# Synthesis and characterization of platinum and palladium pyrrolidinedithiocarbamate complexes

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Abstract Treatment of  $(PPh_3)_2MCl_2$  (M = Pd or Pt) with ammonium pyrrolidinedithiocarbamate  $(NH_4S_2CNC_4H_8)$ in a 1:1 molar ratio gave  $(PPh_3)M(Cl)(\kappa^2S,S-S_2CNC_4H_8)$ [M = Pt (1), Pd (2)]. On the other hand, the interaction of these compounds in a 1:2 [M:L] molar ratio gave  $(PPh_3)Pt-(\kappa S-S_2CNC_4H_8)(\kappa^2S,S-S_2CNC_4H_8)$  (3), which contains both terminal and chelated dithiocarbamato ligands, or a yellow insoluble solid for M = Pd. The bis(diphenylphosphino)ethane platinum or palladium dichlorides [(dppe)MCl\_2] reacted with the same ligand to give the salts [(dppe)M-( $\kappa^2S,S-S_2CNC_4H_8$ )]Cl (M = Pt (4), Pd (5) which have only one chelating dithiocarbamato ligand. The new compounds were characterized by <sup>1</sup>H-, <sup>13</sup>C{<sup>1</sup>H}- and <sup>31</sup>P-n.m.r. spectroscopy, mass spectrometry, elemental analysis and X-ray single crystal structure analysis.

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#### Introduction

The dithiocarbamates  $(R_2NCS_2^{-})$  are versatile ligands capable of bonding to transition as well as main group metals [1–4]. They have been widely investigated because of their importance in fields such as the chemical industry, biology and biochemistry [5–10]. Coordination complexes of dithiocarbamato ligands of Ni, Pd and Pt are known in the literature [11–19]. Complexes of Pt(II) and Pd(II) containing dithiocarbamato groups together with mono- or diamine ligands have been described by Faraglia and others [17-20]. These complexes include neutral  $[M(S_2CNR_2)-$ (amine)(Cl)] or cationic complexes such as [M(S<sub>2</sub>CNR<sub>2</sub>)- $(amine)_2$ <sup>+</sup>. Some of these complexes were tested in vitro against KB tumor cells; sub-line of the ubiquitous KER-ATIN-forming tumor cell line Hela. The derivatives  $[M(S_2CNEt_2)(bipy)]^+$  and  $[M(S_2CNEt_2)(phen)]^+$  showed antitumor activity against leukemic cells [21]. The analogous L-methioninol (=Mol)  $[M(S_2CNR_2)(Mol)]^+$  (R = Me, CH<sub>2</sub>CO<sub>2</sub>Et) complexes have been prepared by the reaction of L-methioninol with [M(S<sub>2</sub>CNR<sub>2</sub>)Cl]<sub>n</sub> in a 1:1 molar ratio, while reaction of the same reactants in 1:2 molar ratio gave the binuclear species [M<sub>2</sub>(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>(Mol)Cl<sub>2</sub>] [22].

Complexes of Pd and Pt with mixed tertiary phosphines and dithiocarbamates have also been described by several groups [23–28]. The interaction of  $(Ph_2P(CH_2)_nPPh_2)$ -PdCl<sub>2</sub> (n = 1–4) with  $R_2NCS_2^-$  in acetonitrile gave the chelate complexes [ $(Ph_2P(CH_2)_nPPh_2)PdS_2CNR_2$ ]<sup>+</sup> [23, 26]. The analogous Pt and Ni complexes [ $(Ph_2P(CH_2)_2PPh_2)$ -M( $S_2CNE_2$ )]<sup>+</sup> were made in a similar way [27]. Complexes of Pt(IV) and Pd(II) of the type [Pt( $S_2CNR_2$ )<sub>2</sub>-(PPh<sub>3</sub>)Cl<sub>2</sub>] and Pd( $S_2CNR_2$ )<sub>2</sub>PPh<sub>3</sub> were prepared from the corresponding dichlorides; [Pt( $S_2CNR_2$ )<sub>2</sub>Cl<sub>2</sub>] or [M( $S_2CNR_2$ )<sub>2</sub>] suspended in CS<sub>2</sub>, with phosphines dissolved in toluene [28]. Our effort in this area involves the preparation of CpRu(PPh<sub>3</sub>)(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>) using ammonium pyrrolidinedithiocarbamate and the chloride CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl [29]. The dithiocarboxylates CpRu(PPh<sub>3</sub>)S<sub>2</sub>CR (R = 2-C<sub>4</sub>H<sub>3</sub>O, 2-C<sub>4</sub>H<sub>3</sub>S, C  $\equiv$  CR') have been obtained by a similar substitution reaction [30]. In the present study, we describe the interaction of ammonium pyrrolidinedithiocarbamate with (PPh<sub>3</sub>)<sub>2</sub>MCl<sub>2</sub> and (dppe)MCl<sub>2</sub> (M = Pd, Pt) which gave different products depending on the phosphine ligands and the molar ratio of reactants.

## Experimental

## Materials and methods

All reactions were performed using standard Schlenk and vacuum-line techniques under argon atmosphere. Solvents (Fisher Scientific) were reagent grade, dried and freshly distilled prior to use according to standard methods. Other chemicals (Acros) were used without further purification.

The <sup>1</sup>H-, <sup>13</sup>C{<sup>1</sup>H}- and <sup>31</sup>P{<sup>1</sup>H}-n.m.r. spectra were recorded on either a Bruker AVANCE 200 or 400 MHz spectrometer using the solvent residual peak (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}) or 85 %  $H_3PO_4$  (<sup>31</sup>P{<sup>1</sup>H}) as reference. The mass spectra were recorded with a Finnigan MAT SSQ 710 instrument. Elemental analyses were obtained with a Leco CHNS-932 apparatus.

Preparation of  $(PPh_3)M(Cl)(\kappa^2 S, S-S_2CNC_4H_8)$ (M = Pt (1), Pd (2))

A solution of  $(PPh_3)_2MCl_2$  (0.14 mmol) and ammonium pyrrolidinedithiocarbamate (23 mg, 0.14 mmol) in THF (50 cm<sup>3</sup>) was stirred for 18 h. After filtration, the THF was removed under reduced pressure. The resulting solid was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the solvent was removed under vacuum.

Complex (1) is a known compound [31], and its structure has recently been reported.

(*PPh*<sub>3</sub>)*M*(*Cl*)( $\kappa^2 S, S - S_2 CNC_4 H_8$ ) (2): Crystals suitable for X-ray diffraction analysis were obtained from CHCl<sub>3</sub>/ pentane solutions at 4 °C. Yield: 75 %. <sup>1</sup>H-n.m.r. (CDCl<sub>3</sub>): δ 1.97 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>); 3.55 (t, 4H, 2NCH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J = 6.8 Hz); 7.31–7.64 (m, 15H, PPh<sub>3</sub>). <sup>13</sup>C-n.m.r. (CDCl<sub>3</sub>): δ 25.3 (CH<sub>2</sub>); 48.9 (NCH<sub>2</sub>); 128.2, 131.2, 132.7 (PPh<sub>3</sub>) 202.0 (CS<sub>2</sub>). <sup>31</sup>P-n.m.r. (CDCl<sub>3</sub>): δ 30.6. DEI-MS (*m*/*z*): 629 (M<sup>+</sup>). C<sub>23</sub>H<sub>23</sub>ClN<sub>2</sub>PPdS<sub>4</sub>·0.5CHCl<sub>3</sub> calcd.: C, 46.3; H, 3.9; N, 2.3; S, 10.5 %. Found: C, 46.9; H, 4.4; N, 2.2; S, 10.9 %.

Preparation of  $(PPh_3)Pt(\kappa S, S_2CNC_4H_8)-(\kappa^2 S, S-S_2CNC_4H_8)$  (3)

A solution of (PPh<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub> (0.11 g, 0.14 mmol) and ammonium pyrrolidinedithiocarbamate (46 mg, 0.28 mmol) in THF (50 cm<sup>3</sup>) was stirred for 48 h. After filtration, the THF was removed under reduced pressure. The resulting solid was extracted with CH<sub>2</sub>Cl<sub>2</sub> and extracts concentrated to dryness. Crystals suitable for X-ray diffraction analysis of (3) were obtained by diffusion of pentane into a  $CH_2Cl_2$ solution at 4 °C. Yield: 81 %. <sup>1</sup>H-n.m.r. (CDCl<sub>2</sub>):  $\delta$  1.95 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>); 2.04 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>); 3.60 (t, 4H,  $2NCH_2CH_2$ ,  ${}^{3}J = 6.8$  Hz); 3.91 (t, 4H,  $2NCH_2CH_2$ ,  ${}^{3}J =$ 6.8 Hz); 7.35–7.55 (m, 15H, PPh<sub>3</sub>). <sup>13</sup>C-n.m.r. (CDCl<sub>3</sub>): δ 25.1, 26.1 (CH<sub>2</sub>); 50.8, 55.1 (NCH<sub>2</sub>); 127.6, 129.5, 133.1 (PPh<sub>3</sub>); 200.5 (CS<sub>2</sub>). <sup>31</sup>P-n.m.r. (CDCl<sub>3</sub>): δ 17.43 (<sup>195</sup>Pt satellites,  ${}^{2}J_{PPt} = 4603$  Hz). DEI-MS (*m/z*): 749 (M<sup>+</sup>). C<sub>28</sub>H<sub>31</sub>N<sub>2</sub>PPtS<sub>4</sub>.0.25C<sub>5</sub>H<sub>10</sub>.2CH<sub>2</sub>Cl<sub>2</sub> calcd.: C, 40.0; H, 4.1; N, 3.0; S, 13.7 %. Found: C, 40.4; H, 4.3; N, 2.8; S, 13.4 %.

Preparation of  $[(dppe)M(\kappa^2 S, S-S_2CNC_4H_8)]Cl (4, 5)$ 

A solution of (dppe)MCl<sub>2</sub> (0.19 mmol) and ammonium pyrrolidinedithiocarbamate (32 mg, 0.19 mmol) in THF (50 cm<sup>3</sup>) was stirred at room temperature for 18 h. The resulting yellow mixture was filtrated, and the solvent was evaporated under reduced pressure. The obtained solid was washed several times with hexane and extracted with  $CH_2Cl_2$ . The final product was recrystallized by diffusion of pentane into  $CHCl_3$  solutions at 4 °C.

 $[(dppe)Pt(\kappa^2 S, S-S_2 CNC_4 H_8)]Cl (4)$ 

Yield: 88 %. <sup>1</sup>H-n.m.r. (CDCl<sub>3</sub>):  $\delta$  2.05 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>); 2.89 (d, 4H, PCH<sub>2</sub>, <sup>2</sup>J<sub>HP</sub> = 18.8 Hz); 3.71 (t, 4H, NCH<sub>2</sub> CH<sub>2</sub>, <sup>3</sup>J = 5.8 Hz); 7.44–7.79 (m, 20H, PPh<sub>2</sub>). <sup>13</sup>C-n.m.r. (CDCl<sub>3</sub>):  $\delta$  28.2 (CH<sub>2</sub>); 49.8 (NCH<sub>2</sub>); 49.6 (PCH<sub>2</sub>); 127.3, 129.7, 132.5 (PPh<sub>2</sub>); 200.3 (CS<sub>2</sub>). <sup>31</sup>P-n.m.r. (CDCl<sub>3</sub>):  $\delta$  46.6 (<sup>195</sup>Pt satellites, <sup>2</sup>J<sub>PPt</sub> = 3888 Hz). DEI-MS (*m*/*z*): 739 (M<sup>+</sup>-Cl). C<sub>31</sub>H<sub>32</sub>ClNP<sub>2</sub>PtS<sub>2</sub> calcd.: C, 48.0; H, 4.2; N, 1.8; S, 8.3 %. Found: C, 48.3; H, 4.4; N, 1.6; S, 8.0 %.

 $[(dppe)Pd(\kappa^2 S, S-S_2 CNC_4 H_8)]Cl (5)$ 

Yield: 75 %. <sup>1</sup>H-n.m.r. (CDCl<sub>3</sub>):  $\delta$  1.95 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J = 6.8 Hz); 2.81 (d, 4H, PCH<sub>2</sub>, <sup>2</sup>J<sub>HP</sub> = 22.2 Hz); 3.74 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J = 6.5 Hz); 7.48–7.75 (m, 20H, PPh<sub>2</sub>). <sup>13</sup>C-n.m.r. (CDCl<sub>3</sub>):  $\delta$  28.7 (CH<sub>2</sub>); 53.3 (NCH<sub>2</sub>); 44.0 (PCH<sub>2</sub>); 126.7, 127.5, 128.3 (PPh<sub>2</sub>); 201.6 (CS<sub>2</sub>). <sup>31</sup>P-n.m.r. (CDCl<sub>3</sub>):  $\delta$  63.27. DEI-MS (*m*/*z*): 651 (M<sup>+</sup>-Cl). C<sub>31</sub>H<sub>32</sub>

ClNP<sub>2</sub>Pd S<sub>2</sub>·1.33H<sub>2</sub>O·CHCl<sub>3</sub> calcd.: C, 46.3; H, 4.3; N, 1.7; S, 7.7 %. Found: C, 46.9; H, 4.5; N, 1.7; S, 7.9 %.

#### Structure determination

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K<sub>a</sub> radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects [32–34]. Crystallographic data as well as structure solution and refinement details are summarized in Table 1. The structures were solved by direct methods (SHELXS [35]) and refined by full-matrix least squares techniques against  $F_0^2$ (SHELXL-97 [35]). All hydrogen atom positions were included at calculated positions with fixed thermal parameters. All non-hydrogen and non-disordered atoms were refined anisotropically [35]. The crystals of compound (5) were very small, so the completeness of the data is less than 90 %. Nevertheless, the ratio of data with  $I > 2\sigma(I)$  to parameters is good enough. Compounds (2) and (3) were co-crystallized with disordered solvent molecules. For compound (2), the methylene chloride is disordered of an inversion center. The molecule is refined with occupancy factor of 0.5. For (3), the solvent molecule is co-crystallized with 50 % and is disordered in 2 and 4 positions. The carbon positions were refined isotropically with occupancy factors of 0.25 and 0.25 XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 877671 for (2), CCDC-806387 for (3) and 806388 for (5).

#### **Results and discussion**

Stirring a THF solution of equimolar amounts of  $(PPh_3)_2MCl_2$ and the dithiocarbamato ligand  $(NH_4S_2CNC_4H_8)$  in THF resulted in the formation of the  $(PPh_3)MCl(\kappa^2S,S-S_2CNC_4H_8)$ complexes (Scheme 1).

Complex (1) has been recently described [31] while (2) is new. Complex (2), which has a chloride, one PPh<sub>3</sub> and one chelating dithiocarbamato ligands, has been characterized by spectroscopic methods, elemental analysis and structural determination. The <sup>1</sup>H-n.m.r. spectrum of (2) contains the resonances of the pyrrolidine protons at 1.97 and 3.55 ppm. The multiplet at 7.31–7.64 ppm is due to the phenyl protons. The single P-atom reveals its presence at 30.6 ppm in the <sup>31</sup>P-n.m.r. spectrum of (2). The <sup>13</sup>C-n.m.r. spectrum of (2) showed six resonances corresponding to the six different carbon types, in which the CS2-carbon was observed at 200.5 ppm.

Treating (PPh<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub> with two equivalents of the dithiocarbamato ligand ( $NH_4S_2CNC_4H_8$ ) gave complex (3) which has both terminal and chelating thiocarbamato ligands in addition to one PPh<sub>3</sub> ligand. The analogous reaction of the Pd-species produced only vellow insoluble materials regardless of the reaction solvent. Complex (3) is stable in the solid state and in solution. The <sup>1</sup>H-n.m.r. spectrum of (3) showed the presence of two sets of the two different methylene protons of the pyrrolidine rings. The first set appears as multiplets due to the CH<sub>2</sub> groups remote from the N-atom at 1.95 and 2.04 ppm, while the other set is assigned to the  $CH_2$ groups bonded to nitrogen, appearing as triplets at 3.60 and 3.91 ppm. In the <sup>13</sup>C-n.m.r. spectrum of (3), the methylene carbon atoms also gave different signals, at 25.1 and 26.1 ppm for one set and at 50.8 and 55.1 for the set bonded to nitrogen. In addition, the spectrum contains three peaks for the carbon atoms of the phenyl groups of the PPh<sub>3</sub> ligand and a weak peak at 200.5 ppm for the carbon atom bonded to the two sulfur atoms. In the  ${}^{31}$ P-n.m.r. spectrum of (3), one singlet at 17.43 ppm with platinum satellites ( $J_{P-Pt} =$ 4603 Hz) was observed. The mass spectrum of (3) displayed the molecular ion peak at m/z = 749 g/mol, in addition to peaks resulted from the fragmentation of this molecule.

The reaction of the bis(diphenylphosphino)ethane complexes (dppe)MCl<sub>2</sub> (M = Pt, Pd) with dithiocarbamate afforded the salts  $[(dppe)Pt(\kappa^2 S, S-S_2CNC_4H_8)]Cl$  (4) and  $[(dppe)Pd(\kappa^2 S, S-S_2 CNC_4 H_8)]Cl(5)$ , respectively, as shown in Scheme 2. These complexes are stable both in solution and in the solid state and are soluble in polar organic solvents. The <sup>1</sup>H-n.m.r. spectra of (4) and (5) showed the two methylene groups of the pyrrolidine ring in the ranges of 1.95-2.05 and 3.71-3.74 ppm which are comparable to those of (2) and (3). The ethylene group of the dppe ligand resonates at 2.89 and 2.81 ppm for (4) and (5), respectively. The spectra of (4) and (5) also showed phenyl resonances in the range of 7.44–7.79 ppm. The <sup>13</sup>C-n.m.r. spectra of (4) and (5) showed the methylene groups of the pyrrolidine ring at 28.2 and 49.8 ppm for (4) and at 28.7 and 53.3 ppm for (5), with that of the dppe ligand at 49.6 and 44.0 ppm for (4) and (5), respectively. The spectra also showed a singlet at 200.3 and 201.6 ppm for (4) and (5), respectively, which is assigned to the CS<sub>2</sub>-carbon. The <sup>31</sup>P n.m.r. spectrum of (4) showed a singlet at 46.6 ppm with a Pt-satellites (J<sub>P-Pt</sub> of 3888 Hz) and that of (5) showed a singlet at 63.3 ppm. The mass spectra of (4) and (5) both showed the molecular peak as  $[(dppe)M(S_2CNC_4H_8)]^+$ .

Crystal structures of (2), (3) and (5)

ORTEP views of the complexes (PPh<sub>3</sub>)Pd(Cl)( $\kappa^2 S, S-S_2$ -CNC<sub>4</sub>H<sub>8</sub>) (2), (PPh<sub>3</sub>)Pt( $\kappa S-S_2$ CNC<sub>4</sub>H<sub>8</sub>)( $\kappa^2 S, S-S_2$ CNC<sub>4</sub>H<sub>8</sub>) (3) and [(dppe)Pd( $\kappa^2 S, S-S_2$ CNC<sub>4</sub>H<sub>8</sub>)]Cl, (5) with the atom numbering schemes are shown in Figs. 1, 2, 3, **Table 1** Crystallographic data and refinement details for (PPh<sub>3</sub>)Pd(Cl)( $\kappa^2 S, S-S_2 CNC_4 H_8$ ) (2), (PPh<sub>3</sub>)Pt( $\kappa S, S_2 CNC_4 H_8$ ) ( $\kappa^2 S, S-S_2 CNC_4 H_8$ ) (3) and [(dppe)Pd( $\kappa^2 S, S-S_2 CNC_4 H_8$ )]Cl, (5)

Compound	(2)	(3)	(5)		
Formula	C <sub>23</sub> H <sub>23</sub> CINPPdS, 0.5 CHCl <sub>3</sub>	C <sub>28</sub> H <sub>31</sub> N <sub>2</sub> PPtS <sub>4</sub> , 0.25 C <sub>5</sub> H <sub>10</sub> , 2 CH <sub>2</sub> Cl <sub>2</sub>	[C <sub>31</sub> H <sub>32</sub> NP <sub>2</sub> PdS <sub>2</sub> ] <sup>+</sup> Cl <sup>-</sup> CHCl <sub>3</sub> , 1.25 H <sub>2</sub> O		
fw (g $mol^{-1}$ )	610.05	937.74	828. 37		
<i>T</i> / °C	-140(2)	-90(2)	-140(2)		
Crystal system	Triclinic Triclinic		Monoclinic		
Space group	Pī Pī		P 2 <sub>1</sub> /n		
a/Å	9.5519(2)	9.3394(4)	32.5310(6)		
b/Å	10.0336(3)	14.9178(8)	12.7723(2)		
c/Å	14.5244(4)	15.6487(9)	34.4507(4)		
α/°	88.728(2)	116.102(3)	90		
β/°	87.543(2)	95.682(3)	97.888(1)		
γ/°	63.202(3)	98.091(3)	90		
$V/Å^3$	1241.37(6)	1906.36(17)	14178.7(4)		
Z	2	2	16		
$\rho \text{ (g cm}^{-3})$	1.632	1.634	1.555		
$\mu (\mathrm{cm}^{-1})$	12.62	42.46	10.62		
Measured data	10,849	13,492	56,100		
Data with $I > 2\sigma(I)$	5,214	6,637	15,372		
Unique data/R <sub>int</sub>	5,619/0.2190	8,638/0.0501	25,707/0.0973		
w $R_2$ (all data, on $F^2$ ) <sup>a)</sup>	0.1820	0.1247	0.2279		
$R_1 (I > 2\sigma(I))^{a}$	0.0673	0.0514	0.0741		
s <sup>b)</sup>	1.012	1.039	1.068		
Res. dens./e $Å^{-3}$	1.651/- 2.336	1.138/- 2.358	2.124/- 1.416		
Absorpt method	Multi-scan	Multi-scan	Multi-scan		
CCDC No.	877671	806387	806388		



Scheme 1 Reactions of  $(PPh_3)_2MCl_2$  with  $NH_4S_2CNC_4H_8$  at different molar ratio

Scheme 2 Preparation of the salts  $[(dppe)M(k^2S,S)$ -

S2CNC4H8)]Cl



M = Pt(4), Pd(5)

(2.2886(11) Å) and the Pd–P bond length (2.2853(9) Å) of

respectively. The crystals of these complexes contain solvent molecules which are omitted from the views of Figs. 1, 2, 3. Selected bond distances and angles for the structures of (2), (3) and (5) are summarized in Table 2. These complexes assume a common square planar geometry around the metal center. The Pd–S distance

views of (2) lie within the range found for the complexes (PPh<sub>3</sub>)Pd-(Cl)( $\kappa^2 S, S-S_2 CNEt_2$ ) and (PPh<sub>3</sub>)Pd( $\kappa S-S_2 PPh_2$ )( $\kappa^2 S, S-S_2$ -Table 2. PPh<sub>2</sub>) [36, 37]. The chelate S–Pd–S angle of (2) is contracted to 75.61(4)°, leaving more space for the other angles around Pd which are in the range of 92.99(4)

Fig. 2 ORTEP drawing of  $(PPh_3)Pt(\kappa S, S_2CNC_4H_8)$  $(\kappa^2 S, S - S_2 CNC_4 H_8)$  (3), the ellipsoids represent a probability of 40 %, hydrogen atoms and solvent molecules are omitted for clarity





С9

CI1 C8

**€**С3

C8

C4

(2)		(3)		(5)				
				Molecule	А	В	С	D
Pd-P1	2.2853(9)	Pt-P1	2.2537(17)	Pd-P1	2.2722(2)	2.271(2)	2.2750(2)	2.258(2)
Pd-S2	2.2886(11)	Pt-S3	2.3270(16)	Pd-P2	2.272(2)	2.2663(2)	2.289(2)	2.2827(2)
Pd-Cl1	2.3354(12)	Pt-S1	2.3360(15)	Pd-S1	2.340(2)	2.3514(2)	2.346(2)	2.3449(2)
Pd-S1	2.3503(9)	Pt-S2	2.3603(18)	Pd-S2	2.3603(2)	2.364(2)	2.3601(2)	2.361(2)
S1-C1	1.708(4)	S1-C1	1.725(7)	S1-C1	1.722(7)	1.711(9)	1.724(7)	1.717(9)
S2-C1	1.738(4)	S2-C1	1.716(7)	S2-C1	1.704(8)	1.734(7)	1.716(9)	1.740(7)
N1-C1	1.302(5)	S3-C6	1.740(7)	N1-C1	1.336(9)	1.316(10)	1.316(9)	1.306(10)
		S4-C6	1.692(7)					
P1-Pd-S2	96.57(4)	P1-Pt-S3	89.42(6)	P1-Pd-P2	85.47(8)	84.99(7)	84.73(8)	84.20(7)
P1-Pd-Cl1	94.58(4)	P1-Pt-S1	100.62(6)	P1-Pd-S1	97.21(7)	101.37(7)	96.99(8)	100.13(7)
S2-Pd-S1	75.61(4)	S3-Pt-S2	95.09(6)	P2-Pd-S2	101.32(7)	98.27(7)	102.71(8)	100.45(7)
Cl1-Pd-S1	92.99(4)	S1-Pt-S2	74.77(6)	S1-Pd-S2	75.83(7)	75.63(7)	75.40(7)	75.89(7)
C1-S1-Pd	85.75(13)	C1-S1-Pt	86.9(2)	C1-S1-Pd	84.5(3)	85.5(2)	85.4(3)	85.7(2)
C1-S2-Pd	87.03(15)	C1-S2-Pt	86.3(2)	C1-S2-Pd	84.2(2)	84.7(3)	85.2(2)	84.7(3)

**Table 2** Selected bond lengths (Å) and bond angles (°) of  $(PPh_3)Pd(Cl)(\kappa^2 S, S-S_2CNC_4H_8)$  (2),  $(PPh_3)Pt(\kappa S, S_2CNC_4H_8)(\kappa^2 S, S-S_2CNC_4H_8)$  (3) and  $[(dppe)Pd(\kappa^2 S, S-S_2CNC_4H_8)]Cl$ , (5)

 $-96.57(4)^{\circ}$ . For compound (3), the Pt–S distances of the chelating dithiocarbamate ligand of 2.3360(15) and 2.3603(18) Å are longer than the Pt–S distances (terminal: 2.3270(16) Å) within the same molecules. The Pt–P bond length in (3) is 2.2537(17) Å. These values are also comparable to those found in the diethylcarbamato analog (PPh<sub>3</sub>)Pt- $(\kappa S, S_2 CNEt_2)(\kappa^2 S, S-S_2 CNEt_2)$  [38]. The S–Pt–S chelate angle of 74.61(14)° is smaller than the corresponding S–Pt–S and P–Pt–S bond angles within (3).

The crystals of compound (5) contain four independent molecules, only one of which is shown in Fig. 3. The Pd–S (2.340(2)-2.364(2) Å) and Pd–P (2.289(2)-2.258(2) Å) bond distances for (5) are similar to those found in (2) and other reported systems [36, 37]. Compound (5) contains two chelate rings with S–Pd–S angles of 75.89(7)–75.40(7)°, while the P–Pd–P angle is in the range 84.20(7)-85.47(8)°. The non-chelate P–Pd–S angles are in the range 96.99(8)–102.71(8)°, consistent with a pseudo-square planar structure for this complex.

# Conclusion

The work presented here shows that either the chloro or the triphenylphosphine ligands of  $(PPh_3)_2MCl_2$  can be replaced by the dithiocarbamato ligand. However, only the chloro ligands are replaced by the dithiocarbamato ligand in the case of  $(dppe)MCl_2$  complexes. The X-ray structures of the synthesized complexes show that the bite angle of the dithiocarbamato ligand, which gives a four-membered

chelate ring, is smaller than the angles within the fivemembered dppe chelate ring or the other non-chelated angles.

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