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Synthesis and crystal structure of palladium(II) complexes with 2-[3-(diphenylphosphino)propyl]thiophene

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Abstract

The reaction of 2-[3-(diphenylphosphino)propyl]thiophene (**P-S3**) with equimolar amount of dichlorobis(benzonitrile)palladium(II) [$PdCl_2(PhCN)_2$] afforded the binuclear complex *trans*-[Pd(μ-Cl)Cl(P-S3)]$_2$ (**I**) with the **P-S3** acting as a monodentate ligand bonded through the phosphorus atom. However, when **P-S3** was allowed to react with dichlorobis(benzonitrile)palladium(II) in a 2:1 molar ratio, the monomeric complex *trans*-[$PdCl_2$(P-S3)$_2$] (**II**) has been isolated. Complex **II** was also isolated from the reaction of complex **I** and **P-S3** ligand in a 1:2 molar ratio. Complexes **I** and **II** and **P-S3** were characterized by elemental analysis, ^1H, ^{13}C and ^{31}P NMR. Single crystal X-ray structures of **I** and **II**, which crystallize in the triclinic space group $P\bar{1}$, have been determined.

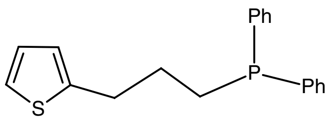
Keywords: Binuclear complexes; Palladium complexes; Hemilabile ligands; P–S ligands

1. Introduction

Chelating ligands with mixed donors that differ in their coordination abilities are called hemilabile ligands [1]. Among the important features of these ligands are their ability to provide vacant coordination site at the metal center during reactions and to stabilize reactive intermediates [2]. With these characteristics, metal complexes having hemilabile ligands have shown improved catalytic activity in many homogenous catalytic processes including hydrogenation [3], alternating CO/olefin copolymerization [4] and ring-opening polymerization [5]. Another interesting characteristic of the hemilabile ligands came from the *trans* effect resulting from the different donor/acceptor properties of the chelating atoms which is found to be effective in the control of certain stereoselective reactions [6,7].

Hemilabile ligands combining phosphorus and sulfur donor sites [8] form stable metal complexes and exhibit different modes of bonding, depending on the carbon backbone between the phosphorus and sulfur atoms and the chemical nature of the sulfur atom [9–11]. In a previous work, palladium complexes with phosphorus-sulfur ligands have been prepared and their catalytic activity towards cyclic olefin polymerization were investigated [12–14].

Herein, we report on the preparation of palladium complexes with the phosphorus–sulfur ligand that combine tertiary phosphine and thiophene, 2-[3-(diphenylphosphino)propyl]thiophene (**P-S3**). The palladium complexes obtained were characterized by ^1H, ^{13}C, ^{31}P NMR and single crystal X-ray analysis.



P-S3

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2. Experimental

2.1. General

All procedures were performed under an atmosphere of dry, purified nitrogen using standard Schlenk techniques. Solvents were distilled and dried by standard methods [15]. Thiophene and 1-bromo-3-chloropropane were purchased from Across. *n*-Butyllithium (1.55 M solution in hexane) was purchased from Aldrich. Potassium diphenylphosphide (0.5 M solution in THF) and palladium(II) chloride were purchased from Fluka. Benzonitrile was purchased from Wardle Chemicals. $[PdCl_2(PhCN)_2]$ [16], and 2-(3-chloropropyl)thiophene [17,18] were prepared as reported. The IR Spectra were recorded, as KBr discs, on Nicolet Impact-400 FT-IR spectrometer. The NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer using TMS as internal reference. The chemical shifts for the ^{31}P NMR spectra are relative to external H_3PO_4. Melting points were determined with Philip-Harris melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratories of AL al-Bayt University, Jordan.

2.2. Syntheses

2.2.1. Preparation of 2-[3-(diphenylphosphino)propyl]-thiophene (**P-S3**)

The compound was prepared following literature procedure [17,18] with modifications. A solution of 2-(3-chloropropyl)thiophene (8.0 g, 0.05 mol) in dry THF (50 mL) was introduced into a 250-mL three-necked round bottomed flask equipped with a nitrogen inlet, dropping funnel, and a condenser that is connected to an oil bubbler. A solution of potassium diphenylphosphide (100 mL of 0.5 M, 0.05 mol) was then slowly added at −45 °C. After the addition was complete, the cooling bath was removed and the reaction mixture was stirred for 2 h at room temperature. Solvent was completely removed under reduced pressure. The residue was dissolved in diethyl ether (100 mL), and the ether solution was washed with distilled water (2 × 100 mL). The ether layer was dried over anhydrous sodium sulfate over night. After filtration, ether was removed under reduced pressure, and the thick yellow residue was dissolved in methanol (50 mL). When the solution was stored at 0 °C a white precipitate was formed. The precipitate was filtered, washed three times with cold methanol, and dried under vacuum at room temperature. Yield: 14.3 g (92%). White powder; m.p. 65–67 °C. Selected IR bands (KBr pellet, cm^{-1}): 3071 (m), 3050 (m), 2931 (m), 2856 (m), 1120 (s) (P–Ph). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.81$ (m, 2H, $-CH_2C\boldsymbol{H}_2CH_2P-$), 2.09 (m, 2H, $-C\boldsymbol{H}_2P-$), 2.94 (t, $J = 13.5$ Hz, 2H, $-C\boldsymbol{H}_2CH_2CH_2P-$), 6.75 (d, $J = 3.1$ Hz, $1H_{thiophene}$), 6.89 (t, $J = 4.2$ Hz, $1H_{thiophene}$), 7.10 (d, $J = 5.0$ Hz, $1H_{thiophene}$), 7.31–7.76 (m, 10H, H_{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$): δ: ($C_{aliphatic}$) 27.3 (d, $^2J_{C-P} = 11.5$ Hz, 1C), 28.0 (d, $^1J_{C-P} = 17.0$ Hz, 1C), 31.2 (d, $^3J_{C-P} = 13.5$ Hz, 1C); δ: ($C_{thiophene}$) 123.2 (s, 1C), 124.5 (s, 1C), 126.8 (s, 1C), 144.6 (s, 1C); δ: (C_{phenyl}) 128.5 (d, $^3J_{C-P} = 6.6$ Hz, 4C), 128.6 (s, 2C), 132.8 (d, $^2J_{C-P} = 18.3$ Hz, 4C), 138.6 (d, $^1J_{C-P} = 12.5$ Hz, 2C). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -12.25$.

2.2.2. Preparatiom of *trans*-$[Pd(\mu\text{-}Cl)Cl(P\text{-}S3)]_2$ (***I***)

A sample of **P-S3** (0.31 g, 1.0 mmol) in dry benzene (20 mL) was slowly added to a filtered solution of $[PdCl_2(PhCN)_2]$ (0.40 g, 1.0 mmol) in dry benzene (30 mL). The solution was stirred for 1 h at room temperature. During that time, the solution changed color gradually from dark brown to orange. Solvent was removed under reduced pressure till a volume of about 10 mL. Upon addition of pet. ether (boiling range of 40–60 °C), an orange precipitate was separated, the product was recrystallized from CH_2Cl_2/pet. ether, washed with pet. ether and dried under vacuum at 50 °C. Yield: 0.48 g (92%). Orange solid; m.p. 225–227 (dec). Selected IR bands (KBr pellet, cm^{-1}): 3056 (m), 2936 (m), 2896 (m), 1102 (s) (P–Ph). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.89$ (m, 4H, $-CH_2C\boldsymbol{H}_2CH_2P-$), 2.50 (m, 4H, $-C\boldsymbol{H}_2P-$), 2.87 (t, $J = 7.2$ Hz, 4H, $-C\boldsymbol{H}_2CH_2CH_2P-$), 6.69 (d, $J = 2.8$ Hz, $2H_{thiophene}$), 6.87 (dd, $J = 3.4$, 5.1 Hz, $2H_{thiophene}$), 7.07 (d, $J = 5.1$ Hz, $2H_{thiophene}$), 7.22–7.68 (m, 20H, H_{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$): δ: ($C_{aliphatic}$) 25.9 (s, 2C), 26.5 (d, $^1J_{C-P} = 35.9$ Hz, 2C), 30.5 (d, $^3J_{C-P} = 17.5$ Hz, 2C); δ: ($C_{thiophene}$) 123.5 (s, 2C), 124.9 (s, 2C), 126.9 (s, 2C), 143.1 (s, 2C); δ: (C_{phenyl}) 127.7 (s, 4C), 128.8 (d, $^3J_{C-P} = 11.9$ Hz, 8C), 131.4 (s, 4C), 133.3 (d, $^2J_{C-P} = 10.2$ Hz, 8C). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 31.81$. *Anal.* Calc. for $[C_{38}H_{38}Cl_4P_2Pd_2S_2]$ (975.34): C, 46.79; H, 3.93; S, 6.57. Found: C, 46.23; H, 3.66; S, 5.51%.

2.2.3. Preparation of *trans*-$[PdCl_2(P\text{-}S3)_2]$ (***II***)

A filtered solution of $[PdCl_2(PhCN)_2]$ (0.40 g, 1.0 mmol) in dry benzene (30 mL) was slowly added to a sample of **P-S3** (0.78 g, 2.5 mmol) in dry benzene (20 mL). The solution was stirred for 1 h at room temperature. Solvent was removed under reduced pressure till a volume of about 10 mL. Upon addition of pet. ether (boiling range of 40–60 °C), a yellow precipitate was formed. The product was collected, recrystallized from CH_2Cl_2/pet. ether washed with pet. ether and dried under vacuum at 50 °C. Yield: 0.50 g (60%). Yellow solid; m.p. 143–144 °C. Selected IR bands (KBr pellet, cm^{-1}): 3081 (m), 3051 (m), 2919 (m), 1431 (s), 1105 (s) (P–Ph). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.88$ (m, 4H, $-CH_2C\boldsymbol{H}_2CH_2P-$), 2.50 (m, 4H, $-C\boldsymbol{H}_2P-$), 2.87 (t, $J = 7.2$ Hz, 4H, $-C\boldsymbol{H}_2CH_2CH_2P-$), 6.68 (d, $J = 2.7$ Hz, $2H_{thiophene}$), 6.86 (dd, $J = 3.4$, 5.1 Hz, $2H_{thiophene}$), 7.07 (dd, $J = 1.1$, 5.1 Hz, $2H_{thiophene}$), 7.34–7.73 (m, 20H, H_{phenyl}). $^{13}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 17.53$. *Anal.* Calc. for $[C_{38}H_{38}Cl_2P_2PdS_2]$ (798.04): C, 57.19; H, 4.80; S, 8.04. Found: C, 57.21; H, 4.79; S, 8.08%.

2.3. Reaction of compound *I* with *P-S3*

To an orange solution of **I** (0.40 g, 0.41 mmol) in dry $CHCl_3$ (30 mL) was slowly added a solution of **P-S3** (0.31 g, 1.0 mmol) in dry $CHCl_3$ (20 mL). The solution was stirred for 2 h at room temperature. During that time, the solution changed color gradually from orange to yellow. Solvent was removed under reduced pressure till a volume of about 10 mL. Upon addition of pet. ether (boiling range of 40–60 °C), a precipitate was separated, washed with pet. ether and dried under vacuum at 50 °C. The product was characterized by its melting point and ^{1}H NMR and found to be identical to compound **II**.

2.4. Crystal structure determination of *trans-[Pd(μ-Cl)Cl(P-S3)]$_2$ (I)*

A suitable single crystal (yellow platelets) of compound **I** was selected for collecting X-ray data. All measurements were made at 293(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3° per frame for 5 s, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART [19] software and refined using SAINTPLUS [20] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPLUS software. Absorption corrections were applied using SADABS [21]. The structure was solved by direct methods and refined by least squares method on F^2 using the SHELXTL program package [22]. The structure was solved in the space group $P\bar{1}$ (#2) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. The thiophene group was rotationally disordered and refined in two positions with refined occupancies of 49:51%. Bond lengths and thermal parameters were loosely restrained. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information. Hydrogen atoms were placed geometrically and refined with a riding model, with U_{iso} constrained to be $1.2U_{eq}$ of the carrier atom.

2.5. Crystal structure determination of *trans-[PdCl$_2$(P-S3)$_2$] (II)*

A suitable crystal (yellow parallelopiped) of compound **II** was selected, attached to a glass fiber and data were collected at 293(2) K using a syntax diffractometer "upgraded to Bruker's P4 specifications" instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low temperature device. Collection and treatment of data were done similar to compound **I** with the exception that cell parameters were retrieved and refined using XSCANS [23] software on all observed reflections. Data reduction and correction for Lp and decay were performed using the SHELXTL [22] software. Absorption corrections were applied using psi scans. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

Table 1
Crystal data for complexes *trans*-[Pd(μ-Cl)Cl(P-S3)]$_2$ (**I**) and *trans*-[PdCl$_2$(P-S3)$_2$] (**II**)

Parameter	[Pd(μ-Cl)Cl(P-S3)]$_2$ (**I**)	[PdCl$_2$(P-S3)$_2$] (**II**)
Chemical formula	$C_{38}H_{38}Cl_4P_2Pd_2S_2$	$C_{38}H_{38}Cl_2P_2PdS_2$
Formula weight	975.34	798.04
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	9.3962(19)	7.9828(10)
b (Å)	9.954(2)	10.699(2)
c (Å)	11.100(2)	10.9374(19)
α (°)	84.62(3)	91.761(17)
β (°)	77.96(3)	105.217(5)
γ (°)	73.51(3)	96.463(14)
V (Å^3)	972.9(4)	893.9(3)
Z	1	1
D_{calc} (Mg/m^3)	1.665	1.483
Absorption coefficient (mm^{-1})	1.416	0.902
$F(000)$	488	408
Crystal dimensions (mm)	0.40 × 0.20 × 0.05	0.40 × 0.30 × 0.15
θ Range for data collection (°)	1.88–25.25	1.92–25.50
Index ranges	$-11 \leqslant h \leqslant 11$, $-11 \leqslant k \leqslant 11$, $-3 \leqslant l \leqslant 13$	$-9 \leqslant h \leqslant 1$, $-12 \leqslant k \leqslant 12$, $-13 \leqslant l \leqslant 13$
Reflections collected	14345	4081
Independent reflections [R_{int}]	3527 [0.0250]	3293 [0.0000]
Data/restraints/ parameters	3527/10/224	3318/0/205
Goodness-of-fit on F^2	1.046	1.068
Final R indices [$I > 2\sigma(I)$]	$R_1^a = 0.0268$, $wR_2^b = 0.0676$	$R_1 = 0.0337$, $wR_2 = 0.0878$
R indices (all data)	$R_1 = 0.0301$, $wR_2 = 0.0699$	$R_1 = 0.0393$, $wR_2 = 0.0915$
Largest difference in peak and hole (e Å^{-3})	0.543 and −0.468	0.709 and −0.475

[a] $R_1 = \sum\{|F_o| - |F_c|\}/\sum|F_o|$.
[b] $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{0.5}$.

3. Results and discussion

3.1. Syntheses

The phosphorus–sulfur ligand, 2-[3-(diphenylphosphino)propyl]thiophene (**P-S3**), was prepared *via* reaction of 2-(3-chloropropyl)thiophene [17,18] with potassium diphenylphosphide in dry THF. The product was collected and recrystallized several times from methanol. It was fully characterized by its IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The ^{1}H NMR spectrum of **P-S3** shows, in addition to the signals due to phenyl protons, two multiplets centered at $\delta = 1.81$ (–CH$_2$C***H***$_2$CH$_2$P–) and 2.09 (–C***H***$_2$P–), and a triplet centered at $\delta = 2.94$ (–C***H***$_2$CH$_2$CH$_2$P–). The three protons of thiophene appear as two doublets centered at $\delta = 6.75$, 7.10 and a triplet centered at $\delta = 6.89$. The ^{13}C NMR spectrum of **P-S3** shows, δ: (C$_{\text{aliphatic}}$) at 27.3 (d, $^2J_{\text{C–P}} = 11.5$ Hz, 1C), 28.0 (d, $^1J_{\text{C–P}} = 17.0$ Hz, 1C), and 31.2 (d, $^3J_{\text{C–P}} = 13.5$ Hz, 1C); δ: (C$_{\text{thiophene}}$) at 123.2 (s, 1C), 124.5 (s, 1C), 126.8 (s, 1C), and 144.6 (s, 1C); δ: (C$_{\text{phenyl}}$) at 128.5 (d, $^3J_{\text{C–P}} = 6.6$ Hz, 4C), 128.6 (s, 2C), 132.8 (d, $^2J_{\text{C–P}} = 18.3$ Hz, 4C), and 138.6 (d, $^1J_{\text{C–P}} = 12.5$ Hz, 2C). The above ^{13}C NMR assignment was confirmed by running Dept-135 experiment that shows, disappearance of the two quaternary carbons at $\delta = 138.6$, and 144.6. The ^{31}P NMR spectrum shows one signal at $\delta = -12.25$.

Reaction of **P-S3** with equimolar amount of [PdCl$_2$(PhCN)$_2$] afforded the binuclear complex *trans*-[Pd(μ-Cl)Cl(P-S3)]$_2$ (**I**). Complex **I** is soluble in acetone, chloroform, and dichloromethane, and insoluble in diethyl ether, dioxane, and hexane. Elemental analysis of **I** for C, H, and S is consistent with the above formulation. The ^{1}H NMR spectrum of **I** shows, in addition to the phenyl proton signals, two multiplets centered at $\delta = 1.89$ (–CH$_2$C***H***$_2$CH$_2$P–) and 2.50 (–C***H***$_2$P–), and a triplet centered at $\delta = 2.87$ (–C***H***$_2$CH$_2$CH$_2$P–). The signals of the thiophene protons appear as doublets centered at $\delta = 6.69$, and $\delta = 7.07$, and a doublet of doublet centered at $\delta = 6.87$. Compared with the free ligand, the ^{31}P NMR signal of complex **I** is downfield shifted to $\delta = 31.81$. The ^{13}C NMR spectrum of **I** shows, δ: (C$_{\text{aliphatic}}$) at 25.9 (s, 2C), 26.5 (d, $^1J_{\text{C–P}} = 35.9$ Hz, 2C), and 30.5 (d, $^3J_{\text{C–P}} = 17.5$ Hz, 2C); δ: (C$_{\text{thiophene}}$) at 123.5 (s, 2C), 124.9 (s, 2C), 126.9 (s, 2C), and 143.1 (s, 2C); δ: (C$_{\text{phenyl}}$) at 127.7 (s, 4C), 128.8 (d, $^3J_{\text{C–P}} = 11.9$ Hz, 8C), 131.4 (s, 4C), and 133.3 (d, $^2J_{\text{C–P}} = 10.2$ Hz, 8C). Comparing the ^{13}C NMR spectrum of **I** with that for the **P-S3** ligand shows no difference on the chemical shift of the thiophene ring carbons, which is consistent with the ligand being coordinated through the phosphorus atom only. The ^{13}C NMR signal for ***C***$_{\text{phenyl}}$–P was shifted upfield upon coordination with the palladium metal to 127.7 ppm and appeared as a singlet. Similarly, the signal for ***C***H$_2$–P was shifted upfield upon coordination with the palladium metal to 26.5 ppm with an increase in J value ($J = 35.9$ Hz). The bidentate mode of bonding for **P-S3** seems to be unfavorable with respect to the formation of the 7-membered chelate ring and the poor donor ability of thiophene sulfur. In view of the above data the complex is believed to have a dimeric structure which was confirmed by single X-ray structure analysis (Fig. 1).

As expected, reaction of the chlorobridged palladium complex **I** with triphenylphosphine in a 1:2 molar ratio afforded the monomeric complex, [PdCl$_2$(P-S3)(PPh$_3$)]. This complex was characterized by its ^{1}H NMR spectrum which shows two multiplets centered at $\delta = 1.89$ (–CH$_2$C***H***$_2$CH$_2$P–), 2.52 (–C***H***$_2$P–) and a triplet centered at $\delta = 2.85$ (–C***H***$_2$CH$_2$CH$_2$P–). The thiophene protons show two doublets centered at $\delta = 6.67$, 7.06 and a triplet centered at $\delta = 6.85$. The phenyl protons appear as a multiplet at $\delta = 7.57$–7.73. Comparing the ^{1}H NMR spectra of **I** and [PdCl$_2$(P-S3)(PPh$_3$)] shows no appreciable differences on the chemical shift of aliphatic and thiophene protons.

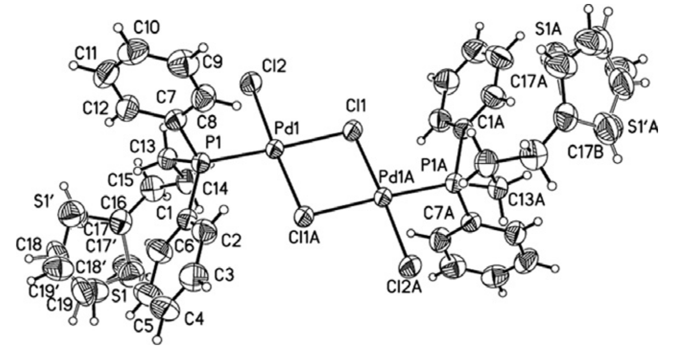

Fig. 1. ORTEP plot of the molecular structure of compound **I**. Showing the rotationally disordered of thiophene group. Thermal ellipsoids are drawn at 50% probability level.

In a similar way, reaction of complex **I** with **P-S3** in a 1:2 molar ratio afforded the monomeric complex, [PdCl$_2$(P-S3)$_2$] (**II**), which is characterized by elemental analysis and NMR spectroscopy. The ^{1}H NMR spectrum of **II** shows, in addition to the phenyl proton signals, a multiplet centered at $\delta = 1.88$ (–CH$_2$C***H***$_2$CH$_2$P–), $\delta = 2.50$ (–C***H***$_2$P–), and a triplet centered at $\delta = 2.87$ (–C***H***$_2$CH$_2$CH$_2$P–). The signals of the thiophene protons appear as a doublet centered at $\delta = 6.68$ and two (doublet of doublet) centered at $\delta = 6.86$ ($J = 3.4$, 5.1 Hz) and $\delta = 7.07$ ($J = 1.1$, 5.1 Hz). Comparing the ^{1}H NMR spectrum of **I** and **II** shows no appreciable differences in both spectra, indicating similar mode of bonding for the ligand in both complexes. The ^{31}P NMR spectrum of **II** shows one signal at $\delta = 17.53$. The greater downfield shift of the ^{31}P peak in complex **I** relative to complex **II** is attributed to the increase in Pd–P bond strength, that is *trans* to bridging Cl ligand.

Complex **II** was also prepared by the direct reaction of [PdCl$_2$(PhCN)$_2$] with **P-S3** in a 1:2.5 molar ratio. The isolated yellow compound was characterized by ^{1}H and ^{13}C NMR and found to be identical with an authentic sample of complex **II** that has been prepared previously by the reaction of complex **I** with **P-S3**.

3.2. The molecular structure of [Pd(μ-Cl)Cl(P-S3)]$_2$ (I)

Yellow platelet-like crystals of **I** were grown from double layer system of CH$_2$Cl$_2$/pet. ether. The solid state structure was established by X-ray crystallography (Fig. 1). Selected bond lengths and angles are collected in Table 2. The two **P-S3** ligands bind to the Pd metal through the phosphorus atoms in a *trans* position. The two chlorobridged ligands form with the palladium atoms a four-membered ring with Cl–Pd–Cl angles of 85.24(3)°, and Pd–Cl–Pd angles of 94.76(3)°. The Pd–Cl bond dis-

Table 2
Selected bond distances (Å) and angles (°) for *trans*-[Pd(μ-Cl)Cl (P-S3)]$_2$

Bond distances (Å)		Bond angles (°)	
Pd(1)–P(1)	2.2239(11)	P(1)–Pd(1)–Cl(2)	86.21(4)
Pd(1)–Cl(2)	2.2747(11)	P(1)–Pd(1)–Cl(1A)	96.89(3)
Pd(1)–Cl(1A)	2.3081(11)	Cl(2)–Pd(1)–Cl(1A)	176.89(3)
Pd(1)–Cl(1)	2.4156(12)	P(1)–Pd(1)–Cl(1)	177.44(2)
Cl(1)–Pd(1A)	2.3080(11)	Cl(2)–Pd(1)–Cl(1)	91.67(4)
P(1)–C(7)	1.812(3)	Cl(1A)–Pd(1)–Cl(1)	85.24(3)
P(1)–C(1)	1.818(3)	Pd(1A)–Cl(1)–Pd(1)	94.76(3)
P(1)–C(13)	1.823(3)	C(7)–P(1)–C(1)	104.28(12)

tance of the terminal chloride is shorter than that of the bridging chloride. It is interesting to note that, the two Pd^1–Cl$_{\text{bridge}}$ (Fig. 1) bond distances are different; the Pd^1–Cl$_{\text{bridge}}$ *trans* to terminal chloride is shorter than the one *trans* to the P-atom. This is consistent with the higher *trans* influence of phosphine ligand compared with Cl. The thiophene ring was rotationally disordered and refined in two positions with refined occupancies of 50% (Fig. 2).

3.3. The molecular structure of [PdCl$_2$(P-S3)$_2$] (**II**)

Yellow crystals of complex **II** were grown by slow evaporation of CH$_2$Cl$_2$/pet. ether solution at room temperature. The solid state structure of **II** is shown in Fig. 3, and selected bond length and angles are collected in Table 3. As indicated in Fig. 3, the two **P-S3** ligands bind to the Pd metal atom through their phosphorus atoms in *trans* positions. The palladium atom is in the center of the symmetry and it displays square planar stereochemistry. The Pd–P distance in **II** is longer than that in **I**, which is consistent with the competition for π-bonding between the *trans* phosphorus atoms in **II**.

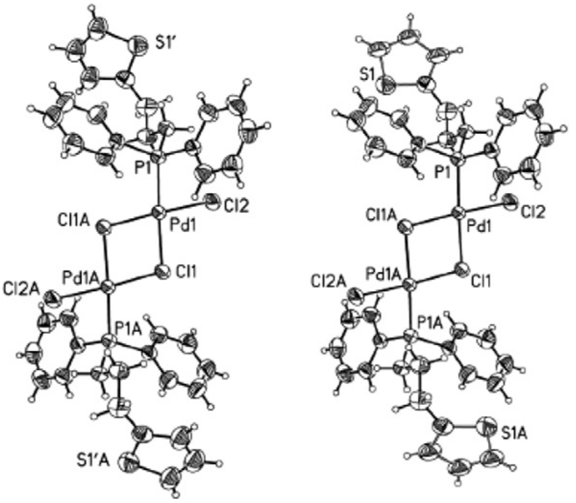

Fig. 2. X-ray crystal structure of the complex **I** showing the rotational disorder of the thiophene ring.

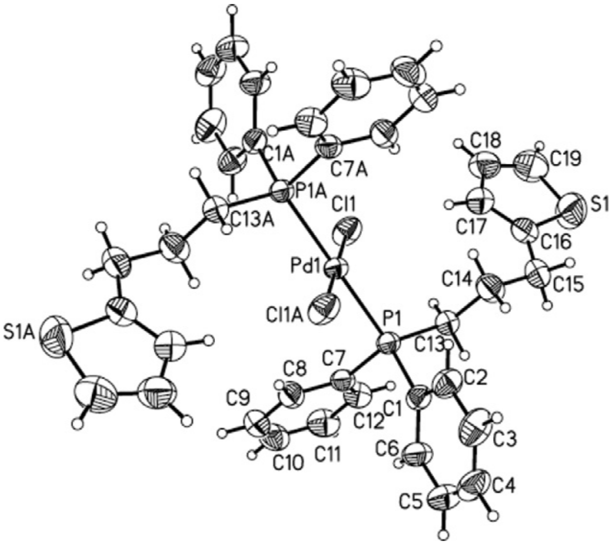

Fig. 3. ORTEP plot of the molecular structure of compound **II** showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 3
Selected bond distances (Å) and angles (°) for the complex *trans*-[PdCl$_2$(P-S3)$_2$] (**II**)

Bond distances (Å)		Bond angles (°)	
P(1)–Pd(1)	2.3356(8)	Cl(1A)–Pd(1)–Cl(1)	180.00(4)
Cl(1)–Pd(1)	2.2952(9)	Cl(1)–Pd(1)–P(1)	86.58(3)
C(1)–P(1)	1.826(3)	Cl(1A)–Pd(1)–P(1)	93.42(3)
C(7)–P(1)	1.819(3)	C(1)–P(1)–Pd(1)	120.76(9)
C(13)–P(1)	1.836(3)	C(7)–P(1)–Pd(1)	106.54(9)
		C(13)–P(1)–Pd(1)	115.07(10)
		C(1)–P(1)–C(7)	104.14(13)
		C(1)–P(1)–C(13)	102.36(14)
		C(7)–P(1)–C(13)	106.79(13)

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Appendix A. Supplementary material

CCDC 611542 and 632706 contain the supplementary crystallographic data for **I** and **II**. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.05.011.

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