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Synthesis and crystal structures of platinum (II) complexes with phosphine sulfide: *cis*-Dichloro[dimethylsulfoxide](triphenylphosphine sulfide) platinum (II) and (-)-*cis*-dichloro[(S)-methyl-p-tolylsulfoxide]-(triphenylphosphine sulfide) platinum (II)

Alexej N. Skvortsov ^{a,*}, Alexander N. Reznikov ^b, Dimitry A. de Vekki ^b, Adam I. Stash ^c, Vitaly K. Belsky ^c, Vitaly N. Spevak ^b, Nickolaj K. Skvortsov ^b

^a Department of Biophysics, St. Petersburg State Polytechnical University, Polytechnicheskaja st. 29, St. Petersburg 195251, Russia
^b St. Petersburg State Institute of Technology (Technical University), Moskowsky pr. 26, St. Petersburg 190013, Russia
^c X-ray Laboratory, L. Ya. Karpov Institute of Physical Chemistry, Vorontsovo Pole St. 10, Moscow 103064, Russia

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Abstract

The addition of triphenylphosphine sulfide (Ph₃PS) to bis-sulfoxide platinum (II) complexes [Pt(Me₂SO)₂Cl₂] and (–)-[Pt(Me-*p*-Tol-SO)₂Cl₂] yields mixed ligand complexes [Pt(Ph₃PS)(Me₂SO)Cl₂] (1) and (–)-[Pt(Ph₃PS)(Me-*p*-TolSO)Cl₂] (2), which are effective catalysts for hydrosilylation reaction. These mixed-ligand complexes were obtained in crystal state and analyzed by X-ray diffraction, ¹H, ³¹P and ¹⁹⁵Pt NMR; **2** was also studied by circular dichroism spectroscopy. Both complexes exist in CDCl₃ solution as a dynamic equilibrium of two geometric isomers with an approximate 1:10 ratio, but only *cis*-isomer is obtained on crystallization. The X-ray structures of the complexes have classical geometry, and phosphine sulfide and sulfoxides are coordinated via sulfur. The new structural data for simple platinum–Ph₃PS coordination bond, unaffected by chelation or bridging, were evaluated. The lengths of this bond are 2.300(4) Å in **1** and 2.305(3) Å in **2**, respectively. PtSP angle equals 105.7(2)° in **1** and 104.05(13)° in **2**, the PtSP plane is almost perpendicular to the coordination plane. The static *trans*-influence of Ph₃PS is estimated to be strong and close to that of *S*-coordinated Me₂SO. The complex **2** exhibits strong circular dichroism at a wavelength below 330 nm, caused both by inherent Me-*p*-TolSO stereogenic center and induced asymmetry of Ph₃PS.

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1. Introduction

The present study is dedicated to synthesis and characterization of neutral platinum (II) complexes with triphenylphosphine sulfide (Ph₃PS) and sulfoxide ligands. The first compound contains dimethylsulfoxide (Me₂SO), while the second contains chiral methyl-*p*-tolylsulfoxide (Me-*p*-TolSO, 1-methylsulfinyl-4-methylbenzene) as a ligand. The complexes were synthesized from respective bis-sulfoxide complexes and Ph_3PS and were subject to spectroscopic and structural studies. The newly prepared complexes arouse particular interest, because they display high catalytic activity in hydrosilylation reactions. Sulfur-containing ligands are rarely used for the preparation of transition metal-based homogeneous catalysts as they are believed to reduce the catalytic activity up to full suppression of

^{*} Corresponding author. Tel.: +7 812 552 79 64; fax: +7 812 552 79 61. *E-mail addresses:* skvor@mail.cytspb.rssi.ru, skvor@phmf.spbstu.ru (A.N. Skvortsov).

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catalytically active centers. However, our studies of Pt(II) complexes with sulfoxide ligands as potent catalysts in hydrosilylation of olefins [1-3], vinylsiloxanes [4], ketones [5–7] and aromatic azomethins [8] have shown that these complexes can exhibit high catalytic activity. Some of the sulfoxide Pt(II) complexes could act as photoinduced catalysts; hence efficient catalysis is triggered by UV-irradiation [9]. The test of the new phosphine sulfide sulfoxide platinum (II) complexes as catalysts in the reaction of 1-heptene with methyldichlorosilane and in the reaction of acetophenone with diphenylsilane [5] showed that under comparable conditions these compounds exhibit even higher catalytic activity than the symmetric bis-sulfoxide complexes. E.g., in the reaction of acetophenone with diphenylsilane at 70 °C and catalyst concentration 0.3 mM, 50% conversion was reached in 19 min for phosphine sulfide sulfoxide catalyst versus 80 min for bis-sulfoxide catalyst. The final conversions in these systems exceeded 80% [5]. In the reaction of selected aromatic azomethins with methyldichlorosilane, catalyzed by phosphine sulfide sulfoxide platinum (II) complexes, the desired product content exceeded 99% [8]. It has been shown previously, that the stereogenic center of Me-p-TolSO is retained upon coordination to platinum, but its absolute configuration is inverted [10–15]. So the chiral sulfoxide phosphine sulfide complex attracts interest for two reasons. On the first hand, it may be a potential catalyst for asymmetric hydrosilylation. On the other hand, Me-p-TolSO proved to be a very useful chiral label for studying ligand exchange at concentrations, relevant to catalytic systems, by circular dichroism (CD) spectroscopy and optical rotation measurements [16-18].

The structure of the complexes under study also has general implication. In contrast to phosphines and phosphine oxides, the information on coordination compounds, containing phosphine sulfide ligands is relatively scarce and discrete. The atom of sulfur incorporated in phosphine sulfide molecules R_3PS is in low oxidation state. All sulfur compounds in lower oxidation states are known to be efficient donors for the majority of heavier metals. In Pearson's terms they are soft bases, and this favors the formation of stable donor-acceptor compounds with soft acids. It is not surprising, then, that phosphine sulfides form stable coordination complexes with heavier metals: gold [19-21], platinum [22,23], iridium [24], palladium [25–28], rhodium [29–32,24], ruthenium [33], niobium [34,35], molybdenum [36] and indium [37,38]. The structural data were also reported for complexes with copper [39-44], silver [45-48], aluminium [49], and diiodine [50-52]. Some related structural data also exist on organometallic compounds of manganese, palladium, platinum, and iridium, containing coordinated phosphine sulfide. In all reported cases, coordination of phosphine sulfide was found to occur via sulfur atom, with phosphorus-sulfurmetal angle ranging from 91° [42] to 117° [29]. Yet, the majority of the structures, studied by X-ray analysis up to date, contain phosphine sulfide as a functional group of a chelating ligand, or belong to organometallic compounds. The mode of coordination in such structures is masked by chelation effects, and influence of metal–carbon bonds, so the information on ligand properties of «simple» phosphine sulfides is even more scant. The present study gives representative example of triphenylphosphine sulfide structure as a ligand in classical platinum (II) coordination compounds. The presence of two different S-donor ligands in the same complex allows us to compare their binding properties. As the structural data for sulfoxide mixed ligand platinum complexes are numerous and well characterized [11-15,50-58], the relative static *trans-* and *cis*effects of phosphine sulfide may be estimated.

2. Experimental

2.1. Materials and physical measurements

2.1.1. The reagents

Acetone, dimethyl sulfoxide, chloroform, and methylene chloride were obtained from "Merck" and used without purification. Triphenylphosphine was obtained from "Merck" and purified by recrystallization from 4:1 methanol–chloroform mixture in argon atmosphere. Triphenylphosphine sulfide (Ph₃PS) was synthesized from triphenylphosphine and equimolar amount of elemental sulfur by standard procedure. The chiral sulfoxide (+)-(R)-Me-p-TolSO was synthesized by the method described in the literature [59]. The enantiomeric purity of the obtained compound exceeded 96% as judged by optical rotation.

2.1.2. ${}^{1}H$, ${}^{31}P$ { ${}^{1}H$ }, and ${}^{195}Pt$ { ${}^{1}H$ } NMR spectra

The ¹H, ³¹P{¹H}, and ¹⁹⁵Pt{¹H} NMR spectra were recorded on a Bruker AC-200 instrument operating at 200.13, 81.01, and 43.03 MHz. Selected ¹H and ¹⁹⁵Pt{¹H} spectra were recorded on a Bruker AM-500 spectrometer, operating at 500.13 and 107.51 MHz, respectively. The spectra were recorded from CDCl₃ saturated solutions in standard 5 mm NMR tubes. Typical parameters for ¹H experiments: 40° pulses, 8 K data points; resolution, 0.61 Hz; 50-100 scans. No internal standard was used for ¹H spectra, the ¹H chemical shifts in ppm from TMS were calculated from deuterium lock frequency. Typical parameters for ³¹P NMR spectra: 8 K data points; resolution 1.0 Hz; 1000–1500 scans. Typical parameters for ¹⁹⁵Pt experiments: 32 K data points; resolution 0.5-3.8 Hz; 1200–1500 scans. Chemical shifts are reported in ppm relative to 85% H₃PO₄ (³¹P{¹H}) and aqueous Na₂PtCl₆ $(^{195}Pt{^1H})$ as respective external standards. The 200.13 MHz ¹H NMR signals of protons coupled to ¹⁹⁵Pt and distorted by effects of ¹⁹⁵Pt chemical shift anisotropy were analyzed by accurate numeric method, that yields correct value of $J_{^{1}H^{-195}Pt}$ [60]. E.s.d.s for calculated coupling constants are given in parentheses.

2.1.3. The UV–Vis properties

Absorption spectra were obtained on scanning spectrophotometer Specord-M40 (Karl Zeiss). Optical rotations $[\alpha]_{D}^{20}$ were measured with polarimeter 241MC (Perkin– Elmer), using 10 cm cells. Circular dichroism (CD) spectra were recorded with dichrograph Mark-V (Jobin-Yvon). (+)-D-10-camphorsulfonic acid was used as calibration standard for CD measurements. Crystals of complex {Pt(Ph₃PS)[(*S*)-Me-*p*-TolSO]Cl₂} from the same preparation as the crystal used for X-ray studies were dissolved in methylene chloride in concentration 5×10^{-4} M. The round fused silica quartz cell with optical pathlengths 1 cm (in wavelength region 350–700 nm) and 0.1 cm (220–350 nm region) were used. Absorbance of solvent and optical activity of cell walls were accounted for. The quantitative spectra of solutions were recorded from 3 independently prepared samples and the magnitudes of ε and $\Delta \varepsilon$ presented below are median values.

2.2. Synthesis of complexes

2.2.1. Synthesis of 1: $[Pt(Ph_3PS)(Me_2SO)Cl_2]$

A sample of platinum dimethyl sulfoxide complex cis- $[Pt(Me_2SO)_2Cl_2]$ (0.11 g, 0.26 mmol), synthesized from K₂PtCl₄ and 2 equivalents of Me₂SO, was placed in a round-bottomed flask with a reflux condenser with 10 ml of acetone. A calculated amount of Ph₃PS (0.156 g, 0.53 mmol) was added, and the mixture was heated at reflux to the full dissolution of the precipitate and the formation of yellow solution. After removal of the solvent, we obtained 0.226 g of a yellow residue. The residue was redissolved in small volume of 1:1 mixture of acetone and methylene chloride. When the solvent partially evaporated, yellow crystals formed. Yield 0.12 g, 70% initial platinum. The product is soluble in chloroform, methylene chloride, less soluble in acetone, insoluble in ethanol and hexane. Melting point 164–165 °C. Anal. Calc. for C₂₀H₂₁Cl₂OPPtS₂: C, 37.62; H, 3.32; Cl, 10.33; Pt 28.43; S 9.35. Found: C, 37.34; H, 3.21; Cl, 10.33; Pt 28.45; S 9.38%. The NMR spectra of CDCl₃ solution of 1 display the presence of two distinct species 1a and 1b with 11:1–13:1 molar ratio. Both of them are consistent with the proposed compound structure. Some of the peaks of minor species 1b are overlapped with stronger 1a resonances. So some quantities could not be calculated for **1b**, and only reliable values are listed. ¹H NMR δ , ppm: **1a** 3.09 t (6H, CH₃), ${}^{3}J_{H-Pt}$ 20.7(2) Hz; 7.92 m (6H, H^{α}[Ph₃PS]), ${}^{3}J_{H-P}$ 13.6 Hz, 7.53 m (6H, H^{β}[Ph₃PS]), ${}^{4}J_{H-P}$ 3.5 Hz; 7.63 m (3H, H^{γ}[Ph₃PS]), ${}^{3}J_{\alpha-\beta}$ 7.9 Hz, ${}^{3}J_{\beta-\gamma}$ 7.8 Hz, ${}^{4}J_{\alpha-\gamma}$ 1.2 Hz; **1b** 3.24 t (6H, CH₃), ${}^{3}J_{H-Pt}$ 22.6(8) Hz; 7.86 m (6H, H^{α}[Ph₃PS]), ³J_{H-P} 13.8 Hz; 7.59 m (3H, H^{γ}[Ph₃PS]), ³J_{$\alpha-\beta$} 7.6 Hz, ³J_{$\beta-\gamma$} 8 Hz. ³¹P{¹H} δ , ppm: **1a** 40.2 t, ²J_{Pt-P} 116(1). ¹⁹⁵Pt{¹H} δ , ppm: **1a** -3326 d, ²J_{Pt-P} 116(2) Hz; **1b** -3232 d, ${}^{2}J_{Pt-P}$ 86(5) Hz.

2.2.2. Synthesis of **2**: (-)-{*Pt*(*Ph*₃*PS*)[(*S*)-*Me*-*p*-*To*|*SO*]*Cl*₂}

Chiral platinum methyl *p*-tolyl sulfoxide complex (-)-*cis*-{Pt[(*S*)-Me-*p*-TolSO]₂Cl₂]} was synthesized from K₂PtCl₄ and (+)-(*R*)-Me-*p*-TolSO as described earlier [13], purified by recrystallization from acetone and checked for purity by optical polarimetry: $[\alpha]_D^{20}$ in CH₂Cl₂ –220°. A sample of [Pt(Me-p-TolSO)₂Cl₂] (0.05 g, 0.087 mmol) was placed in a flask with a reflux condenser and a mixer. Two equivalents of Ph₃PS (0.051 g, 0.17 mmol) and 4 ml of methylene chloride were added. The system was heated at reflux and mixed for 5 h, the initial reagents dissolved completely. The formed solution was cooled and mixed with hexane. A yellow precipitate was formed. The precipitate was collected on Shott filter and dried. Then the precipitate was redissolved in a small volume of 1:1 mixture of acetone and methylene chloride. When the solvent partially evaporated, yellow-green crystals formed. Yield 0.05 g, 80% initial platinum. The product is soluble in chloroform, methylene chloride, less soluble in acetone, insoluble in hexane. Melting point 204 °C. $[\alpha]_D^{20}$ in CH₂Cl₂ –121°. Anal. Calc. for C₂₆H₂₅Cl₂OPPtS₂: C, 43.70; H, 3.52; Cl 10.63; Pt 29.25; S 4.81. Found: C, 43.66; H, 3.47, Cl 10.60; Pt 29.27; S 4.85%. The NMR spectra of CDCl₃ solution of 2 also show the presence of two distinct species 2a and 2b with 10:1–12:1 molar ratio. ¹H NMR δ , ppm: **2a** 2.43 s (3H, CH₃); 3.21 t (3H, SCH₃), ³J_{H-Pt} 20.6(3) Hz; 7.91 d (2H, H^{α} [Tol]), 7.28 d (2H, H^{β} [Tol]), ³J 8.1 Hz; 7.86 m (6H, $H^{\alpha}[Ph_{3}PS]), {}^{3}J_{H-P}$ 13.7 Hz, 7.50 m (6H, $H^{\beta}[Ph_{3}PS]), {}^{4}J_{H-P}$ 3.5 Hz; 7.61 m (3H, H^{γ}[Ph₃PS]), ³ $J_{\alpha-\beta}$ 7.8 Hz, ³ $J_{\beta-\gamma}$ 7.9 Hz, ⁴ $J_{\alpha-\gamma}$ 1.3 Hz; **2b** 2.41 s (3H, CH₃); 3.26 t (3H, SCH₃), ${}^{3}J_{H-Pt}$ 21.5(5) Hz; 7.9 d (2H, H^{α}[Tol]); 7.83 m (6H, H^{α}[Ph₃PS]), ³J_{H-P} 14 Hz, 7.4 m (6H, H^{β}[Ph₃PS]), ⁴ $J_{\text{H-P}}$ 3.6 Hz; 7.59 m (3H, H^{γ}[Ph₃PS]), ³ $J_{\alpha-\beta}$ 7.9 Hz, ³ $J_{\beta-\gamma}$ 7.9 Hz. ¹⁹⁵Pt{¹H} δ , ppm: **2a** -3342 d, ² $J_{\text{Pt-P}}$ 115(3) Hz. The meaningful regions of 500 MHz ¹H NMR spectrum of 2 in CDCl₃ are presented as supplementary material, Fig. S1 and S2.

2.3. X-ray crystallography on the compounds 1 and 2

Crystals of complexes, suitable for X-ray analysis were obtained from the solutions of the compounds in a 1:1 vol. mixture of acetone and methylene chloride by evaporating the solvent gradually.

2.3.1. X-ray crystal structure determination for cis-[Pt(Ph₃PS)(Me₂SO)Cl₂]

A yellow crystal of $1, 0.50 \times 0.12 \times 0.12$ mm, was used for analysis. The X-ray diffraction data were obtained with Enraf-Nonius CAD4 diffractometer with Nb β -filtered Mo K_{α} source (0.71073 Å). The $\theta/2\theta$ scan with $2\theta_{max} = 50^{\circ}$ was used. The intensities of three selected reflections, each monitored for 60 min showed a decay less than 0.2% during the experiment. The temperature of the crystals was (293 ± 2) K. The compound crystallizes in $P2_1nb$ orthorhombic space group. The unit cell parameters are: b = 15.256(3),V =a = 9.090(2),c = 16.596(3) Å, 2301.5(8) Å³, Z = 4, $\rho_{\text{calc}} = 1.843 \text{ g cm}^{-3}$, F(000) = 1232. The data were collected in h k l range 0–10, 0–18, 0–19; 1487 reflections with $I > 2\sigma(I)$ were measured. X-ray absorption, $\mu = 65.88 \text{ cm}^{-1}$, was accounted for. Non-hydrogen atoms were refined anisotropically by full-matrix leastsquares method on *F*. The hydrogen atoms were added at arbitrary positions and refined isotropically. Final R = 0.032, $R_w = 0.080$ for all observed reflections.

2.3.2. X-ray crystal structure determination for (-)-cis-{Pt(Ph₃PS)[(S)-Me-p-TolSO]Cl₂}

A yellow-green crystal of **2**, $0.45 \times 0.25 \times 0.23$ mm, was analyzed with a Syntex P-1 diffractometer with Nb β-filtered Mo K_{α} source (0.71073 Å). The $\theta/2\theta$ scan with $2\theta_{max} = 50^{\circ}$ was used. The intensities of three selected reflections showed a decay less than 0.3% during the whole experiment. The temperature of the crystals was (293 ± 2) K. Complex 2 crystallizes in $P2_12_12_1$ orthorhombic space group. The unit cell parameters are: a = 9.817(2), b = 14.555(3), c = 18.769(4) Å, V = 2681.8(10) Å³, Z = 4, $\rho_{\text{calc}} = 1.770 \text{ g cm}^{-3}, F(000) = 1392.$ The data were collected in h k l range 0-11, 0-16, 0-20; 2280 reflections with $I \ge 2\sigma(I)$ were measured. X-ray absorption, $\mu =$ 56.64 cm^{-1} , was accounted for. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares method on F. The position of hydrogen atoms was determined from difference syntheses and refined isotropically. Final R = 0.032, $R_w = 0.080$ for all observed reflections. Absolute structure was determined by Flack method, the calculated absolute structure factor is -0.010(13). Calculation of geometry properties and illustrations was made with program PLATON [61].

3. Results and discussion

3.1. Synthesis of complexes

The mixed-ligand sulfoxide phosphine sulfide platinum (II) complexes were synthesized from bis-sulfoxide complexes and phosphine sulfide. The reaction occurs by the displacement of one of sulfoxide ligands in the initial complex. Our attempts to synthesize bis-phosphine sulfide platinum complexes failed. No substitution of the second sulfoxide ligand occurs even if phosphine sulfide is taken in over 5-fold excess. The example of ¹H NMR spectrum of the fresh product of the reaction of *cis*-[Pt(Me₂SO)₂Cl₂] with 5-fold excess of Ph₃PS is provided as supplementary material, Fig. S3 and S4. Only the two mixed ligand complexes are formed. The initial bissulfoxide complex is totally consumed in the reaction. We do not propose any precise pathway of the reaction, as the mixed ligand product is subject to fast *cis-trans* isomerization in CDCl₃ (discussed in detail below).

3.2. X-ray structures

The X-ray analysis of the obtained crystals definitely shows that both complexes have *cis*-geometry in crystal state. The bond lengths and angles for the structures are listed in Table 1. The molecular structure, and atom numbering scheme for *cis*-[Pt(Ph₃PS)(Me₂SO)Cl₂] (1) are presented in Fig. 1. The molecular structure, absolute configuration, and atom numbering scheme for (-)- $\{Pt(Ph_3PS)[(S)-Me-p-TolSO]Cl_2\}$ (2) are presented in Fig. 2.

The platinum atom in both structures is in the square planar environment. The sulfoxides and phosphine sulfides in both structures are coordinated via sulfur. The coordination planes of **1** and **2** are almost undistorted square planar, deviation of atoms from coordination plane is less than 0.05 Å. The three angles of coordination plane in **1** differ from right angles by less than 0.5° , so the coordination plane of **1** has almost classical geometry. In slightly less regular structure of **2** the coordination plane is twisted by about 5° .

The lengths of platinum-ligand bonds indirectly indicate the mutual influence of ligands. The platinum-chloride bonds are rather long, as was expected for complexes with sulfoxide, exhibiting very strong static trans- and cis-influences. The two chloride ligands in complex 1 have comparable Pt–Cl distances. In 2 the chloride ligand Cl^1 trans to Ph₃PS is even more withdrawn from the coordination center, while the $Pt-Cl^2$ bond *trans* to sulfoxide is longer in 1 than in 2. The latter fact is consistent with stronger transinfluence of Me₂SO as compared to Me-p-TolSO. It may be concluded that *trans*-influence of Ph₃PS is stronger than that of Me-p-TolSO and comparable to that of Me₂SO, which has almost the strongest *trans*-influence in platinum complexes. The static cis-influence of Ph₃PS could also be estimated. It was shown that in [Pt(Me₂SO)LCl₂] series of complexes, Pt–S distance $(d_{Pt-S(O)}, A)$ increase in the following order of ligands L: NH₃ (2.186), H₂O (2.194), 2methylpyridine (2.200), pyridine and pyrimidine (2.209), benzonitrile (2.215), MeCN (2.220), C₂H₄ (2.223), Me₂SO (2.234, 2.248) [54–57]. The values of $d_{Pt-S(O)}$ for the complex 1 are close to those in the complex with benzonitrile. So we conclude that static *cis*-influence of Ph₃PS is of the same level than that of nitriles.

The two structures show the same positioning of Ph₃PS with respect to coordination plane and sulfoxide ligand, though sulfoxide and rings positions, and packing are different. The RMS fit of coordination planes of the two structures, displaying this fact, is presented in Fig. 3. Thus, we believe that the mode of Ph₃PS coordination is governed only by specific properties of poorly studied triphenylphosphine sulfide-platinum bond. In 1 and 2 Ph₃PS coordinates in such way that the plane, containing PtSP angle is almost perpendicular to coordination plane (the interfacial angle is $89.3(2)^\circ$ for 1 and $89.78(14)^\circ$ for 2). Such position was not observed in platinum complexes, studied earlier [22,23,62-64], probably because PS group in those compounds was a part of the chelating ligand. The PtS¹P angle itself is $105.7(2)^\circ$ in 1 and $104.05(13)^\circ$ in 2. This angle is rather variable in Ph₃PS complexes with different electrophiles, ranging from 102.5° in untypical copper(I) complex [39] to 116–117° in niobium(V) complexes [34,35]. Yet, for most complexes with platinum metals and gold it ranges from 103° to 106°. The difference in the coordination properties of the sulfur atoms in sulfoxides and Ph₃PS is

Table 1 Selected structural parameters for *cis*-[Pt(Ph₃PS)(Me₂SO)Cl₂] and *cis*-[Pt(Ph₃PS)(Me-*p*-TolSO)Cl₂] complexes

	cis-[Pt(Ph ₃ PS) (Me ₂ SO)Cl ₂]	<i>cis</i> -{Pt(Ph ₃ PS) [(S)-Me- <i>p</i> -TolSO]Cl ₂ }	Ph ₃ PS (data from Ref. [66])	(R)-Me- <i>p</i> -TolSO (data from Ref. [67])
Bonds (Å)				
Pt-Cl(1)	2.316(5)	2.322(3)		
Pt-Cl(2)	2.315(3)	2.311(3)		
Pt-S(1)	2.300(4)	2.305(3)		
Pt-S(2)	2.214(3)	2.216(3)		
S(1)–P	2.026(6)	2.018(4)	1.9529(8)	
S(2)–O	1.452(17)	1.470(10)		1.493(10)
S(2) - C(19)	1.778(18)	1.76(2)		1.797(7)
S(2)-C(20)	1.74(3)	1.791(11)		1.796(13)
P-C(1)	1.811(14)	1.788(10)	1.8220(16)	
P-C(7)	1.822(17)	1.788(8)	1.8115(17)	
P-C(13)	1.815(15)	1.799(10)	1.8188(16)	
Angles (°)				
Cl(1)– Pt – $Cl(2)$	89.48(15)	89.22(11)		
Cl(1)– Pt – $S(1)$	177.63(16)	176.17(11)		
Cl(1)-Pt-S(2)	89.75(16)	92.69(11)		
Cl(2)-Pt-S(1)	89.56(15)	89.14(9)		
Cl(2)-Pt-S(2)	176.02(15)	177.37(10)		
S(1)-Pt-S(2)	91.06(16)	89.07(10)		
Pt-S(1)-P	105.7(2)	104.05(13)		
Pt-S(2)-O	118.3(6)	117.0(4)		
Pt-S(2)-C(19)	110.0(6)	111.3(7)		
Pt-S(2)-C(20)	109.0(8)	111.5(4)		
O-S(2)-C(19)	107.4(9)	107.9(8)		106.5(3)
O-S(2)-C(20)	108.7(11)	106.2(5)		105.5(3)
C(19)-S(2)-C(20)	102.3(10)	101.7(8)		97.6(3)
S(1)–P–C(1)	113.9(6)	116.4(3)	113.19(7)	
S(1)-P-C(7)	106.0(6)	106.0(3)	113.02(7)	
S(1)-P-C(13)	114.4(6)	113.6(5)	111.97(7)	
C(1) - P - C(7)	110.1(7)	109.8(5)	103.61(8)	
C(1)–P–C(13)	105.5(7)	105.2(5)	107.38(8)	
C(7)–P–C(13)	106.8(7)	105.5(4)	107.11(8)	
Dihedral angles (°)				
Pt-S(1)-P-C(13)	-85.8(6)	-92.3(4)		
S(2)-Pt-S(1)-P	-90.7(2)	-90.22(14)		
S(1)-Pt-S(2)-O	4.9(8)	27.5(5)		
O-S(2)-C(20)-C(21)		26.1(12)	5.0(15)	

Estimated standard deviations are given in parenthesis.

reflected in the lengths of Pt-S bonds. These are markedly different, which is indicative of stronger bond between Pt(II) and sulfoxides as compared to phosphine sulfide and suggests lower donor power of the latter. The lengths of platinum-triphenylphosphine sulfide bonds are 2.300(4) and 2.305(3) Å in 1 and 2, respectively. It is longer than analogous bond trans to chloride in dichloro-(1-(diphenylphosphino)-8-(diphenylthiophosphoryl)naphthalene-P,S)-platinum(II) (2.286 Å) [22] but it is significantly shorter than the bond *trans* to phosphine sulfide in *trans*bis(2-(diphenylthiophosphinyl)-N-(diphenylphosphino)aniline-P,S)-platinum (2.343 Å) [23]. In platinum organic compounds [62,63] and complex with phosphine sulfide as a bridging ligand [64] the analogous bond is much longer (>2.4 Å). The evaluated data for platinum-Ph₃PS bond may be compared to other Ph₃PS bonds with different electrophiles, known up to date. If we exclude organometallic compounds, the length of Ph₃PS-electrophile bond increases in the following order Au(I) \leq Cu(I) \leq Al(III) \approx

Pt(II) \leq [Fe₂I₄] \ll Mo(V) \leq Nb(V) \leq I₂. The P–S–A (A – acceptor atom) angle increases in the order Pt(II) \approx Au(I) \approx I₂ \leq [Fe₂I₄] \approx Al(III) \approx Cu(I) \leq Mo(V) \leq Nb(V). (The comparison is based on 3 complexes of Au(I) [19–21], 2 complexes of Pt(II) studied in the present work, 3 Nb(V) complexes [34,35], 3 diiodine adducts [50–52], and unique examples for the other metals: Cu [44], Al [49], Mo [36], and Fe [65]).

The coordinated phosphine sulfide ligand undergoes structural changes, as compared to the free molecule [66] (see Table 1). The P–S bond becomes longer, while P–C bonds shorten. The phosphorus atom becomes more tetrahedral on coordination: the S–P–C angles decrease, while C–P–C angles become wider. The same trends are observed for Ph₃PS coordinated to various nucleophiles. They are caused by withdraw of electrons from sulfur and weakening of the P–S bond. These structural changes are more profound in Me₂SO complex. Formally Ph₃PS has C_3v symmetry. But in fact local threefold symmetry of phos-



Fig. 1. Crystal structure of *cis*-[Pt(Ph₃PS)(Me₂SO)Cl₂] (50% probability ellipsoids).



Fig. 2. Crystal structure and absolute configuration of (-)-*cis*-{Pt(Ph₃PS)[(*S*)-Me-*p*-TolSO]Cl₂} (50% probability ellipsoids).

phorus in most of the known structures of free and coordinated Ph_3PS is not realized, distinct single plane of symmetry could be observed instead. Therefore, the two lone pairs at sulfur are not equivalent. In the studied structures, the positioning of the plane of Ph_3PS approximate symmetry with respect to coordination plane is given by the torsion angle $Pt-S^1-P-C^{13}$, which is close to 90°. We suggest that the rotation of unhindered Ph_3PS with respect to P-S bond in 1 and 2 is caused by selective coordination through a certain sulfur lone pair. The structural characteristics of aromatic rings in both structures are fairly typical (taking standard deviations into account). None of the rings is coplanar with P-S bond.



Fig. 3. RMS fit of coordination planes in crystal structures of *cis*- $[Pt(Ph_3PS)(Me_2SO)Cl_2]$ (bold line) and (-)-*cis*- $\{Pt(Ph_3PS)[(S)-Me_{-}P-Tol-SO]Cl_2\}$ (thin line). RMS difference 0.073 Å for atoms in coordination plane.

The sulfoxide ligands in both structures are classically Scoordinated. The relative position of substituents at the sulfur atom in chiral sulfoxide in 2 is retained, so that absolute configuration of Me-p-TolSO is inverted. This fact was previously observed in a number of structures of platinum complexes with Me-p-TolSO [11–15], and may be considered as a general rule. The platinum-sulfoxide bond lengths, structural changes in sulfoxide ligands (contraction of S-O and S-C bonds and flattening of "sulfoxide pyramid") and position of S-O bond of Me₂SO in the coordination plane of 1 are in accordance with general trends for S-coordinated sulfoxides [53]. Our previous X-ray studies [13–15] show that S–O bond of Me-p-TolSO also tends to enter coordination plane, but this tendency is not so pronounced. The negatively charged oxygen atom of sulfoxide in both structures points away from the *cis*-chloride ligand, like in most of the neutral sulfoxide platinum complexes with *cis*-geometry [53–56]. Though partial conjugation between the aromatic system and the electrons of the S-O bond makes the coplanar position of this bond more favorable [68], the S-O bond is not coplanar to tolyl ring in the structure of 2. This described conjugation is of interest, because it significantly affects chiroptic properties of Me-p-TolSO and its complexes. As we noticed in our previous work [15], the conjugation of S–O bond with tolyl ring could be easily overridden by crystal packing requirements and thus it is not necessarily observed in X-ray structures of complexes with Me-p-TolSO.

The packing of complexes shows no peculiar intermolecular contacts or prominent stacking interaction.

3.3. NMR and isomerization of complexes

The discussed complexes are interesting from the viewpoint of their catalytic activity in hydrosilylation reactions. According to modern concepts of catalytic action of platinum complexes in hydrosilylation reaction, the ligands are dynamically exchanged in the catalytic cycle [4,69]. So the isomerization and ligand exchange of the complexes is of particular interest.

The CDCl₃ solutions of both studied sulfoxide phosphine sulfide complexes invariably contain two species, a major form and a minor one, as evidenced by NMR spectra. According to ¹H NMR, both species are fully consistent with the proposed structure of mixed-ligand complexes (Fig. S1-S4). The difference in chemical shifts and Pt-H coupling constants of the two species, calculated from 200 MHz spectra by accurate method [60], is significant (Fig. S5). So these species are not conformational isomers. The observed proportion of isomers is about 10:1 and varies slightly in different preparations. On crystallization only cis-isomer is isolated, as confirmed by X-ray analysis. Nevertheless, even the fresh CDCl₃ solution of the crystals contains both isomers; its NMR spectrum does not change notably with time. Thereby, we suggest that the solutions of complexes 1 and 2 are true equilibrium mixtures of *cis*and *trans*-isomers. The rates of isomerization of the complexes should be relatively high, as it should be faster than crystallization-dissolution process. Yet the isomerization rates are slow on NMR scale: there is no detectable broadening of resonance peaks by chemical exchange.

As the equilibrium settles fast as compared to dissolution, we have by now no trustworthy method to assign major and minor species to cis- and trans-isomers. The general trends that describe the influence of geometry on chemical shifts and coupling constants give controversial results. It is well known, that sulfoxide is a strong π -acceptor. Phosphine sulfide is also supposed to be a good π acceptor, based on its electronic structure and strong static trans-influence. This fact has a direct relation to chemical shifts. It is generally considered, that the back donation of π -electrons to π -acceptor causes the decrease in overall deshielding of the ligand protons. On the contrary the coordination center is slightly deshielded by π -bonding. When two π -acceptors are in *trans*-position to each other, they have to share the same orbitals of coordination center. So the combined action of two π -bonds on chemical shifts is weaker in trans-complexes. Hence, Pt(II) complexes with *cis*-position of two π -acceptors exhibit larger (less negative) ¹⁹⁵Pt chemical shifts and smaller ¹H chemical shifts than the respective trans-isomers. The SCH₃ group of S-coordinated sulfoxides is one of known exceptions: it is affected both by σ -donor and π -acceptor items and its ¹H chemical shift is larger in *cis*-isomers [15,55–58].

Another important trend states that neutral *cis*-complexes of platinum (II) display stronger ¹⁹⁵Pt-ligand spin coupling, than *trans*-complexes. For sulfoxide complexes the most indicative is ${}^{3}J_{Pt-H}$ coupling constant of SCH₃ group. In all the neutral sulfoxide complexes, studied by us previously [11–15], as well as in other sulfoxide complexes [55–58], this rule is obeyed: typical value of ${}^{3}J_{Pt-H}$ is 20–21 Hz for *trans*-isomers and 22–24 Hz for *cis*-isomers.

In major species 1a and 2a the SCH₃ group protons are less deshielded upon coordination (Figs. S1, S3, S5), while

all the other protons are more deshielded than in the corresponding minor species **1b** and **2b** (the difference in ¹H chemical shifts of **1a** and **1b** is larger, than in **2a** and **2b**, it is consistent with stronger π -acceptor properties of Me₂SO as compared to Me-*p*-TolSO). The ¹⁹⁵Pt chemical shift of **1b** is larger than in **1a**. The ³J_{H-Pt} coupling constants are significantly larger in minor species as compared to major species. According to the trends listed above, such properties suggest that the major species is a *trans*- isomer, while the minor is a *cis*- one. The fact, that only minor *cis*isomer is obtained on crystallization, should not be very annoying. The complex could gradually isomerize towards less soluble form, while the latter crystallizes out.

But there is still one controversial fact concerning $^{195}\text{Pt}-^{31}\text{P}$ coupling constants for complex **1**. These constants should be significantly larger in *cis*-isomer, just like $^{3}J_{\text{Pt-H}}$ constants. The major species **1a** displays significantly larger $(116 \pm 2 \text{ Hz})$ $^{3}J_{\text{Pt-P}}$ constant than **1b** $(86 \pm 5 \text{ Hz})$, which is contrary to the assumption that **1a** is *trans*-[Pt(Ph_3PS)(Me_2SO)Cl_2]. The data for **2** are unfortunately absent: we could not detect the $^{195}\text{Pt}\{^{1}\text{H}\}$ signal of **2b** because of its low concentration.

Our attempts to prepare systems, enriched with minor isomer, were by now unsuccessful. Attempts to substitute the solvent for more polar one (water or alcohol), caused decomposition of complexes. So our assignment of major species in CDCl₃ solution to *trans*-[Pt(Ph₃PS)(RR'SO)Cl₂] should be considered tentative.

There are some hints for the mechanism of isomerization from the 500 MHz ¹H NMR spectra of **2**. The thorough analysis of the spectrum (Fig. S1) reveals small traces of uncoordinated sulfoxide (δ 2.69, 2.36 ppm) and two species with S-coordinated sulfoxide (δ 3.46, 2.43; 3.54, 2.46 ppm). The content of traces is about 1% of the total sulfoxide content. The S-coordinated traces were attributed to *cis*- and *trans*-{Pt[(S)-Me-*p*-TolSO]₂Cl₂} based on the chemical shift values. This fact hints for the dissociation of small amount of free sulfoxide from the complex. The free sulfoxide boosts ligand exchange and aids the isomerization.

3.4. Optical activity of (-)-{ $Pt(Ph_3PS)[(S)$ -Me-p-TolSO]Cl₂}

The strong circular dichroism (CD) of enantiomerically pure Me-*p*-TolSO and complexes that contain Me-*p*-TolSO ligand is caused by stereogenic sulfur center. Generally, asymmetric sulfoxides display two electronic transitions of S–O group that fall in the 200–260 nm region. These bands are very broad and overlap significantly with each other and higher energy transitions, so the UV-spectrum is not very informative. However, in chiral sulfoxides these transitions are optically active and show circular dichroism with opposite sign. This results in a characteristic two-band CD spectrum [15]. Partial conjugation of the electrons of tolyl ring and S–O group makes Me-*p*-TolSO strongly asymmetric [68]. So absorption and CD of its S–O bands become far more intensive, than that of aliphatic sulfoxides [70]. For (+)-Me-*p*-TolSO the CD of the low-energy S–O band is strongly positive (Fig. 4, dotted line).

As noted above, Me-p-TolSO coordinates to platinum (II) via sulfur with the retention of the relative position of substituents at the sulfur atom, and the inversion of absolute configuration. Previously, we studied a series of (-)-{PtL[(S)-Me-p-TolSO]Cl₂}, platinum complexes L = Py, Bu_3P , NH_3 , NH_2Me [15]. We noticed that coordination via sulfur causes the change of sign of CD bands. The usual spectral pattern of CD spectra of such complexes in CH_2Cl_2 solutions displays three distinct regions. A strong negative low-energy S-O CD band with a peak at 240-245 nm is observed in far-UV region. Only a rising slope of its positive high energy counterpart may be observed in CH₂Cl₂. Intermediate negative CD band is located at 270-275 nm. It was attributed to electronic transitions of tolyl ring. Its intensity is sensitive to the nature of non-chiral ligands; it increases if a bulky ligand is present in *cis* to Me-*p*-TolSO. Low energy bands of *d*-*d* transitions stretch to the visible region and respond for the color of the complexes. They are highly dependent on ligand nature and complex geometry [71], but their induced CD is very weak.

The CD spectrum of (-)-*cis*-{Pt(Ph₃PS)[(S)-Me-*p*-Tol-SO]Cl₂} is more complicated than the expected pattern



Fig. 4. The UV and CD spectra of (-)-{Pt(Ph₃PS)[(S)-Me-*p*-TolSO]Cl₂} (solid line) and (+)-Me-*p*-TolSO (dotted line) at 20 °C in CH₂Cl₂.

for $\{PtL[(S)-Me-p-TolSO]Cl_2\}$ complexes (Fig. 4, solid line). The two peaks of opposite sign, corresponding to S-coordinated sulfoxide, are readily recognized in far-UV region. But the CD band at 270 nm is positive and a new negative band is observed at 290 nm. We suggest that such appearance of CD spectrum is caused by ligand-ligand interaction. Chiral Me-p-TolSO behaves as the first type of Moffit classification for optically active chromophores [72]. Both electronic and magnetic transition dipoles of such chromophores have significantly non-zero values. The low-energy electronic transitions of nearby Ph₃PS ligand lie in the same region, as that of the low-energy Me-p-TolSO transition. If dipole-dipole interaction is effective, both transitions should be shifted on energy scale and become exciton-coupled. As one of the initial transitions is optically active, both exciton-coupled transitions become optically active (induced optical activity). Usually such transitions have the opposite sign of CD. We should keep in mind yet, that dipole-dipole interaction and induced optical activity could be averaged toward zero by rotation of interacting chromophores with respect to each other. But configuration of Ph₃PS shown by the crystal structure of 2 almost eliminates the possibility of such averaging. The Ph₃PS ligand is very unlikely to rotate through its coordination bond for steric reasons. The rotation of Me-*p*-TolSO only is not enough for effective averaging. Besides in *cis*-isomer Me-*p*-TolSO rotation is also strongly hindered by Ph₃PS. So we suggest that two peaks of opposite sign at 270 and 290 nm are caused by coupling of optically active Me-p-TolSO transitions to lower energy transition of Ph₃PS.

Adding various nucleophiles to **2** causes ligand substitution and change in circular dichroism. The coupled value of the optical rotation $[\alpha]_D^{20}$ also change, this effect was used by us to monitor reactions in models of catalytic systems. The strongest nucleophiles substitute for chiral sulfoxide. The free (+)-Me-*p*-TolSO, released into solution can be easily and quantitatively identified by its strong positive CD and optical rotation [10,16–18].

4. Conclusion

The phosphine sulfide complexes of platinum (II) can be prepared from bis-sulfoxide complexes and equimolar amount of phosphine sulfide. Yet only mixed ligand complexes are formed even with excess phosphine sulfide. The newly synthesized complexes are potent catalysts in hydrosilylation reaction. Triphenylphosphine sulfide (Ph₃PS) sulfoxide platinum (II) complexes exist as a mixture of rapidly turning *cis*- and *trans*-isomers in chloroform solution, but crystallize out as *cis*-isomer. The equilibrium ratio of isomers in chloroform solution is approximately 1:10. The geometry of major isomer was not established because of NMR data controversies, and this subject needs further investigation. The crystal structures of *cis*-isomers are classical platinum (II) complexes. They give the excellent example of simple coordination of phosphine sulfide to platinum, not affected by chelation. The same position of Ph_3PS is observed in both structures: the PSPt plane is almost perpendicular to coordination plane, and to the plane of approximate symmetry of Ph_3PS ligand. We suggest that such positioning of Ph_3PS is governed by specific properties of triphenylphosphine sulfide–platinum bond. Despite Ph_3PS was found to be much weaker donor, than *S*-coordinated sulfoxide, the structural *trans*-influence of Ph_3PS was estimated to be strong and comparable to that of a sulfoxide. The complex with chiral sulfoxide displays strong chiroptic properties with significant induced optical activity of Ph_3PS ligand. The optical activity can be used to monitor ligand exchange at low concentrations, relevant to catalytic systems.

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Appendix. Supplementary data

Crystallographic data (excluding structure factors) for the structures of complexes **1** and **2** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 241253 and 241252, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 0 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.12.007.

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