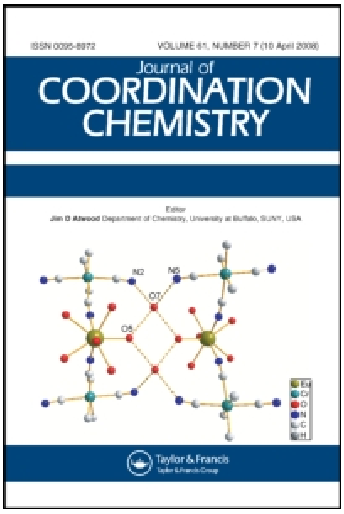

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Palladium(II) Chloride Interaction with Chelating BIS(Phosphine Sulfides). Effect of the Ligand Structure on the Complex Geometry

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PALLADIUM(II) CHLORIDE INTERACTION WITH CHELATING BIS(PHOSPHINE SULFIDES). EFFECT OF THE LIGAND STRUCTURE ON THE COMPLEX GEOMETRY

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Interaction of $PdCl_2$ in chloroform with bis(phosphine sulfides) $Ph_2P(S)–X–P(S)Ph_2$ (X-CH_2, $C(CH_3)_2$, CH_2CH_2, NH, S, and SCH_2S) has been studied. Mechanism of the reaction has been found to vary dramatically with the identity of X. The structures of the resultant complexes were evaluated by UV and IR spectroscopy. Crystal structures were determined by X-ray diffraction for two of the compounds (**A**: $[Ph_2P(S)–(CH_2)_2–P(S)Ph_2]PdCl_2 \cdot CH_3CN$, $P2_1/n$, $Z = 4$, $a = 10.104(2)$, $b = 20.939(4)$, $c = 14.034(3)$ Å, $\gamma = 102.54(2)°$; **B**: $[Ph_2P(S)–N–P(S)Ph_2]_2Pd \cdot 2CHCl_3$, $P\bar{1}$, $Z = 1$, $a = 9.539(1)$, $b = 12.333(3)$, $c = 12.866$ Å, $\alpha = 111.83(2)°$, $\beta = 96.70(3)°$ $\gamma = 99.84(3)°$).

Keywords: Palladium(II) complexes; chelating ligands;
bis(phospine sulfides); crystal structures

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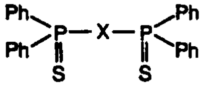
INTRODUCTION

Palladium(II) ions as soft electron acceptors form stable coordination compounds with ligands containing soft phosphorus and sulfur donor atoms[1] which makes such ligands promising for recovery of Pd(II) from wastes. Efficient Pd(II) extractants are esters of thiophosphoric acids[2] and phosphine sulfides.[3,4] Recently, we reported a remarkable Pd(II) extraction ability for chelating bis(phosphine sulfides).[5,6]

Probing the bis(phosphine sulfides) **1–6** as Pd(II) separation agents has revealed that the extraction behavior of these ligands varies significantly with the identity of the bridging moiety –X– between the P=S groups.[6] The most efficient Pd(II) transfer from aqueous chloride solution into chloroform was provided by bis(diphenylthiophosphoryl) alkanes **1–3** that formed multinuclear complexes $L(PdCl_2)_n$ in the organic phase. Surprisingly, ligands **4–6** containing additional soft donor atoms in the –X– unit appear to be weaker Pd(II) extractants than **1–3**. Especially, dramatic loss of binding ability for palladium ions was observed when a thioether moiety was introduced between the P=S groups.



	X
1	CH_2
2	$C(CH_3)_2$
3	CH_2CH_2
4	NH
5	S
6	SCH_2S

Although bis(phosphine sulfides) as a family of chelating agents for transition metal ions has been known for years[7–10] and preparation of the representative Pd(II) complexes with these ligands published,[8–10] the information available in the literature did not explain the observed trends in the extraction behaviors of **1–6** toward Pd(II). Therefore, we studied the effect of bis(phosphine sulfide) structure on the interaction of such ligand with Pd(II) chloride in chloroform, a commonly utilized diluent for solvent extraction.

We now report structures of the complexes resulting from the reactions of **1–6** with $PdCl_2$ in $CHCl_3$ evaluated by means of UV and IR spectroscopy. For two of the Pd(II)-bis(phosphine sulfide) complexes, the molecular structure has been determined by X-ray diffraction.

EXPERIMENTAL

Reagents

Reagent grade $PdCl_2$ purchased from Alfa AESAR was used without purification. Reagent grade chloroform and acetonitrile from Fisher Scientific were purified as described.[11] Bis(phosphine sulfides) **1–5** were prepared according to published procedures.[9,12–14]

Synthesis of Bis(diphenylthiophosphinylthio)methane (6)

As reported[15] earlier, **6** was obtained from potassium diphenyldithiophosphinate and dibromomethane in acetone. Yield 91.5%; m.p. 205°C (2-propanol). Anal. Calcd. for $C_{25}H_{22}P_2S_4$ (%): C 58.59; H 4.30; P 12.11; S 25.00. Found: C 58.24; H 4.42; P 12.12; S 24.95. ^{1}H NMR (C_6D_6): δ 4.92 (t, 2H, CH_2, $^3J_{P-H}$ 15.66 Hz), 7.01 (m, 12H, *m*, *p*-C_6H_5), 7.98 (m, 8H, *o*-C_6H_5). ^{31}P NMR (D_6-acetone): δ 65.5 (s).

General Procedure for Synthesis of Complexes

$PdCl_2$ (0.04 g; 0.2 mmol) was added to a solution of the appropriate bis(phosphine sulfide) (0.2 mmol) in $CHCl_3$ (10 mL) and stored at room temperature. In 1–2 days, the solid was dissolved completely and orange to dark red crystals grew from the colored solution on the walls and bottom of the flask. The crystals were filtered off, washed with $CHCl_3$ and dried *in vacuo*. Yields were 70–80%.

In the case of **5**, several different products, red-orange crystals, dark powder-like solid and an oily residue, separated from the solution. Only the crystals were collected and analyzed.

For **1–4**, the complex preparation procedure was also applied in acetonitrile (with 1 mL ethanol added). The resultant crystalline products had essentially the same melting points and spectral characteristics as those for the complexes obtained in $CHCl_3$. **1·PdCl$_2$**: m.p. 245°C;[5] **2·PdCl$_2$**: m.p. 235°C;[5] **3·PdCl$_2$**: m.p. 225°C, see Crystallography Studies; **Pd{[Ph$_2$P(S)]$_2$N}$_2$**: m.p. 304°C, see Crystallography Studies; **Pd[Ph$_2$P(S)S]$_2$**: m.p. 205°C. Anal. Calcd. for $C_{24}H_{20}P_2S_4Pd$ (%): C 47.7; H 3.31; Pd 17.6. Found: C 48.2; H 3.35; Pd 18.0; **6·(PdCl$_2$)$_2$**: m.p. 165–170°C (decomp). Anal. Calcd. for $C_{25}H_{22}P_2S_4Pd_2Cl_4$ (%): C 34.6; H 2.54; Pd 24.5. Found: C 34.8; H 2.52; Pd 24.2.

Spectral Measurements

UV absorption spectra were recorded with a Specord M-40 (Karl Zeiss, Jena) spectrometer. IR spectra (KBr pellets) were measured with a Specord 75-IR (Karl Zeiss, Jena) spectrometer.

Characterization of the complexes by ^{1}H NMR spectroscopy (200 MHz, $CDCl_3$, 297 K) was attempted with use of an IBM AF-200 spectrometer; however, the NMR spectra were uninformative due to significant broadening of the signals. Since square-planar complexes of Pd(II) are diamagnetic, the observed broadening is believed to arise from fast exchange processes rather than the metal ion properties.

Crystallography Studies

Crystals of **3** · $PdCl_2$ (Structure **A**) suitable for X-ray were grown from an acetonitrile solution of the complex. Crystals of $Pd\{[Ph_2P(S)]_2N\}_2$ were obtained from the complex solutions in chloroform (Structure **B**) and acetonitrile (Structure **C**). Crystallographic parameters are summarized in Table I.

The lattice parameters were obtained by least squares refinement for 22 automatically centered reflections with $12° < \theta < 13°$. Experimental data were collected on four-circle Enraf-Nonius CAD-4 diffractometer using the $\omega/2\theta$ scan technique. The structures were solved by the Patterson method[16]

TABLE I Summary of crystallographic parameters

	Compound		
	3 · $PdCl_2$	$Pd\{[Ph_2P(S)]_2N\}_2$	$Pd\{[Ph_2P(S)]_2N\}_2$
Structure	**A**	**B**	**C**
Unit content	$(C_{26}H_{22}P_2S_2)PdCl_2 \cdot CH_3CN$	$(C_{24}H_{20}NP_2S_2)_2Pd \cdot 2CHCl_3$	$(C_{24}H_{20}NP_2S_2)_2Pd$
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
z	4	1	2
Cell parameters			
a (Å)	10.104(2)	9.539(1)	10.194(3)
b (Å)	20.939(4)	12.333(3)	10.543(3)
c (Å)	14.034(3)	12.866(4)	25.192(5)
α (°)		111.83(2)	84.43(3)
β (°)	102.54(2)	96.70(3)	88.3(3)
γ (°)		99.84(3)	65.65(3)
Volume (Å^3)	2898.3(20)	1357.3(15)	
$R1$ $[I > 2\sigma(I)]/R1$ (all data)	0.038/0.049	0.047/0.073	
$Rw2$ $[I > 2\sigma(I)]/Rw2$ (all data)	0.091/0.097	0.12/0.14	
GooF	1.05	1.04	

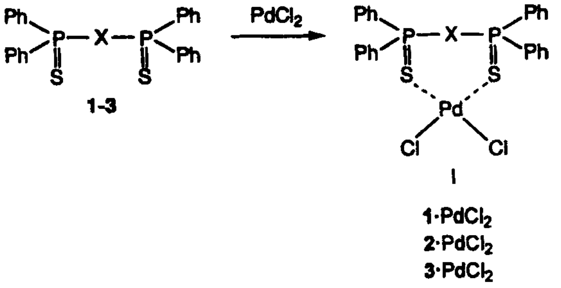
with successive Fourier synthesis. Because low quality data were available for Structure C (fast crystal destruction under the X-ray), refinement was not attempted in this case. All (but hydrogen) atoms of A and B were refined in anisotropic approximation using SHELXL-93.[17a] At the final step of refinement for Structure A with restricted phenyl rings, SHELXL-97[17b] was employed. The geometrically constrained hydrogen atoms were placed in calculated positions and allowed to ride on carbon atoms with fixed isotropic temperature factors ($u = 0.08$).

RESULTS AND DISCUSSION

Interaction of $PdCl_2$ with Bis(Phosphine Sulfides) in Chloroform

Interaction of $PdCl_2$ with the chelating ligands **1**–**6** in chloroform was expected to proceed in accordance with Scheme 1. Indeed, when solid $PdCl_2$ was added to solutions of bis(diphenylthiophosphoryl) alkanes **1**–**3** in $CHCl_3$, it dissolved to give red solutions from which, in a few days, dark-red crystalline products precipitated. These were identified by elemental analysis as complexes $L \cdot PdCl_2$ (earlier, compounds $\mathbf{1} \cdot PdCl_2$[7–9] and $\mathbf{3} \cdot PdHal_2$[10] with Hal = Cl and Br were obtained in a different way).

Complexes $\mathbf{1} \cdot PdCl_2$, $\mathbf{2} \cdot PdCl_2$, and $\mathbf{3} \cdot PdCl_2$ show similar absorption spectra with two intense bands at 38 000 and 31 500 cm^{-1} attributed to the charge transfers Cl → Pd and S → Pd, respectively, in agreement with the earlier published data for square-planar complexes with $[PdS_2Cl_2]$ chromophore.[5,9,18,19] In the IR spectra of these compounds (Table II), $\nu_{P=S}$ are shifted by 43–45 cm^{-1} relative to the spectra of the parent ligands. Evidently Pd(II) is coordinated with two sulfur atoms of the thiophosphoryl groups. Since the complexes are non-electrolytes in acetonitrile solution, both of the



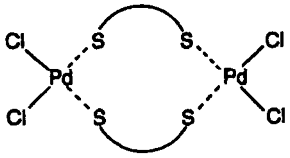
SCHEME 1

TABLE II Selected vibrations (cm^{-1}) in the IR spectra (KBr) of **3**–**6** and the corresponding Pd(II) complexes

Compound	*Vibration*	*Attribution*[a]
3	600	$\nu_{P=S}$
3·$PdCl_2$	557	$\nu_{P=S}$
4	3033	ν_{NH}
	913	ν^{as}_{P-N-P}
	615	ν^{s}_{P-N-P}
	600	$\nu_{P=S}$
$Pd\{[Ph_2P(S)]_2N\}_2$	1150	$\nu_{P=N}$
	813	ν_{P-N}
	553	$\nu_{P=S}$
5	733	ν^{as}_{P-S-P}
	633	$\nu_{P=S}$
	600	ν^{s}_{P-S-P}
$Pd[Ph_2P(S)S]_2$	653	$\nu^{as}_{PS_2}$
	566	$\nu^{s}_{PS_2}$
6	680	ν_{S-CH_2}
	647	$\nu_{P=S}$
6·$(PdCl_2)_2$	665	ν_{S-CH_2}
	573	$\nu_{P=S}$

[a] In accordance with Ref. [20].

Cl^- anions must be coordinated. Therefore, Pd(II) in the complexes L·$PdCl_2$ is assumed to be incorporated into six-membered (for **1** and **2**) or seven-membered (for **3**) chelates as shown in structure I, Scheme 1. For **3**·$PdCl_2$, the contrasting geometry (structure II) with two $PdCl_2$ species coordinated by two bridging ligands was suggested earlier.[10]



II

We determined the crystal structure of **3**·$PdCl_2$ (Figure 1) in which the presence of a seven-membered chelate cycle is clearly evident. The structure is discussed in detail in the section Crystal Structures.

Further investigation of the interaction of $PdCl_2$ with the bis(phosphine sulfides) in $CHCl_3$ has revealed that the reaction mechanism changes radically when heteroatoms, N or S, are introduced in the bridge between the P=S groups. Thus, bis(diphenylthiophosphoryl) amine **4** in this reaction produced a dark-red crystalline product which, in $CHCl_3$ solution, showed a distinctive absorption spectrum with a broad charge transfer band at 33 000–31 000 cm^{-1} and a shoulder at 22 000 cm^{-1}. The P=S vibrations in

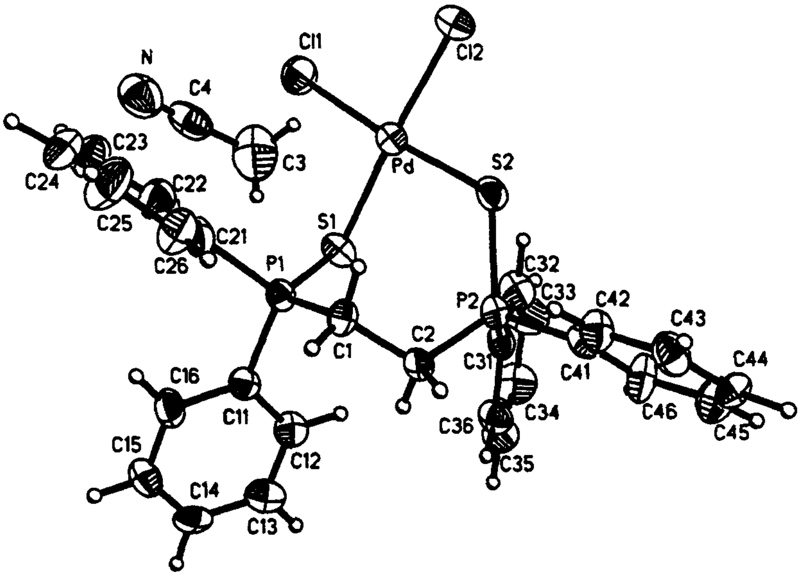


FIGURE 1 An ORTEP diagram for the crystal structure of complex $3 \cdot PdCl_2$ (A).

the IR spectrum, were shifted by 47 cm^{-1} relative to the corresponding band in the spectrum of the parent ligand 4 (Table II) analogously to those in the complexes $1 \cdot PdCl_2$, $2 \cdot PdCl_2$, and $3 \cdot PdCl_2$. This indicates coordination of Pd(II) with sulfur atoms of the P=S groups. Instead of the bands at 3033 (ν_{NH}), 913 (ν^{as}_{P-N-P}), and 615 cm^{-1} (ν^{s}_{P-N-P}) in the IR spectrum of 4, intense vibrations of a P−N=P group[20] were observed in the spectrum of the corresponding Pd(II) complex.

X-ray diffraction was used to determine the molecular structure of the compound. As shown in Figure 2, the compound is a bis-chelate complex $Pd\{[Ph_2P(S)]_2N\}_2$ (see section Crystal Structures for the detailed discussion of the structure).

In earlier work,[21] to obtain $Pd\{[Ph_2P(S)]_2N\}_2$, ligand 4 was deprotonated and reacted with $PdCl_2$ as the potassium salt $K[Ph_2P(S)]_2N$ (see Scheme 2). The present study demonstrated that Pd(II) coordinated with the P=S groups of bis(phosphine sulfide) 4 possesses sufficient electron-withdrawing strength to promote dissociation of the ligand NH proton. The deprotonated ligand, $[Ph_2P(S)]_2N^-$, obviously stabilized by the charge delocalization between the two P=S groups and amine nitrogen, chelated the Pd(II) cation as shown in structure III (Scheme 2).

Reaction of Pd(II) chloride with bis(diphenylthiophosphoryl) sulfide 5, a reaction reported earlier to not occur,[9] gave a series of products

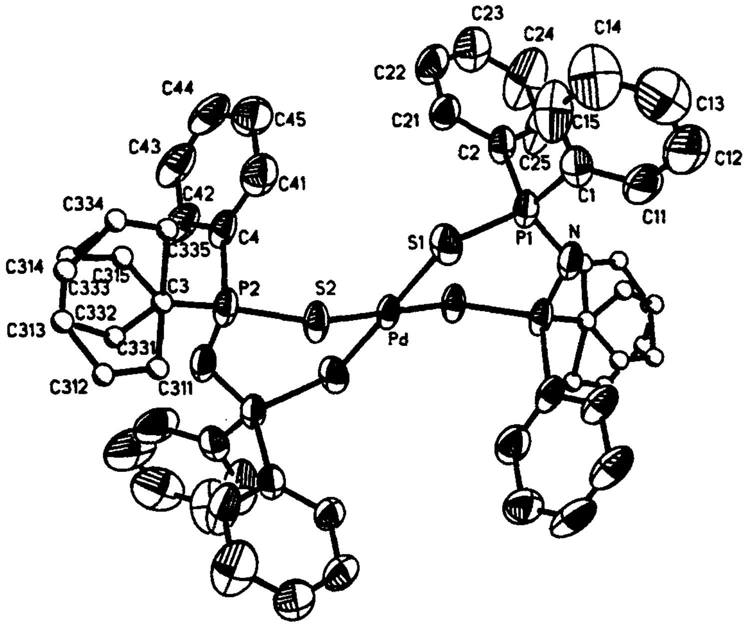
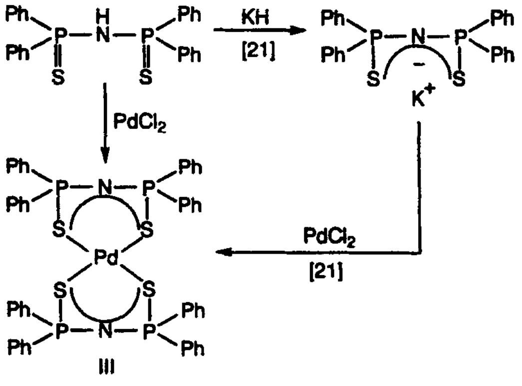
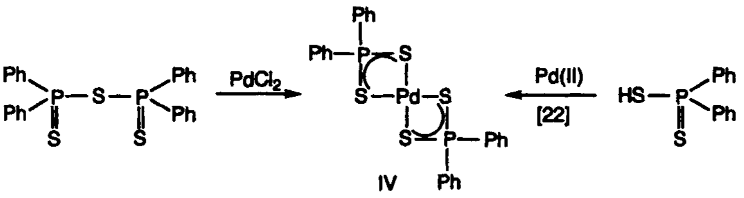


FIGURE 2 An ORTEP diagram for the crystal structure of complex Pd{[Ph$_2$P(S)]$_2$N}$_2$ (B) with hydrogen atoms and solvent molecules omitted for clarity and thermal ellipsoids for the disordered phenyl rings not shown.

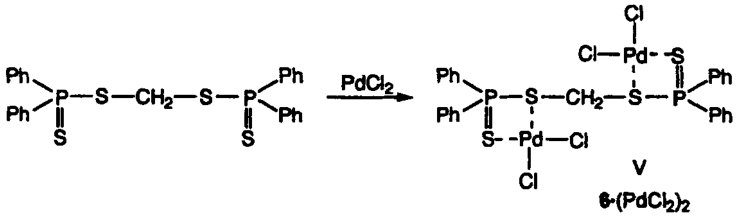


SCHEME 2

(see Experimental section) from which only one, bright red-orange crystals, was examined. By elemental analysis, the compound was identified as a bis-chelate complex Pd[Ph$_2$P(S)S]$_2$ (Scheme 3) which was obtained previously[22] from the corresponding acid, Ph$_2$P(S)SH. IR (Table II) and UV spectra (ν_{max} 31 900 cm^{-1}, S → Pd) of Pd[Ph$_2$P(S)S]$_2$ suggest the presence of two



SCHEME 3



SCHEME 4

four-membered chelate cycles (structure IV) in this intra-complex compound. Obviously, the destruction of **5** upon its interaction with $PdCl_2$ is another indication of the strong electron-withdrawing effect of Pd(II).

In contrast with **5**, less-polarized C–S bonds in the bridging fragment between the P=S groups of ligand **6** did not rupture on interaction with $PdCl_2$. Complex $\mathbf{6}\cdot(PdCl_2)_2$ was formed instead (Scheme 4). Based on the UV spectrum of this compound in $CHCl_3$ (ν_{max} 38 500 and 31 880 cm^{-1}, chromophore $[PdS_2Cl_2]$), and changes observed in the IR spectrum of $\mathbf{6}\cdot(PdCl_2)_2$ relative to the spectrum of the parent ligand (Table II), the complex was ascribed geometry V shown in Scheme 4.

Therefore, the mechanism of $PdCl_2$ interaction with bis(phosphine sulfide) in chloroform varies as the ligand structure is altered. This explains the earlier contrasting extraction behaviors of **1**–**6** for Pd(II).[6] Thus, bis(diphenylthiophosphoryl) alkanes **1**–**3** provide the most efficient Pd(II) chloride separation from aqueous solution into $CHCl_3$ since they form stable six- and seven-membered chelate complexes $L\cdot PdCl_2$ which are capable of adding $PdCl_2$ to give the multinuclear species $L(PdCl_2)_n$.[6] Bis(diphenylthiophosphoryl) amine **4** which deprotonates on interaction with $PdCl_2$ to form bis-chelate complex $Pd\{[Ph_2P(S)]_2N\}_2$, exhibits smaller Pd(II) loading relative to that of **1**–**3**. Although the geometry of $Pd\{[Ph_2P(S)]_2N\}_2$ with charge-delocalization must provide the thermodynamic stability of the complex, it does not suggest formation of multinuclear species, unlike the geometry of $L\cdot PdCl_2$ complexes with L = **1**–**3**. Bis(diphenylthiophosphoryl) sulfide **5** is destroyed on interaction with $PdCl_2$ which interferes with Pd(II) extraction from aqueous chloride solution by this ligand. For compound **6** containing a $S{-}CH_2{-}S$ bridge between two P=S groups, a diminished extraction ability for Pd(II) relative to that of **1–3** may arise from the lower thermodynamic stability of the four-membered chelate cycles in $\mathbf{6} \cdot (PdCl_2)_2$ (structure V) compared with that of the six- and seven-membered chelate complexes $L \cdot PdCl_2$ of **1–3** (structure I).

Crystal Structures

Compounds $\mathbf{3} \cdot PdCl_2$ (Structure **A**, Figure 1) and $Pd\{[Ph_2P(S)]_2N\}_2$ (Structure **B**, Figure 2) exist in the crystal as molecular complexes solvated by acetonitrile and chloroform, respectively. In contrast, crystals of the complex $Pd\{[Ph_2P(S)]_2N\}_2$ grown from acetonitrile (Structure **C**) do not contain solvent molecules. Selected bond lengths and angles are presented in Table III.

In all three of the crystal structures, square-planar coordination of Pd(II) is observed. In **A** and **C**, Pd atoms deviate from the mean plane of four donor atoms by 0.05 and 0.03 Å, respectively. In **B**, Pd occupies a center of symmetry. Pd–S distances in **A** are slightly shorter than those in **B** and **C** (in the latter, Pd–S bonds are 2.36–2.37 Å). P–S separations in **A**, **B**, and **C** are close to those observed for the complexes with the $S{=}PR_3$ ligands.[23] Also typical for the phosphine sulfide complexes are the P–C distances. As expected for the conjugated $P \mathrel{\overset{\cdots}{-}} N \mathrel{\overset{\cdots}{-}} P$ system, all of the P–N distances in **B** are significantly shorter than the corresponding single bond and almost as

TABLE III Selected bond lengths (Å) and angles (°) in the structures of complexes $\mathbf{3} \cdot PdCl_2$ (**A**) and $Pd\{[Ph_2P(S)]_2N\}_2$ (**B**)

Bond type	*Bond*	*Bond length*		*Bond Angle*	*Angle value*	
		A	**B**		**A**	**B**
Pd–S	Pd–S1	2.309(2)	2.329(2)	S1–Pd–S2	97.59(9)	80.86(5)
	Pd–S2	2.304(3)	2.3435(13)	S1–Pd–S2(a)		99.14(5)
Pd–Cl	Pd–Cl1	2.318(3)		Cl1–Pd–Cl2	91.22(9)	
	Pd–Cl2	2.332(2)		S1–Pd–Cl1	88.31(9)	
P–S	P1–S1	1.995(3)	2.026(2)	S2–Pd–Cl2	83.03(8)	
	P2–S2	2.019(3)	2.028(2)	S1–Pd–Cl2	173.03(6)	
P–N	P1–N		1.589(5)	S2–Pd–Cl1	174.02(6)	
	P2–N		1.599(6)	Pd–S1–P1	105.16(7)	109.94(9)
P–C	P1–C1	1.804(9)	1.800(7)	Pd–S2–P2	113.67(8)	103.65(7)
	P1–C2		1.810(5)	S1–P1–N		118.1(2)
	P2–C2	1.819(7)		S2–P2–N(a)		116.0(2)
	P2–C3		1.805(6)	S1–P1–C1	112.1(2)	
	P2–C4		1.802(6)	S2–P2–C2	113.8(3)	

long as the aromatic P=N bond (1.58 ± 0.02 Å).[24] The bond angles around P atoms are close to tetrahedral.

CONCLUSIONS

The geometry of complexes obtained through interaction of $PdCl_2$ with chelating bis(phosphine sulfides) **1–6** in chloroform varies dramatically when the structure of the bridging unit –X– between the P=S groups is altered. Due to strong electron-withdrawing by Pd(II) coordinated with the ligand *via* the thiophosphoryl groups, dissociation of the NH-group proton of **4** and rupture of the P–S bonds in **5** takes place.

Acknowledgments

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Supporting Information

Tables of the crystallographic parameters, atomic coordinates and equivalent isotropic displacement parameters, bond length and angles, observed and calculated structure factors (36 pages) are available from GTT.

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