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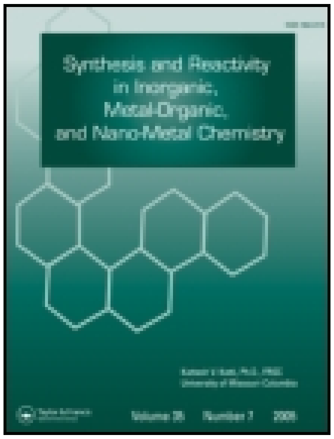

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Palladium Complexes with Some Phosphorus-Sulfur Ligands

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Palladium Complexes with Some Phosphorus-Sulfur Ligands

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The phosphorus-sulfur asymmetric ligands 2-(2-diphenylphosphinoethyl)-thiophene (P-S2), 2-(3-diphenylphosphinopropyl)thiophene (P-S3), and [2-[(methyl-thio)methyl]phenyl]diphenylbenzene (P-SM) have been synthesized and characterized by IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. Reaction of P-S2, P-S3 or P-SM with equimolar amount of dichlorobis(benzonitrile)palladium(II), [Pd(PhCN)Cl_2], gave the complexes [Pd(P-S2)Cl_2], [Pd(P-SM)Cl_2] and [Pd(P-S3)(μ-Cl)Cl]$_2$, respectively. However, reaction of P-S2 with [Pd(PhCN)Cl_2] in a molar ratio of 2:1 afforded the complex [Pd(P-S2)$_2$$Cl_2$]. The above complexes were characterized by microelemental analysis, IR, ^{1}H-NMR and ^{13}C-NMR.

Keywords palladium complexes, phosphorus-sulfur ligands, asymmetric ligands, bidentate ligands

INTRODUCTION

The asymmetric ligands (also called mixed-donor or hemilabile ligands) in general, and those withphosphorus and sulfur donor centers, have received wide spread attention.[1,2]

On one hand, the phosphorus atom in this type of ligands tends to stabilize metal ions in low oxidation state through its effective π-back bonding,[3,4] and on the other hand, the sulfur atom is weakly coordinated to the metal center and thus facilitates the formation of a vacant coordination site.[5] The combined effect of phosphorus and sulfur donor atoms seems to be essential in homogeneous catalysis, since it stabilizes the catalytic intermediates in solution and allows organic substrates to enter into the coordination sphere of the metal.[6,7] Many palladium complexes with phosphinothioether ligands have been utilized in catalytic processes, such as in photochemical carbonylation of benzene,[8] polymerization of norbornene,[9] and arylation of olefin.[2,10] Recently, asymmetric phosphorus-sulfur ligands involving thiophene have been prepared and characterized.[5] The relatively weak donor ability of the sulfur atom of thiophene encourages the preparation of more ligands containing phosphorus and thiophene[5,11] and the use of their metal complexes in variety of catalytic systems.[12,13] Herein, we report on the preparation of palladium complexes with 2-[2-(diphenylphosphino)ethyl]thiophene (P-S2), 2-[3-(diphenylphosphino)propyl]thiophene (P-S3), and [2-[(methylthio)methyl]phenyl] diphenylphosphine (P-SM). The complexes, [Pd(P-S2)$_n$$Cl_2$] (n = 1, 2), [Pd(P-S3)(μ-Cl)Cl]$_2$, and [Pd(P-SM)Cl_2] have been prepared and fully characterized by their microanalytical analysis, IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy.

EXPERIMENTAL

All procedures were performed under an atmosphere of dry, purified nitrogen using standard Schlenk techniques. Solvents were distilled and dried by standard methods.[14] Thiophene, 1-bromo-3-chloropropane, thionyl chloride, 2-bromobenzyl bromide, were purchased from Across. n-Butyllithium (1.55 M solution in hexane) and methanethiol were purchased from Aldrich. Potassium diphenylphosphide (0.5 M solution in THF) and palladium(II) chloride were purchased from Fluka. Ethylene oxide was purchased from BDH. Benzonitrile was purchased from Wardle Chemicals. Chlorodiphenylphosphine was purchased from PFALTZ & BAUER. [$PdCl_2(PhCN)_2$][15] 2-(2-thienyl)ethanol,[16] 2-(3-chloropropyl)thiophene,[11] and 2-bromo-1-[(methylthio)methyl]benzene[17] were prepared following literature procedure. The IR Spectra were recorded, as KBr discs, on a Nicolet Impact-400 FT-IR spectrometer. The NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer using TMS as internal reference. Melting points were determined with a Philip-Harris melting point apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratories of AL al-Bayt University, Jordan.

Preparation of Ligands

Preparation of 2-[2-(diphenylphosphino)ethyl]thiophene (P-S2)

The above ligand was synthesized via the reaction of 2-(2-chloroethyl)thiophene with potassium diphenylphosphide. 2-(2-chloroethyl)thiophene was prepared from 2-(2-thienyl) ethanol[16] as in the following: A solution of 2-(2-thienyl)ethanol (10 g, 78 mmol) in dry benzene (50 mL) was introduced

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into A 250 mL three-necked, round-bottomed flask equipped with a nitrogen inlet, dropping funnel, and a condenser connected to an oil bubbler. a solution of thionyl chloride (11.4 mL, 156 mmol) in dry benzene (50 mL) was then slowly added at 0°C. After addition was complete (~30 min), the solution was stirred at room temperature for 15 min, and then heated for 3 h at (50–60°C). The solvent was removed under reduced pressure, and the black residue was vacuum distilled. The product was collected at 66°C and 7 mmHg as a pale yellow oil. Yield: 7.1 g (62%).

Preparation of (P-S2)

A solution of 2-(2-chloroethyl)thiophene (7.3 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 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. The solvent was then removed under reduced pressure. The residue was dissolved in diethyl ether (100 mL), washed with distilled water (2 × 100 mL). The ether layer was then dried over anhydrous sodium sulfate overnight. After filtration, ether was removed under reduced pressure. The thick yellow residue was dissolved in methanol (50 mL) with vigorous stirring. The solution was stored at 0°C overnight. The white precipitate formed was filtered, washed three times with cold methanol, and dried under vacuum at room temperature. Yield: 10.0 g (71%).

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

The compound was prepared following literature procedure[11] with slight 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 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 then removed under reduced pressure. The residue was dissolved in diethyl ether (100 mL), washed with distilled water (2 × 100 mL). The ether layer was then dried over anhydrous sodium sulfate overnight. After filtration, ether was removed under reduced pressure. The thick yellow residue was dissolved in methanol (50 mL) with vigorous stirring. The solution was stored at 0°C overnight. The white precipitate formed was filtered, washed three times with cold methanol, and dried under vacuum at room temperature. Yield: 14.3 g (92%); m.p.: 65–67°C, [literature[11], 90% yield].

Preparation of [2-[(methylthio)methyl]phenyl]diphenylphosphine (P-SM)

A solution of 2-bromo-1-[(methylthio)methyl]benzene (21.7 g, 0.1 mol) in dry diethyl ether (50 mL) was introduced into a 250 mL three-necked, round-bottom flask equipped with a nitrogen inlet, and a condenser connected to an oil bubbler. The solution was cooled to −65°C and then a solution of n-butyllithium (65 mL of 1.55 M) was slowly added. After the addition was completed, the cooling bath was removed, and the solution was stirred at room temperature for 4 h. Then, a solution of chlorodiphenylphosphine (17.95 mL, 0.1 mol) in dry diethyl ether (20 mL) was slowly added at 0°C. After the addition was complete, the reaction mixture was allowed to warm up to room temperature, and then refluxed for 1 h. Solvent was removed under reduced pressure, and the residue was dissolved in diethyl ether (100 mL). The ether solution was washed with distilled water (2 × 100 mL). The ether layer was then dried over anhydrous sodium sulfate over night. Ether was removed from the filtrate under reduced pressure and the residue was vacuum distilled. The product was collected at 210°C and 5 mmHg as a pale yellow viscous oil. Yield: 13.0 g (40%).

Preparation of the Palladium Complexes

The complexes $[Pd(P\text{-}S2)Cl_2]$ (**I**), $[Pd(P\text{-}S3)(\mu\text{-}Cl)Cl]_2$, (**II**), and $[Pd(P\text{-}SM)Cl_2]$ (**III**), were prepared via the following general procedure:

A sample of ligand (1.1 mmol) in benzene (20 mL) was slowly added to a filtered solution of $[PdCl_2(PhCN)_2]$ (1.0 mmol) in benzene (30 mL). The solution was stirred for 1 h at room temperature. During that time, the solution changed color gradually. Solvent was removed under reduced pressure until reaching a volume of about 10 mL. Upon addition of petroleum ether (boiling range of 40–60°C), a precipitate was separated, washed with petroleum ether (boiling range of 40–60°C) and dried under vacuum at 50°C.

[Pd(P-S2)Cl2] (**I**): Yield: 0.39 g (82%); yellowish brown solid; m.p: 215–218 (dec). Selected IR bands (KBr pellet, cm^{-1}): 3074(m), 3057(m), 2918(m) and 2848(m) (νC-H); 1102(s) (νP-Ph). Calcd. for $[C_{18}H_{17}Cl_2PPdS]$ (473.69): C, 45.64; H, 3.62; S, 6.77. Found: C, 45.92; H, 3.46; S, 6.68%.

$[Pd(P\text{-}S3)(\mu\text{-}Cl)Cl]_2$ (**II**): Yield: 0.45 g (92%); orange solid; m.p: 225–227 (dec). Selected IR bands (KBr pellet, cm^{-1}): 3056(m), 2936(m) and 2896(m) (νC-H); 1102 (s) (νP-Ph). Calcd. for $[C_{38}H_{38}Cl_4P_2Pd_2S_2]$ (975.44): C, 46.79; H, 3.93; S, 6.57. Found: C, 46.23; H, 3.66; S, 5.51%.

$[Pd(P\text{-}SM)Cl_2]$ (**III**): Yield: 0.36 (72%); yellow solid; m.p: 238–240 (dec). Selected IR bands (KBr pellet, cm^{-1}): 3051(m), 2953(m), 2915(m), 2848(m) and 1250(s) (νC-H); 1098(s) (P-Ph). Calcd. for $[C_{20}H_{19}Cl_2PPdS]$ (499.73): C, 48.07; H, 3.83; S, 6.42. Found: C, 48.21; H, 4.08; S, 6.82%.

*Preparation of [Pd(P-S2)$_2$Cl$_2$] (**IV**)*

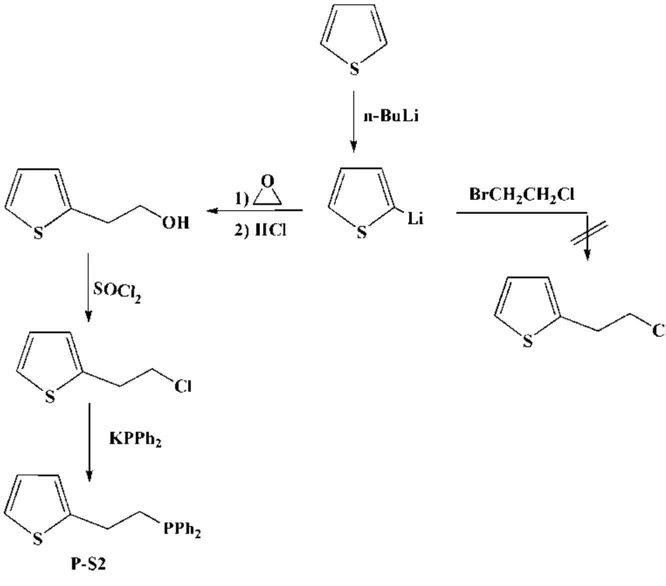
A sample of a filtered solution of [PdCl$_2$(PhCN)$_2$ (0.59 g, 1.5 mmol) in benzene (30 mL) was slowly added to a solution of P-S2 (0.977 g, 3.3 mmol) in benzene (20 mL). The mixture was stirred for 1 h at room temperature. During that time, solution changed color gradually from red-brown to yellow with the formation of precipitate. Solvent was removed under reduced pressure till a volume of about 10 mL. The yellow precipitate was collected, washed with petroleum ether (boiling range of 40–60°C) and dried under vacuum at 50°C. Yield: 1.0 g (87%). Selected IR bands (KBr pellet, cm^{-1}): 3077(m), 3033(m), 2929(m), 2852(m), (νC-H); 1099(s) (P-Ph). Calcd. for [$C_{36}H_{34}Cl_2P_2PdS_2$] (770.06): C, 56.15; H, 4.45; S, 8.33. Found: C, 55.80; H, 4.37; S, 8.27%.

RESULTS AND DISCUSSION

Preparation of the Ligands

Preparation of 2-[2-(diphenylphosphino)ethyl]thiophene (P-S2)

The above ligand was prepared in three steps starting from 2-lithiothiophene. In the first step, 2-(2-thienyl)ethanol was prepared following literature procedure[16] via bubbling of ethylene oxide through a stirred THF solution containing n-butyllithium and thiophene at 0°C (Scheme 1). 2-(2-thienyl) ethanol was isolated and characterized by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy (Table 1). In addition to the thiophene ring vibrations, the IR spectrum of 2-(2-thienyl)ethanol shows absorption due to υOH at 3349 cm^{-1}, indicating the insertion of ethylene oxide. The ^{1}H-NMR (300 MHz, CDCl$_3$) spectrum shows, in addition to the thiophene signals, a broad singlet at $\delta = 2.76$ (-CH$_2$-O$\boldsymbol{H}$), a triplet centered at $\delta = 3.03$ (-C$\boldsymbol{H}_2$CH$_2$OH), and another triplet centered at $\delta = 3.78$ (-CH$_2$C$\boldsymbol{H}_2$OH). The ^{13}C NMR (75 MHz, CDCl$_3$) spectrum shows signals at $\delta = 33.3$ (s,-$\boldsymbol{C}$H$_2$CH$_2$OH, 1C), 63.4 (s,-$\boldsymbol{C}$H$_2$OH. 1C), 124.0 (s, C$_3$, 1C), 125.6 (s, C$_4$, 1C), 127.1 (s, C$_5$, 1C) and 141.0 (s, C$_2$, 1C).



SCH. 1.

In the second step, 2-(2-thienyl)ethanol was reacted with thionyl chloride to give 2-(2-chloroethyl)thiophene. The product was collected as pale yellow liquid by vacuum distillation at 66°C and 7 mmHg. The ^{1}H-NMR (300 MHz, CDCl$_3$) spectrum of the product shows, in addition to thiophene proton signals, two triplets centered at $\delta = 3.27$ (-C$\boldsymbol{H}_2$CH$_2$Cl), and $\delta = 3.71$ (-CH$_2$C$\boldsymbol{H}_2$Cl). Comparing the IR spectra of 2-(2-chloroethyl)thiophene and 2-(2-thienyl)ethanol shows a disappearance of the absorption due to νO-H. Similarly, the signal at $\delta = 2.76$ due to OH proton in the ^{1}H-NMR spectrum of 2-(2-chloroethyl)thiophene has also been disappeared.

Treatment of 2-(2-chloroethyl)thiophene with potassium diphenylphosphide in dry THF affords 2-[2-(diphenylphosphino)ethyl]thiophene (P-S2). The fine white precipitate was filtered and recrystallized three times from methanol. The product was fully characterized by its ^{1}H-NMR, and ^{13}C-NMR spectroscopy (Table 1). The ^{1}H-NMR spectrum (300 MHz, CDCl$_3$) of (P-S2) shows, a multiplet at $\delta = 7.31$–7.76 for the phenyl protons, a triplet centered at $\delta = 2.45$ (-C$\boldsymbol{H}_2$CH$_2$P-), and a quartet centered at $\delta = 2.95$ (-C$\boldsymbol{H}_2$P-). The three protons of thiophene appear as: two doublets centered (at $\delta = 6.80$ and $\delta = 7.12$), and a triplet at $\delta = 6.91$. The ^{13}C-NMR spectrum (75 MHz, CDCl$_3$) of P-S2 shows δ(C$_{\text{aliphatic}}$): 26.5 (d, $^1J_{\text{C-P}} = 19.5$ Hz, 1C), and 30.5 (d, $^2J_{\text{C-P}} = 12.8$ Hz, 1C). δ(C$_{\text{thiophene}}$): 123.3 (s, 1C), 124.2 (s, 1C), 126.85 (s, 1C), and 145.5 (d, $^3J_{\text{C-P}} = 14.3$ Hz, 1C). δ(C$_{\text{phenyl}}$): 138.2 (d, $^1J_{\text{C-P}} = 12.8$ Hz, 2C), 132.8 (d, $^2J_{\text{C-P}} = 18.8$ Hz, 4C), 128.6 (d, $^3J_{\text{C-P}} = 3.3$ Hz, 4C), and 128.7 (s, 2C). The above ^{13}C-NMR assignment were confirmed by running Dept-135 experiment that shows, the disappearance of the two quaternary carbons (at $\delta =$ 138.2 ppm and 145.5 ppm). In Comparison with 2-(2-chloroethyl)thiophene, the IR spectrum of P-S2 shows strong absorption at 1098 cm^{-1}due to ν Ph-P.

Attempts to prepare 2-(2-chloroethyl)thiophene by the addition of 1-bromo-2-chloroethane with a solution containing n-butyllithium and thiophene at low temperature in dry THF were unsuccessful (Scheme 1). Under these conditions, 2-butylthiophene was formed as evidenced by its ^{1}H-NMR spectrum and mass spectrometry. The ^{1}H-NMR spectrum (300 MHz, CDCl$_3$) shows signals at $\delta = 0.97$ (3H, t, $J = 7.26$, -CH$_2$C$\boldsymbol{H}_3$), 1.42 (2H, m, $J = 7.5$, -CH$_2$C$\boldsymbol{H}_2$CH$_3$), 1.70 (2H, q, $J = 7.4$, -CH$_2$C$\boldsymbol{H}_2$CH$_2$-), 2.85 (2H, t, $J = 7.76$, C$_4$H$_3$S-C$\boldsymbol{H}_2$CH$_2$-), 6.80 (1H, d, $J_{3,4} = 3.36$, H-3), 6.93 (1H, dd, $J_{3,4} = 3.59$, $J_{4,5} = 5.09$, H-4), and 7.12 (1H, d, $J_{4,5} = 5.13$, H-5). The mass spectrum shows the molecular peak at (140 m/z).]

TABLE 1
^{1}H-NMR and ^{3}C-NMR data of some starting materials, ligands and Pd-complexes

Compound	^{1}H-NMR	^{3}C-NMR
2-(2-chloroethyl)-thiophene[a]	3.27 (t, J =7.3 Hz, 2H) 3.71 (t, J = 7.3 Hz, 2H), 6.88 (d, J = 3.4 Hz, 1H), 6.95 (dd, J = 3.4, 5.1 Hz, 1H), 7.14 (d, J = 5.1 Hz, 1H)	33.4 (s), 44.9 (s); 124.4 (s), 126.0 (s, 1C), 127.1 (s), 140.3 (s).
P-S2[a]	2.45 (t, J = 8.3 Hz, 2H), 2.95 (q, J = 8.2 Hz, 2H), 6.80 (d, J = 3.0 Hz, 1H), 6.91 (t, J = 5.0 Hz, 1H), 6.80 (d, J = 5.0 Hz, 1H), 7.75–7.34 (m, 10H).	26.5 (d, $^{1}J_{\text{C-P}}$ = 19.5 Hz), 30.5 (d, $^{2}J_{\text{C-P}}$ = 12.8 Hz), 123.3 (s), 124.2 (s), 126.9 (s), 128.6 (d, $^{3}J_{\text{C-P}}$ = 3.3 Hz), 128.7 (s), 132.8 (d, $^{2}J_{\text{C-P}}$ = 18.8 Hz), 138.2 (d, $^{1}J_{\text{C-P}}$ = 12.8 Hz), 145.5 (d, $^{3}J_{\text{C-P}}$ = 14.3 Hz).
P-S3[a]	1.81 (m, 2H), 2.09 (m, 2H), 2.94 (t, J = 13.5 Hz, 2H), 6.75 (d, J = 3.1 Hz, 1H), 7.10 (d, J = 5.0 Hz, 1H), 6.89 (t, J = 4.2 Hz, 1H), 7.76–7.31 (m, 10H)	27.3 (d, $^{2}J_{\text{C-P}}$ = 11.5 Hz), 28.0 (d, $^{1}J_{\text{C-P}}$ = 17.0 Hz), 31.2 (d, $^{3}J_{\text{C-P}}$ = 13.5 Hz), 123.2 (s), 124.5 (s), 126.8 (s), 144.6 (s), 138.6 (d, $^{1}J_{\text{C-P}}$ = 12.5 Hz), 132.8 (d, $^{2}J_{\text{C-P}}$ = 18.3 Hz), 128.5 (d, $^{3}J_{\text{C-P}}$ = 6.6 Hz), and 128.6 (s).
P-SM[a]	1.98 (s, 3H), 3.94 (d, J = 1.5 Hz,2H), 7.46–6.91 (m, 14H).	15.4 (s), 36.9 (d, $^{3}J_{\text{c-p}}$ = 24.5 Hz), 128.6 (d, $^{3}J_{\text{c-p}}$ = 6.8 Hz), 128.7 (s), 129.1 (s), 129.6 (d, $^{3}J_{\text{c-p}}$ = 4.8 Hz), 132.0 (d, $^{3}J_{\text{c-p}}$ = 9.8 Hz),133.8 (d, $^{2}J_{\text{c-p}}$ = 19.5 Hz), 134.2 (s), 136.2 (d, $^{1}J_{\text{c-p}}$ = 13.6 Hz), 136.8 (d, $^{1}J_{\text{c-p}}$ = 10.2 Hz), 142.8 (d, $^{2}J_{\text{c-p}}$ = 24.5 Hz).
[Pd(P-S2)Cl$_2$] (I) [b]	2.88 (m, 2H), 2.74 (m, 2H). 6.86 (dd, J= 3.4, 5.1 Hz, 1H), 7.27 (dd, J= 1.1, 5.1 Hz, 1H), 6.80 (m, 1H), 7.81–7.48 (m, 10H)	24.7 (s), 30.0 (d, $^{2}J_{\text{C-P}}$ = 34.5 Hz), 124.6 (s), 125.3 (s), 127.4 (s), 143.6 (d, $^{3}J_{\text{C-P}}$ = 19.5 Hz), 129.7 (s), 129.1 (d, $^{2}J_{\text{C-P}}$ = 11.3 Hz), 133.6 (d, $^{3}J_{\text{C-P}}$ = 9.8 Hz), 132.0 (s).
[Pd(P-S3)(μ-Cl)Cl]$_2$ (II) [a]	1.89 (m, 2H), 2.50 (m, 2H), 2.87 (t, J = 7.2 Hz, 2H), 6.69 (d, J = 2.8 Hz, 1H), 6.87 (dd, J = 3.4, 5.1 Hz, 1H), 7.07 (d, J = 5.1 Hz, 1H), 7.68–7.22 (m, 20H).	25.9 (s), 26.5 (d, $^{2}J_{\text{C-P}}$ = 35.9 Hz), 30.5 (d, $^{3}J_{\text{C-P}}$ = 17.5 Hz), 123.5 (s), 124.9 (s), 126.9 (s), 143.1 (s), 127.7 (s), 133.3 (d, $^{2}J_{\text{C-P}}$ = 10.2 Hz), 128.8 (d, $^{3}J_{\text{C-P}}$ = 11.9 Hz), 131.4 (s).
[Pd(P-SM)Cl$_2$] (III) [a]	2.45 (s, 3H), 3.45 (dd, $^{2}J_{\text{H-H}}$= 13.6 Hz, $^{4}J_{\text{P-H}}$= 2.7 Hz, 1H), 3.68 (dd, $^{2}J_{\text{H-H}}$= 13.6 Hz, $^{4}J_{\text{P-H}}$= 6.3 Hz, 1H), 6.79–7.72 (m, 14H).	21.9 (s), 36.7 (d, $^{3}J_{\text{c-p}}$ = 11.4 Hz); 124.3 (d, $^{1}J_{\text{c-p}}$ = 49.1 Hz), 125.1 (d, $^{1}J_{\text{c-p}}$ = 42.3 Hz), 125.9 (d, $^{1}J_{\text{c-p}}$ = 46.6 Hz), 128.9 (d, $^{2}J_{\text{c-p}}$ = 12.5 Hz), 129.3 (d, $^{3}J_{\text{c-p}}$ = 11.8 Hz), 130.0 (d, $^{3}J_{\text{c-p}}$ = 8.6 Hz), 132.3 (s), 134.7 (d, $^{2}J_{\text{c-p}}$ = 11.8 Hz, 4C), 134.9 (s), 137.7 (d, $^{2}J_{\text{c-p}}$ = 12.2 Hz), 132.3–132.6 (m).

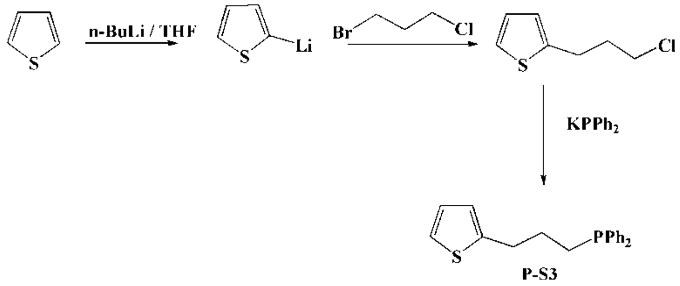
[a] CDCl$_3$ was used as a solvent for both ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz).
[b] DMSO-d$_6$ was used as a solvent for both ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz).

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

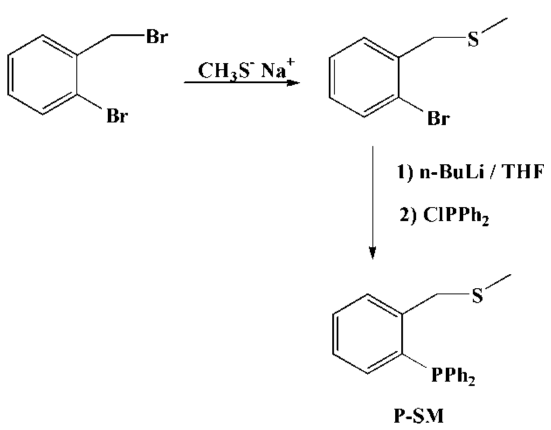
This ligand was prepared by the reaction of 1-bromo-3-chloropropane with a solution containing n-butyllithium and thiophene in dry THF[11] (Scheme 2). Then 2-(3-chloropropyl)thiophene was collected as a pale yellow viscous liquid and used without further purification. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of this derivative shows, in addition to the thiophene signals, a quintet centered at $\delta = 2.12$ ($-CH_2C\boldsymbol{H}_2CH_2Cl$), a triplet centered at $\delta = 3.02$ ($-C\boldsymbol{H}_2CH_2CH_2Cl$), and a triplet centered at $\delta = 3.57$ ($-C\boldsymbol{H}_2Cl$). The ^{13}C NMR (75 MHz, $CDCl_3$) shows $\delta(C_{\text{aliphatic}})$: 26.9 (s, $-CH_2\boldsymbol{C}H_2CH_2Cl$), 34.3 (s, $-\boldsymbol{C}H_2CH_2CH_2Cl$), 43.9 (s, $-CH_2CH_2\boldsymbol{C}H_2Cl$); $\delta(C_{\text{thiophene}})$: 123.5 (s, C_3, 1C), 124.9 (s, C_4, 1C), 126.9 (s, C_5, 1C), 143.2 (s, C_2, 1C). Treatment of 2-(3-chloropropyl)thiophene with potassium diphenylphosphide in dry THF afforded the P-S3 ligand. The product was collected and recrystallized several times from methanol. The P-S3 ligand was fully characterized by its IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. The ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of P-S3 shows, in addition to the phenyl proton signals, a multiplet centered at $\delta = 1.81$ ($-CH_2C\boldsymbol{H}_2CH_2P-$), a multiplet centered at $\delta = 2.09$ ($-C\boldsymbol{H}_2P-$), and a triplet centered at $\delta = 2.94$ ($-C\boldsymbol{H}_2CH_2CH_2P-$). The three protons of thiophene appear as: two doublets centered (at $\delta = 6.75$, and $\delta = 7.10$), and a triplet centered (at $\delta = 6.89$). The ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of P-S3 shows $\delta(C_{\text{aliphatic}})$: 28.0 (d, $^1J_{C\text{-}P} = 17.0$ Hz, 1C), 27.3 (d, $^2J_{C\text{-}P} = 11.5$ Hz, 1C), and 31.2 (d, $^3J_{C\text{-}P} = 13.5$ Hz, 1C); $\delta(C_{\text{thiophene}})$: 123.2 (s, 1C), 124.5 (s, 1C), 126.8 (s, 1C), and 144.6 (s, 1C). $\delta(C_{\text{phenyl}})$: 138.6 (d, $^1J_{C\text{-}P} = 12.5$ Hz, 2C), 132.8 (d, $^2J_{C\text{-}P} = 18.3$ Hz, 4C), 128.5 (d, $^3J_{C\text{-}P} = 6.6$ Hz, 4C), and 128.6 (s, 2C). The above ^{13}C-NMR assignments were confirmed by a running Dept-135 experiment that shows, disappearance of the two quaternary carbons (at $\delta = 138.6$ ppm, and 144.6 ppm). In comparison with 2-(3-chloropropyl)thiophene, the IR spectrum of P-S3 shows, a vibration at the 1120 cm^{-1} due to νPh-P.

Preparation of [2-[(methylthio)methyl]phenyl]diphenylphosphine (P-SM)

The P-SM ligand was prepared from o-bromobenzyl bromide as shown in Scheme 3. 2-bromo-1-[(methylthio)-methyl]benzene was prepared via reaction of o-bromobenzyl bromide with sodium methylsulfide solution in dry ethanol.[17] The colorless, oily product was purified by vacuum distillation at 108–110°C and 5 mmHg. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of 2-bromo-1-[(methylthio)methyl]benzene shows, a singlet at $\delta = 2.04$ ($-SC\boldsymbol{H}_3$), a singlet at $\delta = 3.79$ ($ArC\boldsymbol{H}_2S-$). The four protons of the phenyl ring appear as: a two triplet centered (at $\delta = 7.09$ and $\delta = 7.25$ ppm), and two doublets centered (at $\delta = 7.33$ and 7.55 ppm). The ^{13}C NMR (75 MHz, $CDCl_3$) shows $\delta(C_{\text{ aliphatic}})$: 15.2 (s, 1C, $-S\boldsymbol{C}H_3$), 38.5 (s, 1C, $Ph\boldsymbol{C}H_2S-$); $\delta(C_{\text{phenyl}})$: 124.6 (s, 1C), 127.4 (s, 1C), 128.6 (s, 1C), 130.8 (s, 1C), 133.2 (s, 1C), 137.6 (s, 1C). Reaction of 2-bromo-1-[(methylthio)methyl]benzene with n-butyllithium followed by reaction with chlorodiphenylphosphine affords a pale yellow viscous oil. A pure sample of ligand (P-SM) was obtained by repeated vacuum distillation at 210°C and 5 mmHg.[18] The product was fully characterized by ^{1}H-NMR, and ^{13}C-NMR spectroscopy (Table 1). The ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of P-SM shows, in addition to the phenyl protons signals (at $\delta = 6.91$–7.46 ppm), a singlet at $\delta = 1.98$ ($-SC\boldsymbol{H}_3$), and a doublet centered at $\delta = 3.94$ ($-C\boldsymbol{H}_2SCH_3$), which appeared due to phosphorus-hydrogen coupling ($J = 1.5$ Hz). The ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of P-SM shows signals at $\Delta(C_{\text{aliphatic}})$: 15.4 (s, $S\text{-}\boldsymbol{C}H_3$, 1C), and 36.9 (d, $^3J_{c\text{-}p} = 24.5$ Hz, $Ph\boldsymbol{C}H_2-$, 1C); $\delta(C_{\text{phenyl}})$: 128.6 (d, $^3J_{c\text{-}p} = 6.8$ Hz, 1C), 128.7 (s, 1C), 129.1 (s, 2C), 129.6 (d, $^3J_{c\text{-}p} = 4.8$ Hz, 1C), 132.0 (d, $^3J_{c\text{-}p} = 9.8$ Hz, 4C), 133.8 (d, $^2J_{c\text{-}p} = 19.5$ Hz, 4C), 134.2 (s, 1C), 136.2 (d, $^1J_{c\text{-}p} = 13.6$ Hz, 1C), 136.8 (d, $^1J_{c\text{-}p} = 10.2$ Hz, 2C), and 142.8 (d, $^2J_{c\text{-}p} = 24.5$ Hz, 1C). The above ^{13}C-NMR assignment were confirmed by running a Dept-135 experiment that shows disappearance of the three quaternary carbons (at $\delta = 136.2$, 136.8, and 142.8 ppm). In comparison with 2-bromo-1-[(methylthio)methyl)]benzene, the IR spectra of P-SM shows, a vibration at 1119 cm^{-1}due to νP-Ph.



SCH. 2.



SCH. 3.

Preparation of the Palladium Complexes

*Preparation of [Pd(P-S2)Cl₂] (**I**) and [Pd(P-S2)₂Cl₂] (**IV**)*

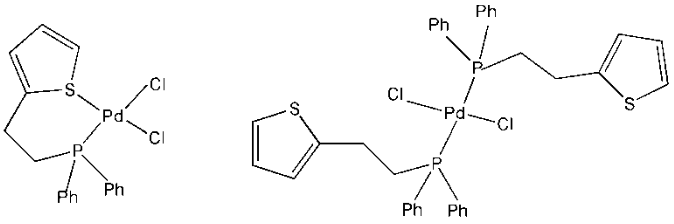
Reaction of P-S2 with equimolar amount of $[Pd(PhCN)_2Cl_2]$ gave the complex [Pd(P-S2)Cl$_2$] with P-S2 acting as a bidentate ligand. However, when the reaction was conducted at a ligand-to-metal molar ratio of 2:1, the complex [Pd (P-S2)$_2$Cl$_2$], was isolated with P-S2 acting as a monodentate ligand. The ^{1}H-NMR spectrum (300 MHz, DMSO-d$_6$) of [Pd(P-S2)Cl$_2$] shows, in addition to the phenyl proton signals at $\delta = 7.48–7.81$, a multiplet at $\delta = 2.88$ (-C$\boldsymbol{H}_2$CH$_2$P-), and another multiplet at $\delta = 2.74$ (-C$\boldsymbol{H}_2$P-). The three protons of thiophene signals appear as: two doublet of doublet centered at $\delta = 6.86$ and 7.27, and a multiplet at $\delta = 6.80$. The ^{13}C-NMR spectrum (75 MHz, DMSO-d$_6$) of [Pd(P-S2)Cl$_2$] shows, δ(C$_{\text{aliphatic}}$): 24.7 (s, 1C), and 30.0 (d, $^2J_{\text{C-P}} = 34.5$ Hz, 1C), δ(C$_{\text{thiophene}}$): 124.6 (s, 1C), 125.3 (s, 1C), 127.4 (s, 1C), and 143.6 (d, $^3J_{\text{C-P}} = 19.5$ Hz, 1C). δ(C$_{\text{phenyl}}$): 129.7 (s, 2C), 129.1 (d, $^2J_{\text{C-P}} = 11.3$ Hz, 4C), 133.6 (d, $^3J_{\text{C-P}} = 9.8$ Hz, 4C), and 132.0 (s, 2C). The above ^{13}C-NMR assignment were confirmed by running the Dept-135 experiment that shows, disappearance of the two quaternary carbons (at $\delta = 129.7$ ppm and 143.6 ppm). In comparison with the ligand (P-S2), the ^{13}C-NMR spectrum of [Pd(P-S2)Cl$_2$] shows an upfield shifted of all carbons. For example, the $\boldsymbol{C}_{\text{phenyl}}$-P in the P-S2 ligand appears at 138.2 ppm as a doublet with a coupling constant of 12.75 Hz, which shifts upfield upon coordination with the palladium metal to 129.7 ppm. Unfortunately, the ^{1}H-NMR and ^{13}C-NMR spectra of the complex [Pd(P-S2)$_2$Cl$_2$] were not informative due to the extremely low solubility of the complex in most deuterated solvents including DMSO-d$_6$. The 2:1 ligand-to-metal ratio for [Pd(P-S2)$_2$Cl$_2$] was confirmed only by the result of its microelemental analysis. The proposed structures of (**I**) and (**IV**) are shown in Figure 1.

*Preparation of [Pd(P-S3)Cl(μ-Cl)]₂ (**II**)*

Reaction of the asymmetric ligand P-S3, with equimolar amount of [Pd(PhCN)$_2$Cl$_2$] gave complex **II**. This palladium complex is soluble in acetone, chloroform, and dichloromethane, and insoluble in petroleum ether, dioxane, and hexane. Microelemental analysis for C, H, and S is inconsistent with the above formation for the complex. The ^{1}H-NMR spectrum (300 MHz, CDCl$_3$) of **II** shows, in addition to the phenyl proton signals, a multiplet centered at: $\delta = 1.89$ (-CH$_2$C$\boldsymbol{H}_2$CH$_2$P-), $\delta = 2.50$ (-C$\boldsymbol{H}_2$P-), and a triplet centered at $\delta = 2.87$ (-C$\boldsymbol{H}_2$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 $\delta = 6.87$. The ^{13}C-NMR spectrum (75 MHz, CDCl$_3$) of **II** shows δ(C$_{\text{aliphatic}}$): 25.9 (s, 2C), 26.5 (d, $^2J_{\text{C-P}} = 35.9$ Hz, 2C), and 30.5 (d, $^3J_{\text{C-P}} = 17.5$ Hz, 2C); δ(C$_{\text{thiophene}}$): 123.5 (s, 2C), 124.9 (s, 2C), 126.9 (s, 2C), and 143.1 (s, 2C); δ(C$_{\text{phenyl}}$): 127.7 (s, 4C), 133.3 (d, $^2J_{\text{C-P}} = 10.2$ Hz, 8C), 128.8 (d, $^3J_{\text{C-P}} = 11.9$ Hz, 8C), and 131.4 (s, 4C). Comparing the ^{13}C-NMR spectrum of [Pd(S-P3)Cl(μ-Cl)]$_2$ with that of the P-S3 ligand shows no difference on the chemical shift of the thiophene ring carbons, which is inconsistent with the ligand being coordinated through the phosphorus atom only. The signal for $\boldsymbol{C}_{\text{phenyl}}$-P was shifted upfield upon coordination with the palladium metal to 127.7 ppm and appeared as a singlet. Similarly, the signal for $\boldsymbol{C}$H$_2$-P was shifted to 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 seems to be unfavorable in case of the P-S3 ligand, probably due to the 7-membered chelate ring that would form. Attempts to obtain the palladium complex with the P-S3 ligand with ligand-to-metal ratio of 2:1 were unsuccessful. This could be due to the steric effect of the side arm containing thiophene ring. In view of the above discussion the complex is believed to have the dimeric structure shown in Figure 2.

*Preparation of [Pd(P-SM)Cl₂] (**III**)*

Reaction of the *P-SM* ligand, with equimolar amount of [Pd(PhCN)$_2$Cl$_2$] affords the complex **III**. This complex is soluble in acetone, chloroform, and dichloromethane, and insoluble in petroleum ether, dioxane, and hexane. Microelemental analysis for C, H, and S are inconsistent with the above formulation of the complex. The ^{1}H-NMR spectrum (300 MHz, CDCl$_3$) of [Pd(*P-SM*)Cl$_2$] shows, in addition to the aromatic proton signals at $\delta = 6.79$-7.72, a singlet at $\delta = 2.45$ (-SC$\boldsymbol{H}_3$), and two signals (doublet of doublet) at $\delta = 3.45$ and 3.68 (-C$\boldsymbol{H}_2$SCH$_3$). These two signals appear as doublet of doublet due to phosphorus and geminal hydrogen coupling. The non-equivalence of the methylene protons is due to the rigid configuration of the ligand upon chelation$^{[19]}$. The ^{13}C-NMR spectrum (75 MHz, CDCl$_3$) of [Pd(*P-SM*)Cl$_2$]



I IV

FIG. 1. Proposed structures of [Pd(P-S2)Cl$_2$] (**I**) and [Pd(P-S2)$_2$Cl$_2$] (**IV**).

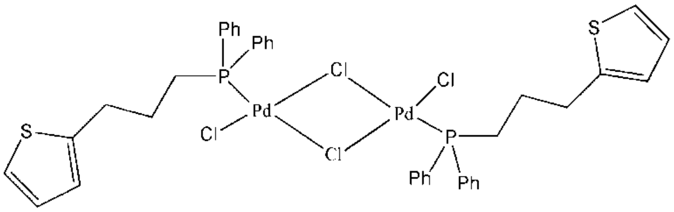


FIG. 2. Proposed structure of [PdCl(μ-Cl) (P-S3)]$_2$.

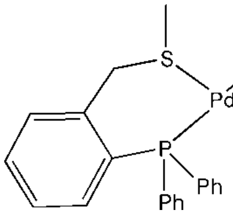


FIG. 3. Proposed structure of [Pd(P-SM)Cl_2].

shows $\delta(\mathrm{C}_{\text{aliphatic}})$: 21.9 (s, 1C), and 36.7 (d, $^{3}J_{\text{c-p}} = 11.4$ Hz, 1C). $\delta(\mathrm{C}_{\text{aromatic}})$: 124.3 (d, $^{1}J_{\text{c-p}} = 49.1$ Hz, 1C), 125.1 (d, $^{1}J_{\text{c-p}} = 42.3$ Hz, 1C), 125.9 (d, $^{1}J_{\text{c-p}} = 46.6$ Hz, 1C), 128.9 (d, $^{2}J_{\text{c-p}} = 12.5$ Hz, 1C), 129.3 (d, $^{3}J_{\text{c-p}} = 11.8$ Hz, 1C), 130.0 (d, $^{3}J_{\text{c-p}} = 8.6$ Hz, 1C), 132.3 (s, 1C), 134.7 (d, $^{2}J_{\text{c-p}} = 11.8$ Hz, 4C), 134.9 (s, 2C), and 137.7 (d, $^{2}J_{\text{c-p}} = 12.2$ Hz, 1C),. The above ^{13}C-NMR assignment were confirmed by Dept-135 experiment that shows, disappearance of the four quaternary carbons at $\delta = 124.3$, 125.1, 125.9, and 137.7 ppm. In view of above discussion, a square planar for [Pd(P-SM)Cl_2] was proposed (Figure 3). Attempts to prepare a complex with ligand-to-metal ratio of 2:1 were unsuccessful. This could be explained due to, the steric effects of ligand P-SM that hinders the bonding two ligands to the same metal center and/or the stability of the chelate ring in compound (**IV**).[2]

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