

Synthesis, molecular structure, and photoluminescence properties of palladium and platinum complexes containing phosphine sulfide-based SCS pincer ligand

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Abstract

3,5-Bis(diphenylphosphinothioyl)toluene (**1**) was prepared by Pd-catalyzed aryl phosphination of 3,5-dibromotoluene with diphenylphosphine followed by sulfurization with elemental sulfur. Cyclometalation of **1** with K_2MCl_4 ($M = Pd, Pt$) occurred at the C-4 position of the central toluene ring and afforded new pincer complexes (**2**: $M = Pd$, **3**: $M = Pt$). Molecular structures of the complexes were characterized by X-ray diffraction. The platinum complex **3** exhibits strong emission in the glassy frozen state as well as in the solid state.

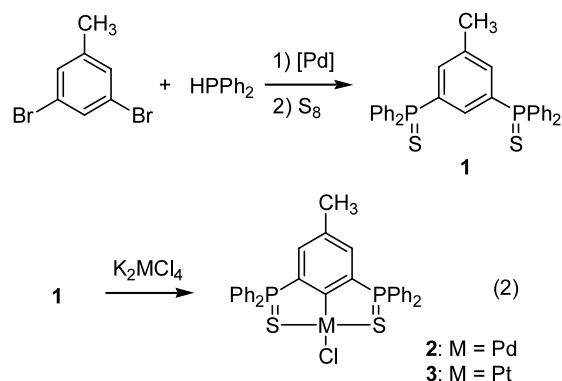
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Keywords: Phosphine sulfide; Pincer ligand; Palladium; Platinum; Photoluminescence

1. Introduction

Pincer ligands play an increasing role in coordination chemistry and catalysis [1]. One of their advantages comes from the possibility to finely tune the reactivity of the metal center by adjusting the nature and the electronic properties of the different pincer ligands. Tridentate cyclometalated platinum(II) complexes have also attracted considerable attention in recent years, mainly because of their interesting photoluminescence properties and their utilization [2]. These have led to the continuous interest that has been devoted to the synthesis of various mixed donor sets incorporating different heteroatoms such as N, P, O, and S. On the other hand, the coordination chemistry of phosphine chalcogenides has been investigated [3], and transition metal complexes containing phosphine sulfide-based tridentate ligands constituted of pyridine and phosphinine have also been recently reported [4]. However, much less attention has been paid to cyclometalation of

aromatic phosphine sulfides, and to our knowledge, there has been no report on phosphine sulfide-based anionic pincer ligands (e.g. $[1,3-(PR_2=S)_2C_6H_3]^-$) and their metal complexes. These ligands also consist of a mixed donor set (η^3-S,C,S -coordination mode); thus, they could be prospective pincer ligands for various transition metals. We report here preparation of the new pincer palladium and platinum complexes. The molecular structures and preliminary photoluminescence properties of the complexes are also described.



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2. Results and discussion

3,5-Bis(diphenylphosphino)toluene was prepared by Pd-catalyzed aryl phosphination of 3,5-dibromotoluene with two equivalents of diphenylphosphine [5]. Sulfurization of the arylenediphosphine with elemental sulfur yielded 3,5-bis(diphenylphosphinothiyl)toluene (**1**) [3,4,5c]. Reaction of **1** with K_2MCl_4 ($M = Pd, Pt$) in acetic acid (AcOH) led to regioselective cyclometalation at the C-4 position of the central toluene ring with Pd(II) and Pt(II), and afforded the corresponding pincer complex ($M(1-H)Cl$: **2**: $M = Pd$, 72%; **3**: $M = Pt$, 89% yield). Since *ortho*-palladation has been shown to be reversible when performed in AcOH [6], these results suggest that the *ortho,ortho*-cyclometalated complexes would be thermodynamically stable. The reaction of **1** with dichlorobis(benzonitrile)palladium ($PdCl_2-(PhCN)_2$) in CH_3CN also yielded **2** (65% yield), whereas **3** was not obtained from the analogous reaction.

In the 1H -NMR spectra of the complexes, the absence of the proton signal assigned to the C-4 position of the central toluene ring and a high-field shift of the proton signal assignable to C-2,6 positions of the toluene ring is observed. The ^{31}P -NMR spectra of the complexes exhibit a down-field shift of the signal assignable to *S*-coordinated phosphine sulfide.

The crystals of **2** and **3** were obtained from a slow diffusion of ethanol into a DMSO solution. The two complexes are isostructural and have the same crystal system and space group. The molecular structure of **2** is shown in Fig. 1, and selected bond lengths, bond angles, and torsion angles for the complexes are given in Table 1. The complexes have a distorted square planar geometry similar to those of the reported pincer palladium and platinum complexes [1,6b,7]. The plane of coordination is somewhat twisted out of the plane of the centered toluene ring. The C–Pd–Cl and S–Pd–S

Table 1

Selected bond lengths (Å), bond angles (°), and torsion angles (°) for complexes **2** and **3**

2: Bond lengths		Bond angles	
Pd(1)–Cl(1)	2.381(4)	Cl(1)–Pd(1)–S(1)	86.88(13)
Pd(1)–S(1)	2.312(4)	Cl(1)–Pd(1)–S(2)	90.30(13)
Pd(1)–S(2)	2.321(4)	S(1)–Pd(1)–S(2)	173.3(1)
Pd(1)–C(1)	2.007(12)	Cl(1)–Pd(1)–C(1)	175.4(3)
S(1)–P(1)	1.995(5)	S(1)–Pd(1)–C(1)	91.5(4)
S(2)–P(2)	2.007(5)	S(2)–Pd(1)–C(1)	91.7(4)
P(1)–C(2)	1.786(13)	Pd(1)–S(1)–P(1)	97.9(2)
P(2)–C(6)	1.766(13)	Pd(1)–S(2)–P(2)	98.8(2)
		S(1)–P(1)–C(2)	107.4(5)
		S(2)–P(2)–C(6)	108.4(5)
Torsion angles			
S(1)–Pd(1)–C(1)–C(2)	14.7(10)		
S(2)–Pd(1)–C(1)–C(6)	4.9(10)		
S(1)–P(1)–C(2)–C(1)	–15.1(11)		
S(2)–P(2)–C(6)–C(1)	–15.8(11)		
3: Bond lengths		Bond angles	
Pt(1)–Cl(1)	2.370(5)	Cl(1)–Pt(1)–S(1)	86.4(2)
Pt(1)–S(1)	2.299(5)	Cl(1)–Pt(1)–S(2)	90.9(2)
Pt(1)–S(2)	2.307(5)	S(1)–Pt(1)–S(2)	174.4(2)
Pt(1)–C(1)	2.02(2)	Cl(1)–Pt(1)–C(1)	175.1(5)
S(1)–P(1)	2.002(7)	S(1)–Pt(1)–C(1)	91.4(5)
S(2)–P(2)	1.996(7)	S(2)–Pt(1)–C(1)	91.7(5)
P(1)–C(2)	1.77(2)	Pt(1)–S(1)–P(1)	97.5(3)
P(2)–C(6)	1.73(3)	Pt(1)–S(2)–P(2)	99.3(3)
		S(1)–P(1)–C(2)	109.8(7)
		S(2)–P(2)–C(6)	105.7(7)
Torsion angles			
S(1)–Pt(1)–C(1)–C(2)	–16.8(15)		
S(2)–Pt(1)–C(1)–C(6)	–4.7(15)		
S(1)–P(1)–C(2)–C(1)	15.6(16)		
S(2)–P(2)–C(6)–C(1)	19.6(18)		

axes are distorted as a consequence of strain of the coordinating plane. The Pd–C, Pd–Cl bond lengths lie in the range of lengths found in related pincer palladium complexes [1,6b,7], while coordination to Pd would

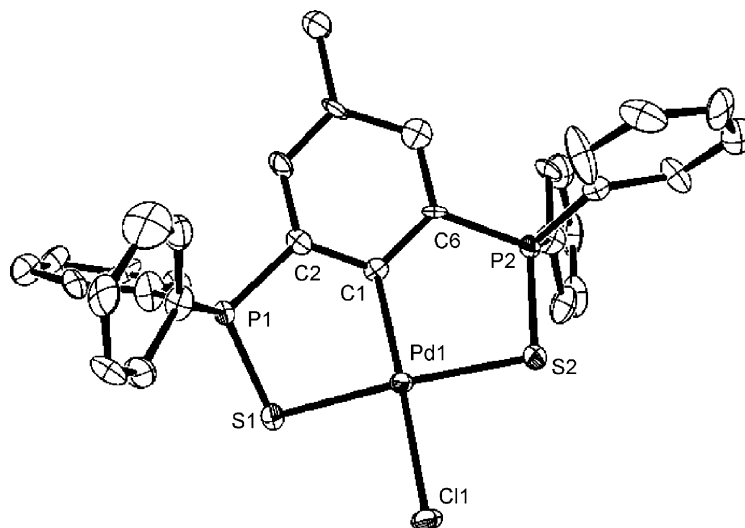


Fig. 1. X-ray crystal structure of **2** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

result in lengthening of the P=S bond length compared with the range of free P=S bond length [3,4,8]. A similar feature was observed with **3**.

The complexes **2** and **3** are not light-emissive in solution at room temperature, whereas photoluminescence was observed in the frozen state. The absorption spectral data and emission data of the complexes are summarized in Table 2. The platinum complex **3** is highly light-emissive even in the solid state at room temperature. Fig. 2 shows emission spectra of **3** in the solid state and in the glassy frozen state. The small difference in energy between the solid state at room temperature and the glassy emission suggests the same electronic origins of the emitting states. Solid state d^8-d^8 and ligand–ligand interactions of the photoluminescent cyclometalated platinum(II) complexes have been investigated [2]. In the present case, however, X-ray diffraction analysis of **3** confirms that the Pt···Pt distance between adjacent complexes is 8.79 Å, indicating that there is no d^8-d^8 interaction, and the large intermolecular plane separation between the two ligand planes (more than 5 Å) would not allow overlap of the π orbitals. We tentatively assigned that the emissive excited state of **3** is related to $^3\text{MLCT}$ formed by intersystem crossing [2]. The stabilized $^3\text{MLCT}$ state seemed to bring about the shift of the emission peak to the longer wavelength. The emission from the triplet state of the metal complex is attracting strong interest in relation to high quantum efficiency in electroluminescence devices.

As described above, new palladium and platinum complexes containing phosphine sulfide-based SCS-pincer ligand have been prepared. The platinum pincer complex exhibits highly emission in the solid state. This procedure should broaden the scope of pincer complexes by changing the structures of ligands and transition metals. Attempts to substitute the chloro ligand with other ligands and to tune their emission properties are being undertaken.

Table 2
Photophysical properties of **2** and **3**

	$\lambda_{\text{max}}^{\text{a}}/\text{nm}$ (ϵ^{b} , $\text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{em}}^{\text{c}}/\text{nm}$	$\phi_{\text{f}}^{\text{d}}$
2	265 (33100), 323 (5500)	580	0.14
3	304 (8900), 345 (3900)	540	0.24

^a Absorption maxima in CH_2Cl_2 at room temperature.

^b Molecular absorption coefficient.

^c Emission maximum in a mixture of CH_2Cl_2 , EtOH, and MeOH matrix at 77 K.

^d Fluorescence quantum yield compared with that of tris(2-phenylpyridine)iridium ($= 0.4 \pm 0.1$) [10].

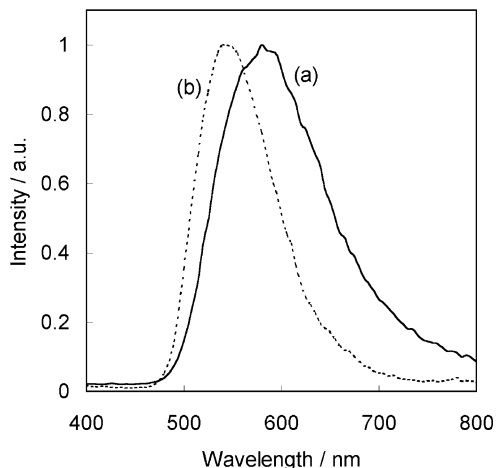


Fig. 2. Emission spectra of **3**: (a) microcrystalline sample at room temperature, (b) in frozen CH_2Cl_2 -MeOH-EtOH matrix (77 K).

3. Experimental

3.1. General procedures

All reactions were carried out under N_2 . AcOH was used as received. $\text{PtCl}_2(\text{PhCN})_2$ was prepared as described previously [9].

3.2. 3,5-Bis(diphenylphosphinothiioyl)toluene (**1**)

A mixture of 3,5-dibromotoluene (1.50 g, 6 mmol) and diphenylphosphine (2.24 g, 12 mmol) was dissolved in DMF (20 ml). Palladium chloride (53 mg, 0.3 mmol) and potassium acetate (1.77 g, 18 mmol) were added to the solution, and the reaction mixture was stirred at 130 °C for 24 h under N_2 . After cooling to room temperature (r.t.), sulfur (480 mg, 15 mmol as elemental sulfur) was added and the reaction mixture was stirred at 120 °C for 4 h under N_2 . After cooling to r.t., an aqueous solution of EDTA-2K (100 ml) and CHCl_3 (200 ml) was added, and the mixture was stirred for 30 min. The organic phase was separated and the solvent was evaporated. The crude product was purified by column chromatography and recrystallization from acetone to give **1** as a white needle (2.21 g, 70% yield).

$^1\text{H-NMR}$ (400 MHz, $\text{Me}_2\text{SO}-d_6$): δ 7.75 (d, 2H, $J = 13.7$ Hz), 7.62–7.48 (m, 20H), 7.41 (t, 1H, $J = 12.9$ Hz), 2.38 (s, 3H). $^{31}\text{P-NMR}$ (160 MHz, $\text{Me}_2\text{SO}-d_6$): δ 42.6. Anal. Found: C, 71.01; H, 5.17; S, 12.13. Calc. for $\text{C}_{31}\text{H}_{26}\text{P}_2\text{S}_2$: C, 70.97; H, 5.00; S, 12.22%.

3.3. Pd(**1-H**)Cl (**2**)

3.3.1. Procedure A

A mixture of **1** (53 mg, 0.1 mmol), K_2PdCl_4 (33 mg, 0.1 mmol), and AcOH (3 ml) was heated at 115 °C for 24 h under N_2 . The resulting yellow precipitate was filtered

and washed with MeOH, water, and ether to give a bright yellow powder of **2** (48 mg, 72% yield).

3.3.2. Procedure B

A mixture of **1** (53 mg, 0.1 mmol), PdCl₂(PhCN)₂ (38 mg, 0.1 mmol), and CH₃CN (10 ml) was heated at 65 °C for 24 h under N₂. The resulting yellow precipitate was filtered and washed with CH₃CN, MeOH, water, and ether to give a yellow powder of **2** (44 mg, 65% yield).

¹H-NMR (400 MHz, Me₂SO-*d*₆): δ 7.82–7.72 (m, 12H), 7.70–7.63 (m, 8H), 7.20 (d, 2H, *J* = 11.7 Hz), 2.16 (s, 3H). ³¹P-NMR (160 MHz, Me₂SO-*d*₆): δ 56.5. Anal. Found: C, 55.59; H, 3.96; Cl, 4.91; S, 9.51. Calc. for C₃₁H₂₅ClP₂PdS₂: C, 55.95; H, 3.79; Cl, 5.33; S, 9.64%.

3.4. Pt(I-H)Cl (**3**)

The procedure A for **2** was adopted using K₂PtCl₄ (42 mg, 0.1 mmol) to afford a yellow powder of **3** (67 mg, 89% yield).

¹H-NMR (400 MHz, Me₂SO-*d*₆): δ 7.82–7.73 (m, 12H), 7.70–7.63 (m, 8H), 7.19 (d, 2H, *J* = 11.7 Hz), 2.09 (s, 3H). ³¹P-NMR (160 MHz, Me₂SO-*d*₆): δ 58.0. Anal. Found: C, 49.26; H, 3.50; Cl, 4.59; S, 8.42. Calc. for C₃₁H₂₅ClP₂PtS₂: C, 49.37; H, 3.34; Cl, 4.70; S, 8.50%.

3.5. Crystal data for **2** and **3**

The diffraction data were collected with a Rigaku Saturn CCD diffractometer using a graphite monochromated Mo-K_α (λ = 0.71070 Å) at –160 °C. The data were corrected for Lorentz and polarization effects, and an absorption correction was applied. The structure was solved by direct methods (SIR 92), and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters.

2: C₃₁H₂₅ClP₂PdS₂, *M* = 665.46, orthorhombic, space group *P*2₁2₁2₁ (No. 19), *a* = 9.890(6), *b* = 14.959(8), *c* = 19.160(11) Å, *V* = 2834.5(27) Å³, *Z* = 4, *D*_{calc} = 1.559 g cm⁻³, μ(Mo-K_α) = 10.30 cm⁻¹, *F*(000) = 1344. A total of 79 603 reflections were measured, 3582 unique. The final cycle of full-matrix least-squares refinement on *F* was based on 3079 observed reflections (*I* > 3σ(*I*), 334 valuable parameters) with factors of *R*₁ = 0.070, *R*_w = 0.118, GOF = 0.94.

3: C₃₁H₂₅ClP₂PtS₂, *M* = 754.15, orthorhombic, space group *P*2₁2₁2₁ (No. 19), *a* = 9.832(6), *b* = 14.978(10), *c* = 19.090(12) Å, *V* = 2811.2(31) Å³, *Z* = 4, *D*_{calc} = 1.782 g cm⁻³, μ(Mo-K_α) = 53.49 cm⁻¹, *F*(000) = 1472. A total of 20 235 reflections were measured, 3222 unique. The final cycle of full-matrix least-squares refinement on *F* was based on 3022 observed reflections

(*I* > 3σ(*I*), 334 valuable parameters) with factors of *R*₁ = 0.089, *R*_w = 0.139, GOF = 0.98.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 209322 (**2**) and 209323 (**3**). 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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