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## New Pt(II) complexes containing hemilabile thioether-pyrazole ligands. Structural analysis by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>195</sup>Pt{<sup>1</sup>H} NMR spectroscopy and crystal structure of [PtCl(bdtp)](BPh<sub>4</sub>) [bdtp = 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane]

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## Abstract

Treatment of the ligand 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane (bdtp) with several platinum starting materials, such as  $K_2PtCl_4$ , PtCl\_2, [PtCl\_2(CH\_3CN)\_2] and [PtCl\_2(PhCN)\_2], have been developed under different conditions. The reactions did not yield pure products. The ratio of the NSN, NS and NN isomers has been calculated through NMR experiments. Subsequent treatment of the mixtures of complexes with NaBPh<sub>4</sub> gave [PtCl(bdtp)](BPh<sub>4</sub>) (1). These Pt(II) complexes were characterised by elemental analysis, conductivity measurements, IR spectroscopy and <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>195</sup>Pt{<sup>1</sup>H} NMR spectroscopy. A mixture of complexes was again obtained when the complex [PtCl(bdtp)](BPh<sub>4</sub>) was heated under reflux in a solution of Et<sub>4</sub>NBr in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1). This proves the hemilability of the ligand bdtp with Pt(II). The X-ray crystal structure of the complex [PtCl(bdtp)](BPh<sub>4</sub>) was determined. The crystal structure contains two kinds of discrete [PtCl(bdtp)]<sup>+</sup> cations, two BPh<sub>4</sub><sup>-</sup> anions and two acetonitrile solvent molecules. In both cations the metal atom is tri-coordinated by the two azine nitrogen atoms and one thioether sulfur atom of the thioether-pyrazole ligand, its coordination (distorted square planar) being completed with one chlorine atom.

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Keywords: Platinum(II); Hemilabile ligands; N ligands; S ligands; Pyrazole complexes; Crystal structure

#### 1. Introduction

Ligands that contain significantly different chemical functions such as hard and soft donors (often called hybrid ligands) find increasing use in chemistry because of the selectivity introduced in the metal–ligand interactions and their possible dynamic behaviour [1]. New molecular interactions and properties may allow the emergence of useful concepts that help tailor molecular structures oriented towards a given property. The term "hemilabile ligand" was introduced in 1979 by Jeffrey and Rauchfuss [2], attrib-

\* Corresponding author. Fax: +34 93 581 31 01. *E-mail address:* Josefina.Pons@uab.es (J. Pons). utable to polydentate chelate ligands containing two types of bonding groups (one labile and one inert). It should be emphatisised than hemilability is not an intrinsic property of the sole ligand and it implies the metal-ligand couple [3].

In the last 5 years, our research group has focused their interest in the chemistry of hemilabile ligands, in particular we have studied and reported the synthesis and characterisation of hemilabile ligands based on the pyrazolyl group and on some other groups containing N [4], P [5], O [6] or S [7] atoms, and their reactivity with Pd(II), Pt(II) and Rh(I). This paper continues the study of the potential hemilability of ligands containing pyrazolyl and thioether groups [7], in particular with the ligand 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane (bdtp) [7c,8]. Previously other authors

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have studied and described in the literature the reactivity of the ligand bdtp with different metals such as Ni(II), Co(II), Cu(I), Zn(II), Ag(I), Cd(II) and Re(I) [9], and our research group recently has reported the reactivity of the ligand bdtp with Pd(II). We have demonstrated the hemilabile properties of this ligand when coordinated to Pd(II) [7c].

In this paper, we have studied the reactivity of the ligand bdtp [7c,8] towards Pt(II), under various conditions and with several platinum starting materials.

## 2. Results and discussion

## 2.1. Synthesis and spectroscopic properties

Reaction of 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane (bdtp) [7c,8] (Scheme 1) with several platinum starting materials, such as  $K_2PtCl_4$ ,  $PtCl_2$ ,  $[PtCl_2(CH_3-CN)_2]$  [10] and  $[PtCl_2(PhCN)_2]$ [11], have been developed under different conditions (Scheme 2). In general, and in contrast to the Pd(II) complexes, these reactions take a longer time and need higher temperatures to occur. This same behaviour is observed with the ligands 1,8-bis-(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo), 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (bddn) and 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2, 5-dithiahexane (bddh) [12].

The reaction did not yield pure products. Unfortunately, isolation of the different isomers by silica gel chromatography was unsuccessful. Recrystallisations of the mixture with different solvents have been carried out but pure products could not be obtained.

The resulting products of these reactions have been characterised by elemental analyses, and infrared and NMR spectra.

The ratio of NS, NSN and NN products has been calculated through <sup>1</sup>H NMR experiments (integration of  $C-H_{pz}$  signals, see Section 4) (see Fig. 1).

The different isomers were distinguished using the following criteria:

*Isomer NSN*: pure NSN complex  $(\delta(C-H_{pz}) = 6.03 \text{ ppm})$  could be obtained when the platinum starting material is [PtCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>].

*Isomer NS*: two signals can be observed for the C–H<sub>pz</sub> of the coordinated ligand in this isomer. One of them appears at the same position as the free ligand ( $\delta$ (C–H<sub>pz</sub>) = 5.76 ppm) and the other one at  $\delta$ (C–H<sub>pz</sub>) = 5.82 ppm. Integration of both peaks is identical.

*Isomer NN*: this is a third isomer, which was characterised by comparison to the complex  $[PdCl_2(bdtp)] (\delta(C-H_{pz}) = 5.90 \text{ ppm}) [7c].$ 

Elemental analyses are consistent with the mixtures.

The IR spectra of the complexes with bdtp show bands at 1555–1553 cm<sup>-1</sup> (v(C=C),  $v(C=N)_{ar}$ , 1465–1418 cm<sup>-1</sup> ( $\delta(C=C)$ ,  $\delta(C=N)_{ar}$ , 1100–1021 cm<sup>-1</sup>  $\delta(C-H)_{ip}$  and 801–800 cm<sup>-1</sup>  $\delta(C-H)_{oop}$ , indicating the presence of the unaltered coordinated ligand [7c,8]. Coordination to platinum is demonstrated in the IR spectra between 500 and 100 cm<sup>-1</sup> of the mixture of compounds. According to IR data, the Pt atom is coordinated to nitrogen atoms [v(Pt-N) between 444 and 441 cm<sup>-1</sup>], sulfur atoms [v(Pt-C) between 419 and 380 cm<sup>-1</sup>] and chlorine atoms [v(Pt-C) between 333 and 326 cm<sup>-1</sup>] [13].

The <sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR, HMQC, COSY and NOESY spectra were recorded in CDCl<sub>3</sub>. The NMR experiments corroborate the obtaining of mixtures and the coordination of the ligands around the metallic centre. This ligand can act as tridentate (NSN) or bidentate (NS or NN) chelates depending on the Pt(II) starting material.

In order to be able to isolate one of the isomers (NSN) from the mixture, treatment of the bdtp mixture with NaBPh<sub>4</sub> was carried out. This reaction gave a compound of the formula  $[Pt(bdtp)](BPh_4)$  (1) as a pure products (NSN isomer).

When the complex 1 was heated under reflux in a solution of  $Et_4NBr$  in  $CH_2Cl_2/MeOH$  (1:1) for 24 h, mixtures of complexes were again obtained (NSN (55%) and NN (45%) isomers with bromides instead of chlorides bonded to the metallic centre). This proves the type III hemilability of the ligand bdtp towards Pt(II) [1a]. The elemental analysis of 1 is consistent with the formula [PtCl(bdtp)](BPh\_4). The positive ionisation electrospray mass spectrum of 1 gave a peak with a m/z value of 509 [PtCl(bdtp)]<sup>+</sup> (molecular peak of the cation is observed with the same isotope



Scheme 1.



The ratio of the species has been calculated through <sup>1</sup>H-NMR experiments, especially from the integration of the pyrazolic proton

Scheme 2.

distribution as the theoretical one). The conductivity measurements in DMF for 1, show that the complex behaves as 1:1 electrolyte in solution [14].

The IR spectrum of complex **1** is similar to that of the ligand, the most characteristic bands being those attributable to the pyrazolyl group: v(C=C), v(C=N) at 1579, 1576 cm<sup>-1</sup> and  $\delta(C-H)_{oop}$  at 799 cm<sup>-1</sup>. The v(B-C) band at 736 cm<sup>-1</sup> is characteristic for **1** [15]. The v(Pt-N), v(Pt-S) and v(Pt-Cl) bands can be attributable to the signals appearing at 442 cm<sup>-1</sup>, 380 cm<sup>-1</sup> and 326 cm<sup>-1</sup>, respectively [13].

<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of compound 1 were recorded in  $[D_6]$  acetone solution, and show the signals of

the coordinated ligands. NMR spectroscopy data are reported in Section 4 (see Fig. 1).

The <sup>1</sup>H NMR spectrum of complex **1** shows that the two protons of each CH<sub>2</sub> moiety in the S–CH<sub>2</sub>–CH<sub>2</sub>–N chains are diastereotopic, thus leading to four groups of signals, which can be associated to a single hydrogen atom in each chain. This happens because of the rigid conformation of the ligand when complexed. Thus, each group of signals can be assigned as doublets of doublets of doublets (Fig. 2). The HMQC spectrum allowed us to assign the two doublets of doublets of lower  $\delta$  to 7-H and the ones at higher  $\delta$  to 6-H (Fig. 3). Study of the S– CH<sub>2</sub>–CH<sub>2</sub>–N fragment as an AA'XX' system gave a set



Fig. 1. <sup>1</sup>H NMR 250 MHz spectrum of the mixture bdtp + [PtCl<sub>2</sub>(PhCN)<sub>2</sub>].



Fig. 2. The 250-MHz  $^{1}$ H NMR and the simulated gNMR spectrum for the NCH<sub>2</sub>CH<sub>2</sub>S fragment of [PtCl(bdtp)](BPh<sub>4</sub>) (1) including the numbering and the dihedral angles for the NCH<sub>2</sub>CH<sub>2</sub>S fragment.

of coupling constants (Table 1). These constants were consistent with the simulated spectra obtained with the aid of the gNMR program [16].

In the NOESY spectrum it can be seen that the methyl group at  $\delta = 2.48$  ppm shows a NOE interaction with the doublet of doublets of doublets at  $\delta = 4.87$  ppm, but not with the one at  $\delta = 5.19$  ppm. From the X-ray structure

of 1, it can be observed that the nearest proton to the CH<sub>3</sub>(5) moiety is 6S-H (Figs. 2 and 4) and therefore it should be the one with the NOE interaction (2.70 Å cation A and 2.73 Å cation B). This information leads us to assign 6S-H to the doublet of doublets of doublets at  $\delta = 4.87$  ppm and 6R-H to the signal at  $\delta = 5.19$  ppm. The coupling constants enabled us to differentiate 7S-H



Fig. 3. The 250-MHz 2D HMQC spectrum of [PtCl(bdtp)](BPh<sub>4</sub>) (1).

Table 1  ${}^{1}$ H NMR results: chemical shifts (ppm) and  ${}^{1}$ H,  ${}^{1}$ H coupling constants (Hz) for 1 in [D<sub>6</sub>]acetone

Compound	1
$\delta$ 6R-H	5.19
$\delta$ 6S-H	4.87
δ 7S-H	3.79
$\delta$ 7R-H	3.38
<sup>2</sup> <i>J</i> (6R-H, 6S-H)	15.24
<sup>2</sup> <i>J</i> (7R-H, 7S-H)	14.90
$^{3}J(6R-H, 7R-H)$	12.03
<sup>3</sup> <i>J</i> (6S-H, 7S-H)	2.85
$^{3}J(6R-H, 7S-H)$	2.99
<sup>3</sup> <i>J</i> (6S-H, 7R-H)	2.09

and 7R-H. These coupling constants agree with the conformation of the S–CH<sub>2</sub>–CH<sub>2</sub>–N chain as seen in the X-ray crystal structure (Figs. 2 and 4). Geminal <sup>2</sup>J and ca. 180°, <sup>3</sup>J coupling constants have significantly higher values than ca. 30° and ca. 60° <sup>3</sup>J coupling constants. Thus, 7R-H should correspond to the doublet of doublets of doublets at 3.38 ppm and 7S-H to the one at  $\delta = 3.79$  ppm [15,17].

Additional <sup>195</sup>Pt{<sup>1</sup>H} NMR experiments for complex 1 at 298 K revealed only one band ( $\delta = -1880$  ppm). The <sup>195</sup>Pt{<sup>1</sup>H} chemical shifts are downfield compared to other complexes with [PtN<sub>2</sub>SCl] cores (-4098, -2312 ppm) [18].

## 2.2. Crystal structure of [PtCl(bdtp)](BPh<sub>4</sub>)-CH<sub>3</sub>CN

The crystal structure of **1** contains two kinds of discrete  $[PtCl(bdtp)]^+$  cations (cations **A** and **B**) (Fig. 4), two  $BPh_4^-$  anions and two acetonitrile solvent molecules. Table 2 lists some selected bond distances and angles.

The cations A and B have the same structure, [PtCl-(bdtp)<sup>+</sup>. In both, the cationic complex is mononuclear, and the Pt(II) is coordinated to the bdtp ligand by its three donor atoms (two nitrogen atoms of the pyrazolyl group and one sulfur atom), along with one chlorine atom, in a slightly distorted square-planar geometry. Tetrahedral distortion can be observed from the bond angles and from the largest deviation to the mean plane (0.039(4) Å cation A)and 0.072(4) Å cation **B**) of the atoms coordinated to the Pt atom in relation to the mean plane that contains these four atoms and the Pt atom (cation A: N(1), N(4), S(1), Cl(1); cation **B**: N(8), N(5), S(2), Cl(2)). The dihedral angle between the planes N(1)-Pt(1)-Cl(1) and N(4)-Pt(1)-S(1); and N(5)-Pt(2)-Cl(2) and N(8)-Pt(2)-S(2) are  $4.10(2)^{\circ}$ and 5.88(2)°, respectively. The bdtp ligand acts as a tridentate chelate and forms two six-membered rings, with a boat form for Pt(1)S(1)C(8)C(9)N(3)N(4) and Pt(1)S(1)C(7)C(6) N(2)N(1) (cation A) and with a twist-boat form for Pt(2)S(2)C(22)C(23)N(7)N(8) and a boat conformation for Pt(2)S(2)C(21)C(20)N(6)N(5) (cation **B**).

The [PtN<sub>2</sub>SCl] core is present in 45 complexes in the literature. Only in 13 of them is the S a thioether [19]. The Pt–Npz bond lengths [2.025(4) and 1.999(5) Å (cation A); 2.008(4) and 2.014(4) Å (cation B)], the Pt–S bond lengths [2.2616(12) Å (cation A); 2.2559(12) Å (cation B)] and the





Fig. 4. ORTEP drawing of  $[PtCl(bdtp)]^+$  (a: cation **A**, b: cation **B**) showing all non-hydrogen atoms and the atom numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

Table 2 Selected bond lengths (Å) and bond angles (°) for  $[PtCl(bdtp)](BPh_4)\cdot CH_3CN$ 

- 5			
Cation A			
Pt(1)–N(1)	2.025(4)	Pt(1)-S(1)	2.2616(12)
Pt(1)-N(4)	1.999(5)	Pt(1)-Cl(1)	2.3168(14)
N(4)-Pt(1)-N(1)	179.44(17)	N(4)-Pt(1)-S(1)	91.87(15)
N(4) - Pt(1) - Cl(1)	91.05(15)	N(1)-Pt(1)-S(1)	88.60(11)
N(1)-Pt(1)-Cl(1)	88.47(11)	S(1)-Pt(1)-Cl(1)	174.97(5)
Cation <b>B</b>			
Pt(2) - N(8)	2.008(4)	Pt(2)-S(2)	2.2559(12)
Pt(2)-N(5)	2.014(4)	Pt(2)–Cl(2)	2.3139(14)
N(8)-Pt(2)-N(5)	177.62(15)	N(8)-Pt(2)-S(2)	91.81(11)
N(8)-Pt(2)-Cl(2)	91.06(11)	N(5)-Pt(2)-S(2)	86.42(11)
N(5)-Pt(2)-Cl(2)	90.86(12)	S(2)-Pt(2)-Cl(2)	173.63(5)

Pt–Cl bond lengths [2.3168(14) Å (cation A); 2.3139(15) Å (cation B)] can be regarded as normal compared with the distances found in the literature. For Pt–N<sub>pz</sub>, the literature describes values between 1.930 and 2.021 Å [20], for Pt–S(thioether) between 2.18 and 2.46 Å [19,21], and for Pt–Cl between 2.198 and 2.381 Å [20].

The N<sub>pz</sub>-Pt-S bite angles of the ligand are  $91.87(15)^{\circ}$  and  $88.60(11)^{\circ}$  (cation **A**) and  $91.81(11)^{\circ}$  and  $85.42(11)^{\circ}$  (cation **B**), and are similar to the corresponding bite angles in the complex [PdCl(bdtp)](BF<sub>4</sub>) (90.5(2)^{\circ} and 88.5(2)^{\circ}) [7c].

#### 3. Conclusion

Reaction of the bdtp ligand with different Pt(II) starting materials forms different mixtures of the NN, NS and NSN isomers. A similar reaction with  $[PdCl_2(CH_3CN)_2]$  as the starting material yielded the NN and NS isomers (the NSN isomer was not observed with Pd before addition of AgBF<sub>4</sub>) [7c] in a dynamic equilibrium in solution at room temperature. This equilibrium is not observed for the Pt(II) mixture on the NMR timescale (under the same conditions), showing that Pt(II) forms more inert complexes with bdtp than Pd(II).

In order to isolate the NSN isomer, we performed the reaction of the bdtp mixture of isomers with NaBPh<sub>4</sub>, obtaining [Pt(bdtp)](BPh<sub>4</sub>) as a pure product. In this case, the only coordination observed is NSN (similar behaviour to Pd(II)). When this product is refluxed in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH in the presence of Et<sub>4</sub>NBr a new mixture of NN, NS and NSN isomers is obtained. This proves the hemilability of this ligand with Pt(II) [1a], as was observed for Pd(II).

## 4. Experimental

#### 4.1. General details

The reactions were carried out under nitrogen atmosphere using vacuum line and Schlenk techniques. Solvents were dried and distilled according to standard procedures and stored under nitrogen. Elemental analyses (C, H, N, S) were carried out by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature (r.t.) in  $10^{-3}$  M DMF solutions, employing a CyberScan CON 500 (Euthech instrument) conductimeter. Infrared spectra were run on a Perkin-Elmer FT spectrophotometer, series  $2000 \text{ cm}^{-1}$  as KBr pellets or polyethylene films in the range 4000–100 cm<sup>-1</sup>. <sup>1</sup>H NMR, <sup>13</sup>C {<sup>1</sup>H} NMR, HMQC, COSY, NOESY spectra were recorded on a NMR-FT Bruker AC-250 MHz spectrometer in CDCl<sub>3</sub>, and [D<sub>6</sub>]acetone solutions at room temperature. <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra were recorded at 25 °C and 77.42 MHz on a DPX-360 Bruker spectrometer using aqueous solutions of  $[PtCl_6]^{2-}$  (0 ppm) as an external reference and delay time 0.01 s. All chemical shifts values ( $\delta$ ) are given in ppm. Positive ion ESI-MS mass spectrometer experiments were performed by the Scientific technique Services of the Universitat de Barcelona on a ZQ (Micromass Instruments, UK). The electrospray interface (pneumatically assisted) was operated under the following conditions: the nebulizing nitrogen gas flow was  $251 \text{ h}^{-1}$ and the drying nitrogen  $2501h^{-1}$ , source temperature 100 °C with a capillary voltage of 3.5 kV and cone voltage 20 V. The flow rate was 100  $\mu$ l min<sup>-1</sup>. Samples were dissolved in a 1:1 mixture of H<sub>2</sub>O/CH<sub>3</sub>CN.

Samples of  $[PtCl_2(CH_3CN)_2]$  [10] and  $[PtCl_2(PhCN)_2]$ [11] were prepared as described in the literature. 1,5bis(3,5-dimethyl-1-pyrazolyl)-3,7-thiapentane (bdtp) [7c,8] was prepared according to the published methods (Scheme 1).

## 4.2. Reactions of bdtp with $K_2PtCl_4$ in $H_2O$

0.23 mmol (0.065 g) of the bdtp ligand dissolved in 10 ml of water was added to a solution of 0.23 mmol (0.095 g) of  $K_2PtCl_4$  in 10 ml of water. The solution was stirred at room temperature for 24 h (until the red colour of the starting material  $K_2PtCl_4$  had completely disappeared), and a yellow solid precipitated. It was filtered off, washed twice with 5 ml of cold water and dried in vacuum.

## 4.3. Reactions of bdtp with $PtCl_2$

To 0.26 mmol (0.070 g) of PtCl<sub>2</sub> in 15 ml of chloroform, 0.27 mmol (0.070 g) of the bdtp ligand dissolved in 15 ml of the same solvent was quickly added. The mixture was refluxed for 48 h. The yellowish solution was filtered to separate Pt(0) and the starting material PtCl<sub>2</sub>. The solvent was evaporated to dryness leaving a white solid, which was filtered off, washed with 10 ml of CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether (1:1) and dried in vacuum.

#### 4.4. Reactions of bdtp with $[PtCl_2(CH_3CN)_2]$

0.24 mmol (0.067 g) of the bdtp ligand dissolved in 15 ml of acetonitrile was added to a solution of 0.24 mmol (0.085 g) PtCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> in 15 ml of acetonitrile. The solu-

tion was refluxed for 24 h. The solvent was evaporated to dryness leaving a yellow solid, which was filtered off, washed with 10 ml of  $CH_2Cl_2/diethyl$  ether (1:1) and dried in vacuum.

## 4.5. Reaction of bdtp with $[PtCl_2(PhCN)_2]$

0.20 mmol (0.055 g) of the bdtp ligand dissolved in 15 ml of chloroform was added to a solution of 0.20 mmol (0.095 g) of [PtCl<sub>2</sub>(PhCN)<sub>2</sub>] in 15 ml of the same solvent. The mixture was refluxed 24 h. From the yellow solution the solvent was evaporated to dryness yielding a yellow solid, which was filtered off, washed with 10 ml of CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether (1:1) and dried in vacuum.

#### 4.5.1. $bdtp + K_2PtCl_4$

Yield: 93%. Anal. Calc. for C<sub>14</sub>H<sub>22</sub>N<sub>4</sub>SCl<sub>2</sub>Pt: C, 30.89; H, 4.07; N, 10.29; S, 5.89. Found: C, 31.10; H, 4.33; N, 10.40; S, 5.51%. Conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, 1.05 ×  $10^{-3}$  M in DMF): 152. IR (KBr, cm<sup>-1</sup>): 3159 v(C-H)<sub>ar</sub>, 2968, 2922  $\nu$ (C–H)<sub>al</sub>, 1553 ( $\nu$ (C=C),  $\nu$ (C=N))<sub>ar</sub>, 1461, 1421 ( $\delta$ (C=C),  $\delta$ (C=N))<sub>ar</sub>, 1069, 1034  $\delta$ (C-H)<sub>ip</sub>, 801  $\delta$  $(C-H)_{oop}$ . (Polyethylene, cm<sup>-1</sup>): 442 v(Pt-N), 394 v(Pt-S), 326 v(Pt-Cl). <sup>1</sup>H NMR (CDCl<sub>3</sub> solution, 250 MHz)  $\delta$ : NS: (59%) 5.83 [1H, s, CH(pz)], 5.76 [1H, s, CH(pz)], 5.25/4.41 [1H/1H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 4.08 [2H, t, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 3.43/2.90 [1H/1H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 2.82 [2H, t, SCH<sub>2</sub>CH<sub>2</sub>S], 2.63 [3H, s, CH<sub>3</sub>(pz)], 2.34 [3H, s, CH<sub>3</sub>(pz)], 2.24 [3H, s, CH<sub>3</sub>(pz)], 2.19 [3H, s, CH<sub>3</sub>(pz)] ppm. NSN: (33%) 6.00 [1.12H, s, CH(pz)], 5.25/4.78 [1.12H/1.12H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 3.98 [1.12H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 2.67 [3.36H, s, CH<sub>3</sub>(pz)], 2.40 [3.36H, s, CH<sub>3</sub>(pz)] ppm. NN: (8%) 5.90 [0.27H, s, CH(pz)], 5.30 [0.55H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 2.90 [0.55H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 2.70 [0.82H, s, CH<sub>3</sub>(pz)], 2.38 [0.82H, s, CH<sub>3</sub>(pz)] ppm  $^{13}C{^{1}H} NMR (CD_{3}Cl solution, 63 MHz) \delta: NS + NSN +$ NN: 153.3-147.9 (pz-C), 144.4-139.3 (pz-C), 108.8, 108.7, 106.0, 105.1 (CH(pz)), 62.0-48.6 (NpzCH<sub>2</sub>CH<sub>2</sub>S), 46.3-32.4 (SCH<sub>2</sub>CH<sub>2</sub>S), 15.4–11.2 (CH<sub>3</sub>(pz)) ppm.

## 4.5.2. $bdtp + PtCl_2$

Yield: 70%. Anal. Calc. for C14H22N4SCl2Pt: C, 30.89; H, 4.07; N, 10.29; S, 5.89. Found: C, 31.16; H, 3.98; N, 9.95; S, 5.45%. Conductivity  $(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, 1.12 \times 10^{-3} \text{ M}$  in DMF): 46. IR (KBr,  $cm^{-1}$ ): 3193 v(C–H)<sub>ar</sub>, 2964, 2930 ν(C-H)<sub>al</sub>, 1555 (ν(C=C), ν(C=N))<sub>ar</sub>, 1465, 1418 (δ(C=C),  $\delta(C=N)_{ar}$ , 1100, 1021  $\delta(C-H)_{ip}$ , 800  $\delta(C-H)_{oop}$ . (Polyethylene, cm<sup>-1</sup>): 441 v(Pt–N), 419 v(Pt–S), 328 v(Pt–Cl). <sup>1</sup>H NMR (CDCl<sub>3</sub> solution, 250 MHz)  $\delta$ : NS: (31%) 5.82 [0.57H, s, CH(pz)], 5.76 [0.57H, s, CH(pz)], 5.25/4.40 [0.57H/0.57H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 4.07 [1.13H, t, N<sub>pz</sub>CH<sub>2</sub> CH<sub>2</sub>S], 3.50/2.83 [0.57H/0.57H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 2.81  $[1.13H, t, SCH_2CH_2S], 2.63 [2.84H, s, CH_3(pz)], 2.34$ [2.84H, s, CH<sub>3</sub>(pz)], 2.23 [2.84H, s, CH<sub>3</sub>(pz)], 2.19 [2.84H, s, CH<sub>3</sub>(pz)] ppm. NSN: (55%) 6.01 [2H, s, CH(pz)], 5.25/ 4.76 [2H/2H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 3.98/2.90 [2H/2H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 2.67 [6H, s, CH<sub>3</sub>(pz)], 2.40 [6H, s, CH<sub>3</sub>(pz)] ppm. NN: (14%) 5.92 [0.53H, s, CH(pz)], 5.30 [1.05H, m, N<sub>pz</sub>CH<sub>2</sub>- CH<sub>2</sub>S], 2.79 [1.05H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 2.52 [1.58H, s, CH<sub>3</sub>(pz)], 2.38 [1.58H, s, CH<sub>3</sub>(pz)] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>Cl solution, 63 MHz)  $\delta$ : NS + NSN + NN: 153.1–148.6 (pz-*C*), 143.6–142.2 (pz-*C*), 108.8, 107.4, 106.0, 105.1 (*C*H(pz)), 61.9–49.7 (NpzCH<sub>2</sub>CH<sub>2</sub>S), 38.6 (SCH<sub>2</sub>CH<sub>2</sub>S), 15.3–11.4 (*C*H<sub>3</sub>(pz)) ppm.

#### 4.5.3. $bdtp + [PtCl_2(CH_3CN)_2]$

Yield: 68%. Anal. Calc. for C<sub>14</sub>H<sub>22</sub>N<sub>4</sub>SCl<sub>2</sub>Pt: C, 30.89; H, 4.07; N, 10.29; S, 5.89. Found: C, 30.36; H, 4.38; N, 9.68; S, 5.91%. Conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, 0.98 × 10<sup>-3</sup> M in DMF): 65. IR (KBr, cm<sup>-1</sup>): 3147 v(C–H)<sub>ar</sub>, 2967, 2917 v(C–H)<sub>al</sub>, 1553 (v(C=C), v(C=N))<sub>ar</sub>, 1465, 1422 ( $\delta$ (C=C),  $\delta$ (C=N))<sub>ar</sub>, 1093, 1032  $\delta$ (C–H)<sub>ip</sub>, 801  $\delta$ (C– H)<sub>oop</sub>. (Polyethylene, cm<sup>-1</sup>): 444 v(Pt–N), 380 v(Pt–S), 333 v(Pt–Cl). <sup>1</sup>H NMR (CDCl<sub>3</sub> solution, 250 MHz)  $\delta$ : NSN: (100%) 6.03 [2H, s, CH(pz)], 5.30/4.76 [2H/2H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 3.98/2.81 [2H/2H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 2.67 [6H, s, CH<sub>3</sub>(pz)], 2.40 [6H, s, CH<sub>3</sub>(pz)] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>Cl solution, 63 MHz)  $\delta$ : NSN: 153.2 (pz-C), 143.9 (pz-C), 108.9 (CH(pz)), 51.5 (NpzCH<sub>2</sub>CH<sub>2</sub>S), 38.6 (SCH<sub>2</sub>CH<sub>2</sub>S), 15.6, 12.5 (CH<sub>3</sub>(pz)) ppm.

## 4.5.4. $bdtp + [PtCl_2(PhCN)_2]$

Yield: 56%. Anal. Calc. for C<sub>14</sub>H<sub>22</sub>N<sub>4</sub>SCl<sub>2</sub>Pt: C, 30.89; H, 4.07; N, 10.29; S, 5.89. Found: C, 31.05; H, 4.40; N, 10.58; S, 5.74%. Conductivity  $(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, 1.05 \times$  $10^{-3}$  M in DMF): 20. IR (KBr, cm<sup>-1</sup>): 3181 v(C-H)<sub>ar</sub>, 2967, 2922 v(C-H)<sub>al</sub>, 1553 (v(C=C), v(C=N))<sub>ar</sub>, 1465, 1422 (δ(C=C), δ(C=N))ar, 1097, 1026 δ(C-H)ip, 800 δ  $(C-H)_{oop}$ . (Polyethylene, cm<sup>-1</sup>): 443 v(Pt-N), 396 v(Pt-S), 328 v(Pt–Cl). <sup>1</sup>H NMR (CDCl<sub>3</sub> solution, 250 MHz)  $\delta$ : NS: (67%) 5.80 [1H, s, CH(pz)], 5.76 [1H, s, CH(pz)], 5.24/4.39 [1H/1H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 4.06 [2H, t, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 3.44/2.90 [1H/1H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 2.80 [2H, t, SCH<sub>2</sub>CH<sub>2</sub>S], 2.62 [3H, s, CH<sub>3</sub>(pz)], 2.34 [3H, s, CH<sub>3</sub>(pz)], 2.23 [3H, s, CH<sub>3</sub>(pz)], 2.19 [3H, s, CH<sub>3</sub>(pz)] ppm. NSN: (26%) 6.00 [0.78H, s, CH(pz)], 5.24/4.76 [0.78H/0.78H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 3.98 [0.78H, m, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 2.67 [2.33H, s, CH<sub>3</sub>(pz)], 2.40 [2.33H, s, CH<sub>3</sub>(pz)] ppm. NN: (7%) 5.90 [0.22H, s, CH(pz)], 2.54 [0.65H, s, CH<sub>3</sub>(pz)], 2.38 [0.65H, s, CH<sub>3</sub>(pz)] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>Cl solution, 63 MHz)  $\delta$ : NS + NSN + NN: 153.1–147.9 (pz-C), 143.6–139.3 (pz-C), 108.7, 106.0, 105.2, 105.1 (CH(pz)), 61.9–48.6 (NpzCH<sub>2</sub>CH<sub>2</sub>S), 46.3– 29.2 (SCH<sub>2</sub>CH<sub>2</sub>S), 15.3–11.2 (CH<sub>3</sub>(pz)) ppm.

#### 4.6. Complexes $[PtCl(bdtp)](BPh_4)$ (1)

A solution of NaBPh<sub>4</sub> (0.14 mmol, 0.050 g) in 10 ml acetonitrile/methanol 1:1 was added dropwise with vigorous stirring to a solution of  $[PtCl_2(bdtp)]$  (0.14 mmol, 0.075 g) in 10 ml of acetonitrile/methanol 1:1. The solution was stirred at room temperature for 12 h. The yellowish solution was filtered to separate NaCl. When the volume of the resultant solution had been reduced to roughly 5 ml,

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diethyl ether (5 ml) was then added to induce precipitation. The resulting precipitate was then filtered and washed with 5 ml diethyl ether.

Yield: 79% (0.076 g). Anal. Calc. for C<sub>38</sub>H<sub>44</sub>N<sub>4</sub>SClPtB: C, 65.82; H, 4.72; N, 5.31; S, 5.41. Found: C, 65.80; H, 4.71; N, 5.74; S, 5.39%. MS (m/z) (%) = 509 (100%) [PtCl(bdtp)]<sup>+</sup>. Conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, 1.06 × 10<sup>-3</sup> M in DMF): 90. IR (KBr, cm<sup>-1</sup>): 3442 v(C–H)<sub>ar</sub>, 2984, 2927 v(C–H)<sub>al</sub>, 1579, 1556 (v(C=C), v(C=N))<sub>ar</sub>, 1476, 1425 ( $\delta(C=C)$ ,  $\delta(C=N)$ )<sub>ar</sub>, 1067, 1031  $\delta$ (C–H)<sub>ip</sub>, 799  $\delta$ (C–H)<sub>oop</sub>, 736 v(B–C). (Polyethvlene,  $cm^{-1}$ ): 442 v(Pt-N), 380 v(Pt-S), 326 v(Pt-Cl). <sup>1</sup>H NMR ([D<sub>6</sub>]acetone solution, 250 MHz)  $\delta$ : 7.31–6.78 [20H, Ph], 6.22 [2H, s, CH(pz)], 5.19 [2H, ddd, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 4.87 [2H, ddd, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 3.79 [2H, ddd, N<sub>pz</sub>CH<sub>2</sub>-CH<sub>2</sub>S], 3.38 [2H, ddd, N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S], 2.66 [6H, s, CH<sub>3</sub>(pz)], 2.48 [6H, s,  $CH_3(pz)$ ] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR ([D<sub>6</sub>]acetone solution, 63 MHz)  $\delta = 165.8 - 122.0$  (Ph), 153.1 (pz-C), 144.8 (pz-C), 108.8 (CH(pz)), 50.5 (N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>S), 39.2 (N<sub>pz</sub>CH<sub>2</sub>-CH<sub>2</sub>S), 14.9 (CH<sub>3</sub>(pz)), 11.4 (CH<sub>3</sub>(pz)) ppm. <sup>195</sup>Pt{<sup>1</sup>H} NMR (CD<sub>3</sub>CN solution, 77.42 MHz)  $\delta$  = singlet at -1880 ppm.

# 4.7. X-ray crystal structure for compound $[PtCl(bdtp)](BPh_4) \cdot CH_3CN$

Suitable crystals for X-ray diffraction of compound *cis*- $[PtCl(bdtp)](BPh_4) \cdot CH_3CN$  were obtained through

Table 3

Crystallographic data for [PtCl(bdtp)](BPh<sub>4</sub>) · CH<sub>3</sub>CN

Empireal formula	CHB.Cl.N. D+ S	
Emplicationnula Formula weight	C <sub>82</sub> I 193 <b>D</b> <sub>2</sub> Cl <sub>2</sub> N <sub>11</sub> Fl <sub>2</sub> S <sub>2</sub> 1770 40	
Tomporature (K)	202(2)	
Crystal system	295(2)	
Space group	<i>P</i> 1	
Unit cell almensions	14.446(6)	
$a(\mathbf{A})$	14.446(6)	
b (A)	15.306(6)	
$c(\mathbf{A})$	19.500(4)	
α (°)	88.71(2)	
$\beta$ (°)	74.43(2)	
γ (°)	76.08(2)	
$V(\text{\AA}^3)$	4027(2)	
Ζ	2	
$D_{\text{calc}} (\text{g cm}^{-3})$	1.467	
$\mu (\mathrm{mm}^{-1})$	3.638	
<i>F</i> (000)	1788	
Crystal size $(mm^{-1})$	$0.2 \times 0.1 \times 0.1$	
$\theta$ Range (°)	2.62-30.00	
Index range	$-19 \leq h \leq 20$ ,	
-	$-19 \leq k \leq 19$ ,	
	$0 \le l \le 27$	
Reflexions collected/unique $(R_{int})$	39970/20296 (0.0393)	
Completeness to $\theta$ (%)	86.3	
Absorption correction	empirical	
Data/restraints/parameters	20296/3/917	
Goodness-of-fit	1 188	
Final $R_1$ w $R_2$	0.0469_0.1146	
$R_1$ (all data) $wR_2$	0.0476_0.1152	
Extinction coefficient	0.00310(14)	
Maximum and minimum residual	0.715  and  -0.596	
electron density (e $Å^{-3}$ )	0.715 and -0.590	

crystallisation from an acetonitrile:*n*-pentane solution. A prismatic crystal was selected and mounted on a MAR345 diffractometer with a image plate detector. Unit-cell parameters were determined from 8310 reflections  $(3 \le \theta \le 31^\circ)$  and refined by least-squares method. Intensities were collected with graphite-monochromatised Mo K $\alpha$  radiation. 39970 reflections were measured in the range  $2.62^\circ \le \theta \le 30.00^\circ$ , 20296 of which were non-equivalent by symmetry ( $R_{int}(\text{ on } I) = 0.039$ ). 19908 reflections were assumed as observed applying the condition  $I \ge 2\sigma(I)$ . Lorentz-polarisation but no absorption corrections were made.

The structure was solved by direct methods, using the SHELXS computer program [22], and refined by the fullmatrix least-squares method with SHELX-97 computer programs [23] using 39970 reflections (very negative intensities were not assumed). The function minimised was  $\sum w||F_o|^2 - |F_c|^2|^2$  where  $w = [\sigma^2(I) + (0.0444P)^2 + 6.5332P]^{-1}$ , and  $P = (|F_o|^2 + 2|F_c|^2)/3$ . All H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor and  $R_w(F^2)$  values as well as the number of parameters and other details concerning the refinement of the crystal structure are gathered in Table 3.

#### 5. Supplementary material

CCDC 620335 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc. cam.ac.uk.

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