCT transitions is not favored since such metal-to-ligand transitions are observed as commented above at shorter wavelengths in $(\text{NPr}_4)_2[\text{cis-PtCl}_2(\text{SnCl}_3)_2]$ [22]. The related pentafluorophenyl derivative $(\text{NBu}_4)[\text{trans-Pt}(\text{SnCl}_3)_2(\text{C}_6\text{F}_5)(\text{PPh}_3)]$ **4**, in addition to two high energy bands at 235 and 265 nm, shows one relatively intense ($\epsilon \approx 900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) low energy feature at 324 nm but its assignment is less certain. The high energy bands in both complexes **4** and **5** are tentatively assigned to both intraligand C_6X_5 and MLCT $\text{Pt}(d) \rightarrow \pi^*(\text{PPh}_3)$ transitions; It is now recognized that for π back bonding the P–R antibonding σ orbitals are utilized [24]. The absorption spectrum of the binuclear derivative $(\text{NBu}_4)_2[\text{Pt}_2(\mu\text{-Cl})_2(\text{C}_6\text{Cl}_5)_2(\text{SnCl}_3)_2]$ (**7**) displays only bands at 234 ($69900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 275 ($33090 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 320 nm ($\epsilon \approx 3350 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) probably due to intraligand transitions, whereas for its corresponding precursor $(\text{NBu}_4)_2[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{C}_6\text{Cl}_5)_2]$ (see Table 3) one additional absorption of low intensity ($530 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) is also observed at low energy (411 nm) which is probably ligand field in nature.

The luminescence behavior of **1**, **4**, **5** and **7** in glassy CH_2Cl_2 solutions at 77 K has been also examined (Table 3). In solution, complex **4** is non-emissive at room temperature, while for the remaining complexes the emission is extremely weak. The low temperature spectrum of **4** in CH_2Cl_2 revealed a broad and Gaussian-shaped band with a maximum at 584 nm upon excitation at 380 nm. When the emission is monitored at 580 nm,

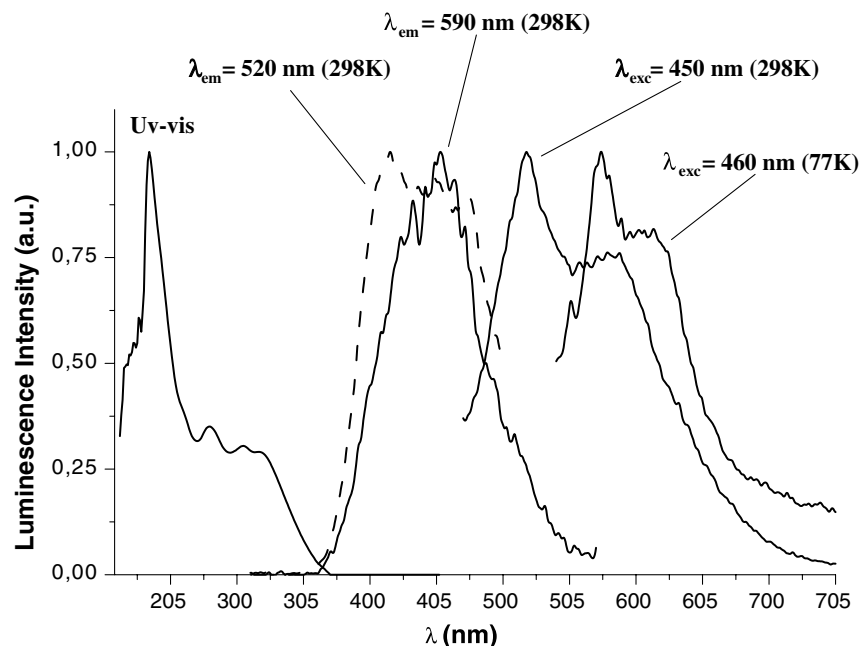


Fig. 3. UV-vis, emission and excitation spectra of complexes **5** in CH_2Cl_2 (77 K and 298 K).

the excitation spectrum exhibits a pronounced maximum at 356 nm. The large Stokes shift and the lack of luminescence at room temperature suggests that the emission originates from a low-lying predominantly spin-forbidden ligand field excited state, though excited states of mixed ligand field (d–d) and MLCT Pt(d)– π^* (PPh₃ or d π SnCl₃[–]) parentage cannot be excluded [24]. The related pentachlorophenyl derivative (NBu₄)[*trans*-Pt(SnCl₃)₂(C₆Cl₅)(PPh₃)] (**5**) differs by emitting weakly in fluid solutions at room temperature, and also by exhibiting an emission profile with two features (λ_{max} 519 and 588 nm at room temperature). At low temperature (77 K), the two bands seem to be distinctly red shifted giving one overall structured emission profile with a maximum at 574 nm and a shoulder at 615 nm (see Fig. 3). By monitoring the emission at λ_{max} 574 nm, two clear and pronounced excitation maxima (429 and 460 nm) with a shoulder at 475 nm are observed at 77 and, as is shown in Fig. 3 the excitation spectrum at room temperature is dependent on the monitored emission energy. It is also remarkable that these excitation maxima do not match with the absorption maxima. The behavior of this complex could be tentatively attributed to a multistate excited manifold. Upon excitation at $\lambda < 400$ nm the emission spectrum of the complex (NBu₄)₂[*trans*-Pt(SnCl₃)₂(C₆F₅)₂] (**1**) in CH₂Cl₂ (77 K) also exhibits (Fig. 4) two different features at 515 and 580 nm and a shoulder at 594 nm, which are related to two excitation maxima at 325 and 399 nm. To assist in the assignment of these features, the emission spectrum of the precursor (NBu₄)₂[*trans*-PtCl₂(C₆F₅)₂] was also investigated in glassy CH₂Cl₂ solution (Table 3). Upon excitation at $\lambda = 345$ nm, this complex displays a structureless emission centered at 580 nm, but on excitation at shorter wavelengths (300 nm) an additional, structured, weak high energy emission is also observed (369 and 425 nm). We tentatively assign the low energy emission to excited states that are ligand field in nature

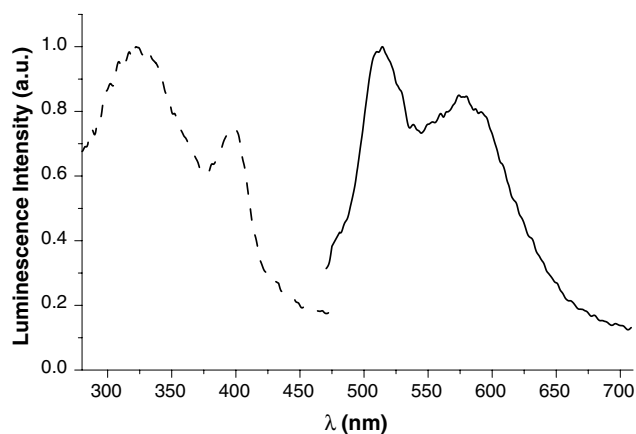


Fig. 4. Emission and excitation spectra of complex **1** in frozen solution (77 K) in CH₂Cl₂.

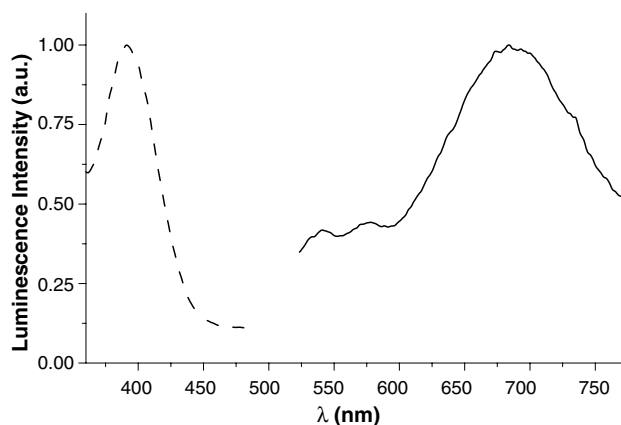


Fig. 5. Excitation at λ_{em} 420 nm (---) and emission λ_{exc} 360 nm (—) for complex **7** in frozen solution (77 K) in CH₂Cl₂.

and the weak high energy emission to excited states located in the C₆F₅ ligands. In complex **1**, the emissions at 515 and 580 nm are probably due to spin-forbidden excited states of mixed ligand-field (d–d) and MLCT (Pt(d) → d π SnCl₃[–]) parentage. As can be observed in Fig. 5, the binuclear derivative (NBu₄)₂[Pt(μ -Cl)₂(C₆Cl₅)₂(SnCl₃)₂] (**7**), in glassy CH₂Cl₂ solution, displays, upon excitation at 400 nm, a broad and Gaussian shape low energy emission centered at 690 nm. A similar emission but slightly blue-shifted is seen in the corresponding chloride precursor (NBu₄)₂[Pt(μ -Cl)₂Cl₂(C₆Cl₅)₂] which exhibits a band at 626 nm related to two excitation maxima at 463 and 354 nm. These emissions are also tentatively assigned to spin-forbidden ligand field excited states.

4. Supporting information

Crystallographic data (excluding structure factors) for the structure analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC numbers 185835 and 185836 for compounds **1** and **6**, respectively. Copies of this information may be obtained 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>) and are available upon request.

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