



# Synthesis and characterization of new dimethylplatinum(IV) complexes with *o*-(diphenylphosphino)thioanisole and its chalcogenide derivatives as ligands. Crystal structure of *trans*-[Me<sub>2</sub>PtBr<sub>2</sub>{*o*-Ph<sub>2</sub>P(S)C<sub>6</sub>H<sub>4</sub>SMe–S,S'}]

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## Abstract

The compound *o*-(diphenylphosphino)thioanisole can be oxidized by S or Se in benzene leading to the derivatives Ph<sub>2</sub>P(E)C<sub>6</sub>H<sub>4</sub>SMe [EPSMe; E = S (1), Se (2)]. These compounds act as bidentate chelate ligands in reactions with the platinum(IV) complex [Me<sub>2</sub>PtBr<sub>2</sub>]<sub>n</sub> to form *trans* and *cis* isomers of the general formula [Me<sub>2</sub>PtBr<sub>2</sub>(L<sub>2</sub>)] [L<sub>2</sub> = SPSMe (3, 4); SePSMe (5, 6)]. The reaction of the complex [Me<sub>2</sub>PtBr<sub>2</sub>]<sub>n</sub> with the starting ligand Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>SMe (PSMe) led to a reductive elimination affording the neutral complex [PtBr<sub>2</sub>(PSMe)] (7). The structure of the complex [Me<sub>2</sub>PtBr<sub>2</sub>{*o*-Ph<sub>2</sub>P(S)C<sub>6</sub>H<sub>4</sub>SMe}] was established by X-ray crystallography. The platinum atom has a distorted octahedral coordination and it is bonded to two methyl carbons, two bromide atoms and two sulfur atoms of the (*o*-diphenylphosphinesulfide)thioanisole bidentate ligand. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Platinum; Phosphino–thioether complexes; Dimethylplatinum(IV) complexes; Reductive elimination reaction; Dichalcogenide complexes

## 1. Introduction

A large number of neutral and cationic trimethylplatinum(IV) complexes have been prepared from the starting tetranuclear complex [{Me<sub>3</sub>PtI}<sub>4</sub>]. In particular, complexes containing phosphines and pyridines have attracted special attention because some of them undergo a reductive elimination reaction with the formation of platinum(II) complexes and ethane [1]. This type of reaction occurs in dialkylplatinum(IV) derivatives containing phosphines as ligands [1d,2]. However, the synthesis of dimethylplatinum(IV) complexes has been scarce, mainly due to the difficulty in preparing the precursor compound [Me<sub>2</sub>PtBr<sub>2</sub>]<sub>n</sub> [3]. Some examples of the reported dimethylplatinum(IV) compounds derived from this precursor are of the [Me<sub>2</sub>PtBr<sub>2</sub>L<sub>2</sub>] type, where

L = glycinate [4–6], glyphosate [7], aspartate [8] and iminodiacetate [9]. In addition, neutral dimethylplatinum(IV) complexes have been synthesized through an oxidative addition reaction of dimethylplatinum(II) complexes containing bidentate N-donor ligands [10–15].

Thioether ligands have been widely studied as coordinated species in organometallic platinum(IV) compounds. Studies on these types of ligands are quite ancient and, generally, they have been focalized on their fluxional property. In particular, there has been much interest in the inversion of the pyramidal environment about the sulfur atom [16–18]. On the other hand, phosphine–thioether ligands can be coordinated to a metallic center as monodentate P-donor or bidentate chelate P,S-donor ligands, behavior which is an essential condition for the generation of potential catalytic active systems [19,20]. One of the most used phosphine–thioether ligands is the *o*-(diphenylphosphino)-

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thioanisole, which usually acts as a bidentate chelate ligand and has been studied mainly in demethylation or methyl transfer reactions from the methylthioether groups [21–23].

In this paper we report the synthesis and characterization of sulfur and selenium derivatives of *o*-(diphenylphosphino)thioanisole, EPSMe (E = S, Se), and the *trans* and *cis* dimethylplatinum(IV) complexes formed from these ligands. A reductive elimination reaction was observed in the reaction of  $[\text{Me}_2\text{PtBr}_2\text{-(THF)}_x]$  with *o*-(diphenylphosphino)thioanisole. The structure of the complex  $[\text{Me}_2\text{PtBr}_2\{o\text{-Ph}_2\text{P(S)C}_6\text{H}_4\text{-SMe}\}]$ , determined by single-crystal X-ray diffraction, is also reported.

## 2. Experimental

### 2.1. Materials and physical measurements

All reactions were carried out by Schlenk techniques under a dry nitrogen atmosphere. Reagent grade solvents were dried, distilled and stored under a nitrogen atmosphere. The starting complexes  $[\text{Me}_3\text{PtI}]_4$  [24],  $[\text{Me}_2\text{PtBr}_2]_n$  [25] and the ligand *o*-(diphenylphosphino)thioanisole [26] were synthesized according to the literature procedures.

Elemental analyses were carried out with a Perkin–Elmer 240C microanalyzer. IR spectra were recorded in a Bruker IFS-25 spectrophotometer using KBr pellets.  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded in a Bruker AC-200P spectrometer. Chemical shifts are reported in parts per million relative to  $\text{Me}_4\text{Si}$  ( $^1\text{H}$ ) and 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}\{^1\text{H}\}$ , positive shifts downfield) as internal and external standards, respectively.

### 2.2. Synthesis of the ligands

#### 2.2.1. *o*- $\text{Ph}_2\text{P(E)C}_6\text{H}_4\text{SMe}$ [E = S (**1**), Se (**2**)]

To a solution of *o*-(diphenylphosphino)thioanisole (1.5 g; 4.4 mmol) in benzene (150  $\text{cm}^3$ ), an excess amount of the element E [4.8 mmol; E = S (0.156 g); Se (0.385 g)] was added. The resulting mixture was stirred under reflux for 2 h. The solution obtained was concentrated to a small volume and the compounds precipitated as pale-yellow solids by the addition of *n*-hexane. The ligands were filtered, washed with carbon disulfide and diethyl ether, and dried in vacuum. **1**: Yield 1.24 g (75%). Found: C, 67.0; H, 3.4; S, 18.3. *Anal.* Calc. for  $\text{C}_{19}\text{H}_{17}\text{PS}_2$ : C, 67.0; H, 3.9; S, 18.8%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.32 (s, 3H, SMe).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  40.6 (s). **2**: Yield 1.88 g (99%). Found: C, 59.1; H, 3.8; S, 8.1. *Anal.* Calc. for  $\text{C}_{19}\text{H}_{17}\text{PSSe}$ : C, 58.9; H, 3.4; S, 18.3%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.33 (s, 3H, SMe).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  31.1 [t,  $^1J(\text{PSe}) = 730$  Hz].

### 2.3. Synthesis of the complexes

#### 2.3.1. *trans* and *cis*- $[\text{Me}_2\text{PtBr}_2(\text{L}_2)]$ [ $\text{L}_2 = \text{SPSMe}$ (**3**), **4**]; $\text{SePSMe}$ (**5**, **6**)]

To a solution of the complex  $[\text{Me}_2\text{PtBr}_2]_n$  (100 mg; 0.260 mmol) in methanol (30  $\text{cm}^3$ ), a stoichiometric amount of the corresponding bidentate ligand (SPSMe, 88.5 mg; SePSMe, 100.6 mg), dissolved in chloroform (10  $\text{cm}^3$ ), was added. The mixture was stirred under reflux for 3 h and the solution obtained was evaporated to dryness at reduced pressure. The solid residue was dissolved in the minimal volume of dichloromethane and chromatographed on silicagel. The *trans*-isomer was isolated using dichloromethane as the eluent while the *cis*-isomer was isolated by elution with acetone. The solutions obtained were concentrated to a small volume and the complexes precipitated by the addition of diethyl ether or *n*-hexane. The solids were filtered, washed with diethyl ether and dried in vacuum. **3**: Yield 54 mg (29%). Found: C, 34.4; H, 3.4; S, 8.5. *Anal.* Calc. for  $\text{C}_{21}\text{H}_{23}\text{Br}_2\text{PPtS}_2$ : C, 34.8; H, 3.2; S, 8.8%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.99 [s, 3H,  $^2J(\text{PtH}) = 72.0$  Hz, Pt–Me (*trans* to SMe)], 2.38 [s, 3H,  $^2J(\text{PtH}) = 73.5$  Hz, Pt–Me (*trans* to  $\text{SPh}_2$ )], 2.57 [s, 3H, SMe,  $^3J(\text{PtH}) = 10.9$  Hz].  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  36.2 [s,  $^2J(\text{PtP}) = 43.7$  Hz]. **4**: Yield 49 mg (26%). Found: C, 34.5; H, 3.3; S, 8.4. *Anal.* Calc. for  $\text{C}_{21}\text{H}_{23}\text{Br}_2\text{PPtS}_2$ : C, 34.8; H, 3.2; S, 8.8%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.64 [s, 3H,  $^2J(\text{PtH}) = 72.5$  Hz, Pt–Me (*trans* to Br)], 1.24 [s, 3H,  $^2J(\text{PtH}) = 72.4$  Hz, Pt–Me (*trans* to SMe)], 2.57 [s, 3H, SMe,  $^3J(\text{PtH}) = 11.6$  Hz].  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  35.6 [s,  $^2J(\text{PtP}) = 46.2$  Hz]. **5**: Yield 61 mg (30%). Found: C, 32.9; H, 3.1; S, 3.9. *Anal.* Calc. for  $\text{C}_{21}\text{H}_{23}\text{Br}_2\text{PPtSSe}$ : C, 32.7; H, 3.0; S, 4.2%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.01 [s, 3H,  $^2J(\text{PtH}) = 71.0$  Hz, Pt–Me (*trans* to SMe)], 2.32 [s, 3H,  $^2J(\text{PtH}) = 73.3$  Hz, Pt–Me (*trans* to  $\text{SePh}_2$ )], 2.58 [s, 3H, SMe,  $^3J(\text{PtH}) = 11.0$  Hz].  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  23.0 [s,  $^2J(\text{PtP}) = 44.0$  Hz,  $^1J(\text{PSe}) = 628$  Hz]. **6**: Yield 74 mg (37%). Found: C, 32.5; H, 2.8; S, 4.0. *Anal.* Calc. for  $\text{C}_{21}\text{H}_{23}\text{Br}_2\text{PPtSSe}$ : C, 32.7; H, 3.0; S, 4.2%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.65 [s, 3H,  $^2J(\text{PtH}) = 72.8$  Hz, Pt–Me (*trans* to Br)], 1.26 [s, 3H,  $^2J(\text{PtH}) = 71.6$  Hz, Pt–Me (*trans* to SMe)], 2.57 [s, 3H, SMe,  $^3J(\text{PtH}) = 11.5$  Hz].  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  21.9 [s,  $^2J(\text{PtP}) = 46.0$  Hz,  $^1J(\text{PSe}) = 630$  Hz].

#### 2.3.2. $[\text{PtBr}_2(\text{PSMe})]$ (**7**)

The complex was prepared by the two following methods. (i) To a solution of the complex  $[\text{Me}_2\text{PtBr}_2]_n$  (100 mg; 0.260 mmol), in a mixture of methanol–chloroform (30–10  $\text{cm}^3$ ), a stoichiometric amount of the PSMe (80 mg, 0.26 mmol) was added. The mixture was stirred under reflux for 3 h. The solution obtained was evaporated to dryness at reduced pressure and the solid residue extracted with dichloromethane. The complex, precipitated as a yellow solid by the addition of diethyl

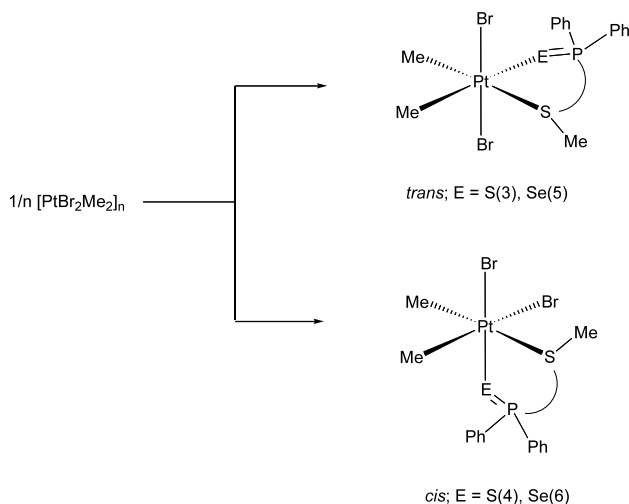
ether, was filtered, washed with diethyl ether or *n*-hexane, and dried in vacuum. Yield 90 mg (52%). Found: C, 34.5; H, 2.3; S, 4.7. *Anal.* Calc. for  $C_{19}H_{17}Br_2PtS$ : C, 34.4; H, 2.6; S, 4.8%. (ii) To a solution of the complex  $K_2PtBr_4$  (200 mg; 0.337 mmol) in methanol (30 cm<sup>3</sup>) a stoichiometric amount of PSMes (199.8 mg; 0.337 mmol) in chloroform (10 cm<sup>3</sup>) was added. The mixture was stirred for 1 h, the solution evaporated to

Table 1  
Crystal data and structure refinement parameters for complex 3

Empirical formula	$C_{21}H_{23}Br_2PtS_2$
Formula weight	725.39
Temperature (K)	293(2)
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	8.764(1)
<i>b</i> (Å)	11.301(2)
<i>c</i> (Å)	12.669(3)
$\alpha$ (°)	74.76(2)
$\beta$ (°)	85.12(2)
$\gamma$ (°)	83.17(2)
<i>V</i> (Å <sup>3</sup> )	1200.1(4)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	2.007
Absorption coefficient (mm <sup>-1</sup> )	9.420
Crystal size (mm)	0.44 × 0.26 × 0.14
$\theta$ Range (°)	1.67–27.56
Index ranges	$0 \leq h \leq 11, -14 \leq k \leq 14, -16 \leq l \leq 16$
Reflections collected	5876
Independent reflections	5518 [ <i>R</i> <sub>int</sub> = 0.0173]
Parameters refined	244
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.035
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.039, <i>wR</i> <sub>2</sub> = 0.099
<i>R</i> indices (all data) <sup>b</sup>	<i>R</i> <sub>1</sub> = 0.051, <i>wR</i> <sub>2</sub> = 0.104
Largest difference peak and hole (e Å <sup>-3</sup> )	1.341 and -1.901

$$^a R_1(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2(F^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum \{w(F_o^2)^2\}]^{1/2}; \text{ where } w = (1 / [\sigma^2(F_o^2) + 0.0678P]) \text{ and } P = (F_o^2 + 2F_c^2) / 3.$$



Scheme 1.

dryness at reduced pressure and the solid residue extracted with chloroform. The addition of *n*-hexane led to the precipitation of a solid, which was filtered, washed with diethyl ether and dried in vacuum. Yield 202 mg (90%). Found: C, 34.3; H, 2.4; S, 4.6%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.15 [s, 3H, <sup>3</sup>*J*(PtH) = 45.0 Hz, SMe]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 37.2 [s, <sup>1</sup>*J*(PtP) = 3498 Hz].

#### 2.4. X-ray crystal structure determination for *trans*-[Me<sub>2</sub>PtBr<sub>2</sub>(SPSMe)] (3)

Suitable crystals for X-ray diffraction determination were obtained from a slow diffusion of diethyl ether into a solution of complex 3 in dichloromethane. Intensity data were collected at room temperature (r.t.) on a Siemens R3m/V diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) by the θ–2θ scan method. Semiempirical corrections based on ψ scans were applied for absorption. The structure was solved by direct methods and refined on *F*<sup>2</sup> by full-matrix least-squares calculations with SHELXL-97 [27]. A riding model was applied to the H atoms, and placed at calculated positions with C–H = 0.96 Å. Relevant crystal data and refinement parameters are summarized in Table 1.

### 3. Results and discussion

The bidentate ligand *o*-(diphenylphosphino)-thioanisole (*o*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>SMe, PSMes) reacts with elemental sulfur or selenium by the oxidation of the phosphorus atom to give the corresponding chalcogenide derivatives of the type Ph<sub>2</sub>P(E)C<sub>6</sub>H<sub>4</sub>SMe (EPSMe, E = S or Se) (1).



These compounds were characterized by elemental analyses and NMR (<sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H}) spectroscopy. The <sup>1</sup>H NMR spectra of ligands 1 and 2 exhibited a singlet resonance at δ 2.32 and 2.33 ppm, respectively, assigned to the methylthioether group [28]. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the ligands 1 and 2 showed a singlet signal at δ 40.6 and 31.1 ppm [<sup>1</sup>*J*(PSe) = 730 Hz], respectively.

The reaction of the bidentate ligands EPSMe (E = S or Se) with the solvated platinum(IV) complex [Me<sub>2</sub>PtBr<sub>2</sub>(MeOH)<sub>x</sub>] (formed by dissolving the polymer [Me<sub>2</sub>PtBr<sub>2</sub>]<sub>n</sub> in methanol), in a mixture of methanol–chloroform at room temperature, afforded the formation of *trans*- and *cis*-isomer complexes of the general formula [Me<sub>2</sub>PtBr<sub>2</sub>(EPSMe)] (E = S or Se) (Scheme 1).

Table 2  
NMR<sup>a</sup> chemical shifts ( $\delta$ ) and coupling constants (Hz) for the platinum(IV) complexes (3–6)

Complex	$\delta_{\text{H}}$					$\delta_{\text{P}}$	
	Pt–Me	$^2J(\text{Pt–H})$	<i>trans</i> Atom	Sme	$^3J(\text{Pt–H})$	P	$^2J(\text{Pt–P})$
<b>3</b>	1.99(s)	72.0	SMe	2.57(s)	10.9	36.2(s)	44
	2.38(s)	73.5	S				
<b>4</b>	0.64(s)	72.5	Br	2.57(s)	11.6	35.6(s)	46
	1.24(s)	72.4	SMe				
<b>5<sup>b</sup></b>	2.01(s)	71.0	SMe	2.58(s)	11.0	23.0(s)	44
	2.32(s)	73.3	Se				
<b>6<sup>c</sup></b>	0.65(s)	72.8	Br	2.57(s)	11.5	21.0(s)	46
	1.26(s)	71.6	SMe				

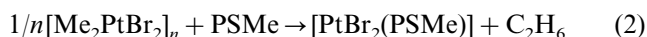
<sup>a</sup> Measured in CDCl<sub>3</sub> at room temperature. Chemical shifts relative to SiMe<sub>4</sub> and 85% H<sub>3</sub>PO<sub>4</sub> as standards. All complexes show multiplets in the region  $\delta$  6.8–7.9 ppm corresponding to the phenyl groups of the ligands.

<sup>b</sup>  $^1J(\text{PSe}) = 628$  Hz.

<sup>c</sup>  $^1J(\text{PSe}) = 630$  Hz.

Relevant NMR chemical shifts and coupling constants are summarized in Table 2. The  $^1\text{H}$  NMR spectra of complexes 3–6 show, in the methyl–platinum region, two singlet resonances in a 1:1 intensity ratio with the corresponding satellites due to  $^{195}\text{Pt–H}$  coupling. The methyl–platinum resonances at the *trans* position of the SMe, Br or EP groups are assigned on the basis of the  $^2J(\text{Pt–H})$  coupling values [15,29–31]. In addition, all the  $^1\text{H}$  NMR spectra show a singlet resonance at  $\delta$  2.57 ppm [ $^3J(\text{Pt–H}) = 10.9$ –11.5 Hz] attributed to the methylthioether protons. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of complexes 3–6 show a singlet signal in the range  $\delta$  21.0–36.2 ppm with a coupling of  $^2J(\text{PtP}) = 44$ –46 Hz [32,33]. The spectra of complexes 5 and 6 present, moreover, the corresponding  $^1J(\text{P–Se})$  coupling with values of 628 and 630 Hz, respectively [34].

Interestingly, the treatment of complex  $[\text{Me}_2\text{PtBr}_2]_n$  with the precursor ligand (PSMe) in methanol solution at room temperature led to a reductive elimination reaction yielding the neutral complex  $[\text{PtBr}_2(\text{PSMe})]$  (7) and ethane (Eq. (2)).



As expected, complex 7 can be prepared alternatively by the reaction of the salt  $\text{K}_2\text{PtCl}_4$  with the precursor ligand (PSMe) in a mixture of methanol–chloroform at room temperature. Its  $^1\text{H}$  NMR spectrum shows a singlet signal at  $\delta$  3.15 [ $^3J(\text{PtH}) = 45$  Hz] assigned to the protons of the methyl–thioether group. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum exhibited a singlet resonance at  $\delta$  37.2 [ $^1J(\text{PtP}) = 3498$  Hz]. The magnitude of the coupling constant is typical of a phosphorus atom *trans* to a bromide ligand in platinum(II) complexes [35].

### 3.1. Crystal structure of complex

#### $[\text{Me}_2\text{PtBr}_2\{\text{Ph}_2\text{P}(\text{S})\text{C}_6\text{H}_4\text{SMe}\}]$ (3)

A perspective ORTEP view of the structure of complex

3 with atom labeling is shown in Fig. 1. Relevant bond lengths and bond angles are given in Table 3. The platinum atom shows a distorted octahedral coordination and is bonded to two methyl carbons, two bromide atoms and two-sulfur atoms of the (*o*-diphenylphosphinesulfide)thioanisole bidentate ligand.

The Pt–C(Me) bond lengths [Pt–C(1) = 2.106(5) and Pt–C(2) = 2.065(6) Å] are similar to those found in the related dimethyl–platinum(IV) complexes  $[\text{Me}_2\text{PtI}_2\{(\text{pz})_2(\text{thi})\text{CH}\}]$  [Pt–C: 2.070(7) and 2.097(9) Å] [11] and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-pz})_3\text{PtMe}_3]$  [2.079(9) and 2.059(12) Å] [36]. The Pt–Br bond lengths [2.447(1) and 2.460(1) Å] are comparable to the terminal Pt–Br distances in complexes  $[\text{Pt}(\text{en})\text{Br}_4]$  [2.480 Å] [37],  $[(\eta^5\text{-C}_5\text{Me}_5)\text{PtMe}_2\text{Br}]$  [2.498(2) Å] [38] and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{PtMeBr}_2]$  [2.462(2) and 2.496(2) Å] [38], but shorter than the bridging Pt–Br distance in  $[(\text{Me}_3\text{PtBr})_4] \cdot 0.5$  toluene [2.677(3) Å] [39].

The Pt–S(2) distance [2.515(2) Å] is slightly larger than Pt–S(2) [2.501(2) Å] implying a greater strength of the Pt–C(1) bond compared with Pt–C(2). According of the *trans* influence arguments, the Pt–C(1) will be larger

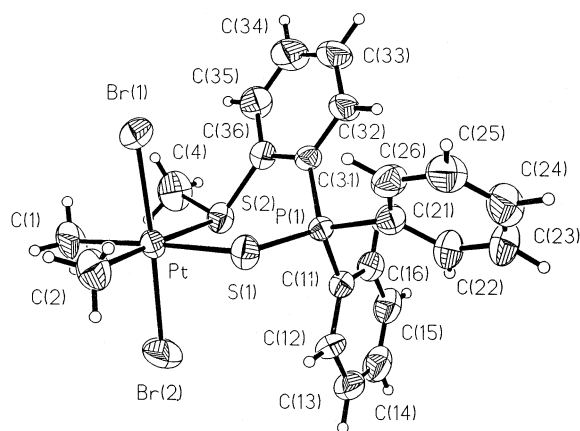


Fig. 1. ORTEP view of the structure of the complex cation 3 with atom numbering scheme (thermal ellipsoids at 50% probability level).

Table 3  
Selected bond lengths (Å) and bond angles (°) for complex 3

<i>Bond lengths</i>			
Pt–C(1)	2.106(5)	Pt–C(2)	2.065(6)
Pt–Br(1)	2.4474(9)	Pt–Br(2)	2.4597(10)
Pt–S(1)	2.501(2)	Pt–S(2)	2.515(2)
S(1)–P(1)	1.986(2)	S(2)–C(36)	1.780(6)
S(2)–C(4)	1.801(6)	P(1)–C(21)	1.793(5)
P(1)–C(11)	1.797(6)	P(1)–C(31)	1.818(5)
<i>Bond angles</i>			
C(1)–Pt–C(2)	86.6(3)	C(2)–Pt–Br(1)	90.1(2)
C(1)–Pt–Br(1)	88.0(2)	C(2)–Pt–Br(2)	89.1(2)
C(1)–Pt–Br(2)	88.7(2)	Br(1)–Pt–Br(2)	176.65(3)
C(2)–Pt–S(1)	85.6(2)	C(1)–Pt–S(1)	172.2(2)
Br(1)–Pt–S(1)	92.09(5)	Br(2)–Pt–S(1)	91.08(5)
C(2)–Pt–S(2)	177.4(2)	C(1)–Pt–S(2)	95.8(2)
Br(1)–Pt–S(2)	91.06(4)	Br(2)–Pt–S(2)	89.91(5)
S(1)–Pt–S(2)	91.94(5)	P(1)–S(1)–Pt	107.28(7)
C(36)–S(2)–C(4)	103.1(3)	C(36)–S(2)–Pt	106.4(2)
C(4)–S(2)–Pt	107.4(3)	C(21)–P(1)–C(11)	106.2(3)
C(21)–P(1)–C(31)	108.9(2)	C(11)–P(1)–C(31)	106.7(2)
C(21)–P(1)–S(1)	107.4(2)	C(11)–P(1)–S(1)	115.0(2)
C(31)–P(1)–S(1)	112.3(2)		

than Pt–C(2), as in fact occurs in this case, and this is reflected in the NMR coupling constants, where the value for the Me(C1) group [ $^2J(\text{PtH}) = 72.0$  Hz] is smaller than that for the Me(C2) group [ $^2J(\text{PtH}) = 73.5$  Hz]. The Pt–S(1) and Pt–S(2) distances are larger than the distances found in the related Pt(IV) and Ir(III) complexes containing thioether as ligands [ $\text{Me}_3\text{PtI}-(\text{MeS})_4(\text{CH}_2)_2$ ] [average: 2.433(7) Å] [40] and [ $(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}\{\eta^2\text{-Ph}_2\text{PCH}_2\text{SPh}\}\text{BF}_4 \cdot \text{Me}_2\text{CO}$ ] [2.402(3) Å] [41], or in complexes with tertiary phosphinesulfide derivatives as ligands, such as  $[\text{PtCl}(\text{PEt}_3)\{\text{Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Bu}_2\}]\text{ClO}_4$  [2.282(2) Å] [32] and [ $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\{\text{P}(\text{O})(\text{OMe})_2\}\{\eta^2\text{-(SPPH}_2)_2\text{CH}_2\}\text{BF}_4$ ] [average: 2.398(2) Å] [34a].

#### 4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 154567. 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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