

Synthesis and Characterization of Palladium (II) Complexes Containing Mixed Ligands with Pyrrolidine Dithiocarbamate and Phosphines

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Abstract

This work includes preparation and characterization of new four mono nuclear complexes of palladium metal ion result from treating palladium chloride with ammonium pyrrolidine dithiocarbamate (PDTC), tertiary phosphines(dppe, dppp) and 2-phenyl pyridine (Hppy) in different molar ratios. All complexes have been characterized by spectroscopic methods{IR, UV-Vis, ^1H NMR} spectroscopy, in addition to elemental analysis (C.H.N) and conductivity measurement. pyrrolidine dithiocarbamate ligand behaves like bidentate in the complexes $[\text{Pd}(\text{PDTC})(\text{dppe})]\text{Cl}$ and $[\text{Pd}(\text{PDTC})(\text{ppy})]$ but it behaves as mono dentate in the complexes $[\text{Pd}(\text{PDTC})_2(\text{dppp})]$ and $[\text{Pd}(\text{PDTC})_2(\text{dppe})]$, while tertiary phosphines and 2-phenyl pyridine behave like bidentate ligand. [DOI: [10.22401/JNUS.21.2.03](https://doi.org/10.22401/JNUS.21.2.03)]

Keywords: palladium, pyrrolidine dithiocarbamate, phosphines.

1.Introduction

The copper and zinc complexes with pyrrolidine dithiocarbamate works as antiviruses drug [1,2]. Dupont [3] and his assistants explain effectiveness of some diethiocarbamic acid derivatives in the elimination of fungus and bacteria (Antifungid and Antibacterial activity) [4,5]. Dithiocarbamate used in agriculture as insecticides [6-8]. They are also used in vulcanization of rubber liners [8,9]. and in the concentration of sulphide ores by froth floatation process for concentration of sulphide ores, it was also used as lubricants and antioxidants [9], and in solar cell regeneration technology [10], and also known as anticancer agents [6]. Josh Ghosh and his associates were also able to prepare the vanadium complexes with thiocarbamate used as a contraceptive method [11]. Pyrrolidinedithiocarbamate (PDTC) is used as an antiviruses that cause influenza by defeat of the gene responsible for the formation of this virus [12,13]. while the Bis (diphenylphosphino)ethane (dppe) and Bis (diphenylphosphino)propan (dppp) behave as bidentate chelate [14] or behave as bridge ligands between two metal atoms [5,15], the complexes of phosphine with palladium used as assistant agent cyclic or heterocyclic by increase stability of medial compound [16] and used in olefins polymer [17], 2-phenyl pyridine (ppy) is heterocyclic organic

compound ligands [18,19] is metelated and coordinated as chelate through the carbon atom of the phenyl ring and the N atom of the pyridine ring, it easy to be complex with palladium [20], also (ppy) used in fabrication of electroluminescent devices at laboratory scale as phosphorescent [21], there are a lot of complexes for (ppy) with palladium we can find in literary [21-23].

2.Experimental

2.1. Physical Measurements and Analysis

The ^1H NMR spectra were recorded on a Varian Unity spectrometer in CDCl_3 or $\text{d}^6\text{-dmso}$. while FT-IR spectra were taken on a Shimidzu FT-IR 8400 spectrophetometer in range $400\text{--}4000\text{cm}^{-1}$ range using KBr. Electronic spectra were obtained using UV-vis 1650PC Spectrophotometer at room temperature in DMSO solvent. Elemental analysis was recorded using a Euro vector EURO EA 300 elemental analyzer.while Melting points recorded on a Gallenkamp melting point apparatus. Condu-ctivity measurements were carried out on 0.001M solutions using a digital conductivity meter.

2.2. Chemicals

PdCl_2 , Pyrrolidine dithiocarbamate (PDTC) prepared by Sigma company, 2-phenylpyridine (ppy) Prepared by a Aldrich company, Bis (diphenylphosphino)ethane (dppe), Bis (diphenylphosphino)propan (dppp)

Prepared by BDH company, were purchased and used as received. The complexes $[Pd(PDTC)Cl]_n$ ($n=1-2$) preparation was according to literature published in [24], while $[Pd_2(ppy)_2(\mu-Cl)_2]$ in literature published in [21].

2.3.Preparation of Complexes

1- $[Pd(PDTC)(dppe)]Cl$

A (dppe) (0.065g, 0.163mmol) dissolved in $CHCl_3$ (10 ml) was added to a solution of $[Pd(PDTC)Cl]$ (0.050g, 0.170mmol) in $CHCl_3$ (10 ml).

The mixture was stirred at 25°C for 4 h. The resulting solid yellow was collected by filtration, and washed with n-Pentane then dried under vacuum. It was recrystallized from n-Pentane/ $CHCl_3$ (1:1) to afford yellow crystalline solid. with yield percent 86% (0.080g), M.p:138-140°C. Elemental analysis calculation for $C_{31}H_{28}NP_2PdS_2Cl$: C,53.96, H,4.78, N,2.12 found C,54.2, H,4.70, N,2.04 Molar conductivity in (DMSO): 35.2 Λ ($ohm^{-1}.cm^2.mol^{-1}$). IR (KBr): 3053w, 2920w, 1438m, 528m, 1525s, 997w, 426vw cm^{-1} . 1H NMR (dms $o-d^6$) δ 7.29-7.77 (m, 20H), δ 3.75(s, 2H), δ 2.95-3.07(m, 4H), δ 1.98 (m, 4H) ppm.

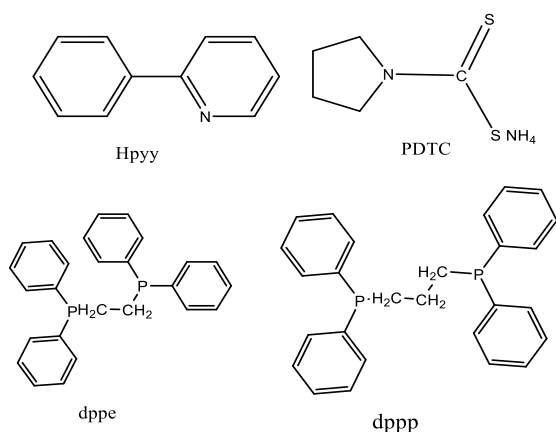


Fig.(1): 2-phenylpyridine (ppy), Pyrrolidinedithiocarbamate (PDTC), Bis(diphenylphosphino)ethane(dppe), Bis(diphenylphosphino)propane(dppp).

2- $[Pd(PDTC)(ppy)]$

A $[PdTC]$ (0.022g, 0.134 mmol) in MeOH (10 ml) was added to $[Pd_2(ppy)_2(\mu-Cl)_2]$ (0.05g, 0.134mmol) dissolved in CH_2Cl_2 (10 ml) The mixture was stirred at 30°C temperature for 4h. The resulting green yellow precipitate was collected by filtration, washed

with MeOH, leaving at room temperature for one day to dry. It was recrystallized from n-Pentane/ $CHCl_3$ (1:1) to afford yellow crystalline solid. with yield percent 91% (0.050g), M.p:237°C. Elemental analysis calculation. for $C_{16}H_{12}N_2PdS_2$: C,47.29, H,3.98, N,6.84 found C,47.23, H,3.96, N,6.89. Molar conductivity (DMSO):14.8 Λ ($ohm^{-1}.cm^2.mol^{-1}$). IR (KBr): 3047w, 2913w, 1596w, 1566s, 1010w cm^{-1} . 1H NMR (dms $o-d^6$) δ 8.25(d, H1), δ 8.12(d, H4), δ 8.06(t, H2), δ 7.77(d, H5), δ 7.38(t, H3), δ 7.12 (t, H6), δ 7.07(t, H7), δ 6.92(d, H8), δ 3.75(t,4Ha), δ 2.02 (p, 4H6) ppm.

3- $[Pd(PDTC)_2(dppe)]$

A solution of (dppe) (0.05g, 0.13mmol) in CH_2Cl_2 (10 ml) was added to a solution of $[Pd(PDTC)_2]$ (0.053g, 0.14mmol) in CH_2Cl_2 (10 ml) [21]. The mixture was mixed at 25°C for 3 h. The resulting solid yellow was collected by filtration, washed with n-Pentane and dried in vacuum. It was recrystallized from n-Pentane/ $CHCl_3$ (1:1) to afford yellow crystalline solid. yield 0.070g, 71%. Elemental analysis calculation. for $C_{36}H_{32}N_2P_2PdS_4$: C,54.33, H, 5.13, N,3.56 found C,54.23, H, 5.06, N, 3.51.

Molar conductivity (DMSO): 2.5 Λ ($ohm^{-1}.cm^2.mol^{-1}$). IR (KBr): 3051w, 2948w, 1436m, 526m, 526m, 1529s, 1000w 412vw cm^{-1} . 1H NMR (dms $o-d^6$). δ 7.60-7.74(m,20H), δ 3.71 (s,8Ha), δ 2.98 (m,4H), δ 2.03(m,8Hb) M.p: 134-136°C.

4- $[Pd(PDTC)_2(dppp)]$

A solution of (dppp) (0.06g, 0.15mmol) in CH_2Cl_2 (10 ml) was added to a solution of $[Pd(PDTC)_2]$ [21]. (0.053g, 0.14mmol) in CH_2Cl_2 (10 ml) The all compound was stirred at 25°C temperature for 3 h. The resulting solid yellow was collected by filtration and washed with n-Pentane and in vacuum dried. It was recrystallized from n-Pentane/ $CHCl_3$ (1:1) to afford yellow crystalline solid. yield 0.060g, 66%. Elemental analysis calculation. for $C_{37}H_{34}N_2P_2PdS_4$: C,54.83, H,5.23, N,3.51, found C,54.77, H,5.22, N,3.45. Molar conductivity (DMSO): 12.8 Λ ($ohm^{-1}.cm^2.mol^{-1}$). IR (KBr):3049w, 2948w, 1438m, 511w, 1517s, 996w, 418vw cm^{-1} . 1H NMR (dms $o-d^6$) δ 7.45-7.09 (m,20H), δ 3.64(m,8Ha), δ 3.00(m,4H), δ 1.95(m,8Hb)ppm.M.p:268-270°C.

3. Results and Discussion

3.1. [Pd(PDTC)(dppe)]Cl

In addition of one equivalents of Bis(diphenylphosphino)ethane (dppe) to a CH₂Cl₂ solution of [Pd(PDTC)Cl][21] resulting yellow solid yield 86%. In the infrared spectra Table (4) of this complex appeared two functional groups of $\nu(\text{P-Ph})$, $\nu(\text{P-C})$ in (528, 1438cm⁻¹), and it appeared strong absorption at the site (1525cm⁻¹) stretching back to the frequency range $\nu(\text{C=N})$ for Pyrrolidine dithiocarbamate (PDTC), while the frequency range (1332)cm⁻¹ back to $\nu(\text{C=S})$, and very weak shifted in (426cm⁻¹) back to $\nu(\text{P-Pd})$, The spectrum showed a weak shifted in (997cm⁻¹) back to $\nu(\text{CSS})$ this shifted special for (PDTC) [27] Appearance of one single frequency for a group $\nu(\text{CSS})$ evidence of the link (PDTC) bidentate in the complexes, [25].

¹H NMR spectrum Showed ¹H{³¹P} NMR of the complex [Pd (PDTC)(dppe)] Cl Table(3) measured in the solvent DMSO multi-position signal at the shifted (1.98ppm) correspond to four protons of the value of integration of chemical and displacement this reference to the two sets of methylene protons (4Hb) to ring pyrrolidine, while multiple single in (3.01ppm) back to four protons of methylene protons (CH₂)₂P of phosphine, also showed the spectrum mono signal at the site (3.75ppm) belonging to the four protons of methylene to ring of pyrrolidine (4Ha), multiple signal in the range (7.29-7.77)ppm back to the vinyl protons rings of phosphine [26] Fig.(2).

3.2.[Pd(PDTC)(ppy)]

The interaction between (NH₄(PDTC)) with the complex [Pd₂(ppy)₂(μ-Cl)₂] [21,23] afford yellow crystalline solid yield 91%. In the infrared spectra Table (4) of this complex appeared strong shift in 1566cm⁻¹ back to the frequency range $\nu(\text{C=N})$, middle shift in (1485)cm⁻¹ refer to $\nu(\text{C-N})$, while 1596cm⁻¹ back to frequency range of $\nu(\text{C=C})$, the frequency range in (1260)cm⁻¹ refers to $\nu(\text{C=S})$, and very weak shifted in (412)cm⁻¹ back to $\nu(\text{P-Pd})$, The spectrum showed a weak shift in (1010cm⁻¹) back to $\nu(\text{CSS})$, evidence of the link (PDTC) bidentate in the complexes [21].

¹H NMR spectrum showed Table (3)

¹H{³¹P} NMR of the complex Penta signal at the (2.08 ppm) back to four protons of methylene protons (4Hb) to ring pyrrolidine, while. The tripartite signal in (3.75ppm) back to four protons of methylene protons (4Ha) to ring pyrrolidine, The doublets signal in (6.92ppm) refer to (H8), tripartite signal in (7.07ppm) to (H7), tripartite signal in (7.12ppm) back to (H6), tripartite signal in (7.38ppm) to (H3), doublets signal in (7.77ppm) to (H5), tripartite signal in (8.06ppm) to (H2), doublets signal in (8.12ppm) to (H4), doublets signal in (8.35ppm) to (H1), all These signals back to proton of ring phenylpyridine [27] Fig.(3).

3.3.[Pd(PDTC)₂(dppe)]

This complex was prepared from interaction between Bis(diph enylphosphino) ethane(dppe), with the complex [Pd(PDTC)₂] [21] to afford yellow crystalline solid, yield 71%. Pyrrolidine dithiocarbamate ligand behaves as mono dentate. IR spectra Table (4) of this complex appeared two functional groups of $\nu(\text{P-Ph})$, $\nu(\text{P-C})$ in (526, 1436cm⁻¹), and it appeared strong absorption at the site (1529cm⁻¹) stretching back to the frequency range $\nu(\text{C=N})$ for pyrrolidinedi thiocarbamate (PDTC), while the frequency range in (1249)cm⁻¹ refer to $\nu(\text{C=S})$ The spectrum showed a two weak shifting in (996-1000cm⁻¹) back to $\nu(\text{CSS})$ appearance of a single frequency for a group $\nu(\text{CSS})$ evidence of the link (PDTC) behaves as mono dentate.

¹H NMR spectrum Table (3) showed multiple single in (2.03)ppm refer to eight protons (8Hb) to ring of pyrrolidine, while multiple single in (2.98ppm) back to four protons of methylene protons (CH₂)₂P of phosphine also showed the spectrum mono signal at the site (3.71ppm), belonging to the eight protons for methylene protons to ring of pyrrolidine, multiple signal with in the range (7.60-7.74)ppm back to the twenty protons of vinyl protons rings phosphine Fig.(4).

3.4.[Pd(PDTC)₂(dppp)]

This complex was prepared from interaction between Bis(diphenylphosphino) Propan (dp pp) and [Pd(PDTC)₂] complex [21]. The resulting was yellow crystalline solid of [Pd(PDTC)₂(dppp)] yield 66%. pyrrolidine

dihtiocarbamate ligand behaves as mono dentate. IR spectra Table (4) of this complex appear two functional groups of $\nu(\text{P-Ph})$, $\nu(\text{P-C})$ in $(511, 1438\text{cm}^{-1})$, and it appeared strong absorption at the site (1517cm^{-1}) stretching back to the frequency range $\nu(\text{C=N})$ for Pyrrolidinedi thiocarbamate (PDTC), while the frequency range in $(1328)\text{cm}^{-1}$ refer to $\nu(\text{C=S})$, and very weak shifting in (426cm^{-1}) back to $\nu(\text{P-Pd})$, The spectrum showed a two weak shifting in $(968, 1000\text{cm}^{-1})$ back to $\nu(\text{CSS})$ and the emergence of a single frequency for a group $\nu(\text{CSS})$ evidence of the link (PDTC) behaves as mono dentate [25].

^1H NMR spectrum Table (3) Showed multiple single in $(1.95)\text{ppm}$ refer to ten protons eight for (8Hb) to ring of pyrrolidine, and two protons of the methylene group distant from the phosphorus atom $(\text{CH}_2)\text{CH}_2$ of phosphine, while multiple single in (3.00ppm) back to four protons of methylene protons $(\text{CH}_2)_2\text{P}$ of phosphine also showed the spectrum mono signal at the site (3.64ppm) , belonging to the eight protons for methylene protons to ring of pyrrolidine, multiple signal in the range $(7.45-7.69)\text{ppm}$, back to the vinyl protons rings phosphine [26] (Fig 5).

3.5 Electronic Spectra of [PdL1L2]Complex

Three different absorbs appeared in three different locations for each prepared complexes which are assigned to $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{E}_{1g}$ were the third absorbency refer to correspond to $\text{L} \rightarrow \text{PdCT}$ transitions [27], the position of these bands are in good agreement with that reported for square planer geometry [24,28]. In addition the measured magnetic moment for this complex was found

to be 0.0B.M, while the conductance measurements indicate that the complex was to be nonionic except the first complex, $[\text{Pd}(\text{PDTC})(\text{dppe})]\text{Cl}$ was ionic Table (2).

4. Conclusion

In this paper, we succeeded to prepare new four mono nuclear complexes based on another complexes by replacement ligands, the (PDTC) ligand behaves in the prepared complexes as a bidentate and coordinate through two sulfur atoms to metalion, The prepared tertiary phosphines complexes showed that the tertiary phosphines are coordinated as a bidnetate via two phosphor (P) atoms, with ppy ligands is metelated and coordinated as chelate through the carbon atom of the phenyl ring and the N atom of the pyridine ring that make the new complexes more stable, all prepared complexes showed square planer shape and all complexes have been characterized by spectroscopic methods, in addition to elemental analysis(C.H.N) and conductivity measurement.

Table (1)
Elemental analyses and some other data of the complexes.

Complexes	Molecular formula	M.W (g/mol)	Color	M.P. °C	Yield %	Elemental analysis Found(cal)%		
						C	H	N
$[\text{Pd}(\text{PDTC})(\text{dppe})]\text{Cl}$	$\text{C}_{31}\text{H}_{28}\text{NP}_2\text{PdS}_2\text{Cl}$	682.52	Pale Yellow	138-140	86	53.96 (54.23)	4.78 (4.70)	2.12 (2.04)
$[\text{Pd}(\text{PDTC})(\text{ppy})]$	$\text{C}_{16}\text{H}_{12}\text{N}_2\text{PdS}_2$	402.82	Pale Yellow	237-239	91	47.29 (47.23)	3.98 (3.96)	6.84 (6.89)
$[\text{Pd}(\text{PDTC})_2(\text{dppe})]$	$\text{C}_{36}\text{H}_{32}\text{N}_2\text{P}_2\text{PdS}_4$	789.29	Pale Yellow	134-136	70	54.33 (54.23)	5.13 (5.06)	3.56 (3.51)
$[\text{Pd}(\text{PDTC})_2(\text{dppp})]$	$\text{C}_{37}\text{H}_{34}\text{N}_2\text{P}_2\text{PdS}_4$	802.32	Pale Yellow	268-270	66	54.83 (54.77)	5.23 (5.22)	3.51 (3.45)

Table (2)
Decomposed Electronic spectra, conductance in DMOS solvent and magnetic moment (B.M) for metal complex.

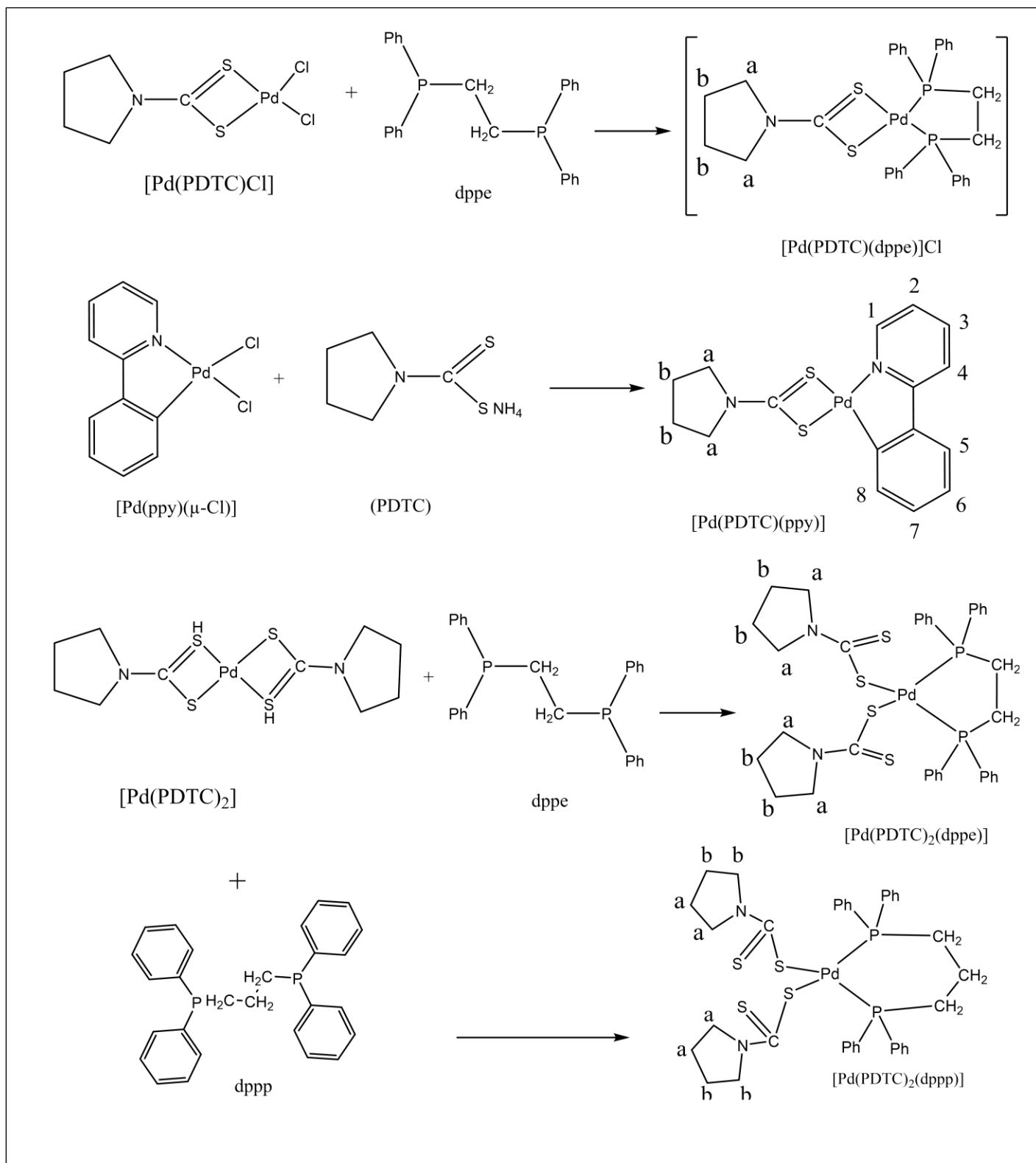
Complexes	$\lambda(\text{nm}) \text{ cm}^{-1}$	Assignment Bands for all complexes	$\mu_{\text{eff.}}$ B.M	Moler. cond ($\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) Λ	Suggested geometry
[Pd(PDTC)(dppe)]Cl	246, 316, 381	$^1A_{1g} \rightarrow ^1B_{1g}$ $A_{1g} \rightarrow ^1E_{1g}$ $L \rightarrow \text{PdCT}$	0.0	35.2	Square planer
[Pd(PDTC) ₂ (dppe)]	362, 307, 522			2.5	
[Pd(PDTC) ₂ (dppp)]	262, 295, 582			12.8	
[Pd(PDTC)(ppy)]	250, 320, 495			14.8	

Table (3)
¹HNMR data for complexes.

Complexes	δH rings ppy	δH rings (Phos.) (ppm)	δH (PDTC) H a H b (ppm)	δH (Phos.) CH ₂ CH ₂ (ppm)
[Pd(PDTC)(dppe)]Cl	-	7.29-7.77 m	1.88-2.09 m 3.75 s	- 2.95-3.07 m
[Pd(PDTC) ₂ (dppe)]	-	7.60-7.74 m	1.97-2.09 m 3.71 s	- 2.95-3.00 m
[Pd(PDTC) ₂ (dppp)]	-	7.45-7.69 m	1.87-2.02 m 3.52-3.77 m	1.87-2.02 m 3.00 s
[Pd(PDTC)(ppy)]	H ₁ = 8.35 d H ₄ = 8.12 d H ₂ = 8.06 t H ₅ = 7.77 d H ₃ = 7.38 t H ₆ = 7.12 t H ₇ = 7.07 t H ₈ = 6.92 d	-	2.08 p 3.75 t	-

Table (4)
The most important bands (cm^{-1}) of the infrared spectra of the complexes.

Complexes	$\nu(\text{C-H})$		diphosphin		$\nu(\text{C=N})$	$\nu(\text{CSS})$	$\nu(\text{C=S})$	$\nu(\text{P-Pd})$
	Ar	Alph	$\nu(\text{P-C})$	$\nu(\text{P-Ph})$				
[Pd(PDTC)(dppe)]Cl	3053w	2925w	538m	1431m	1525s	997w	1332w	426
[Pd(PDTC) ₂ (dppe)]	3051w	2948	526m	1436m	1529s	996w	1249w	412
[Pd(PDTC) ₂ (dppp)]	3049w	2948w	511m	1438m	1517s	968w	1328m	418
[Pd(PDTC)(ppy)]	3047w	2913w	-	-	1566s	1010w	1260m	-



Scheme (1) : Reactions between mixed ligands and complexes.

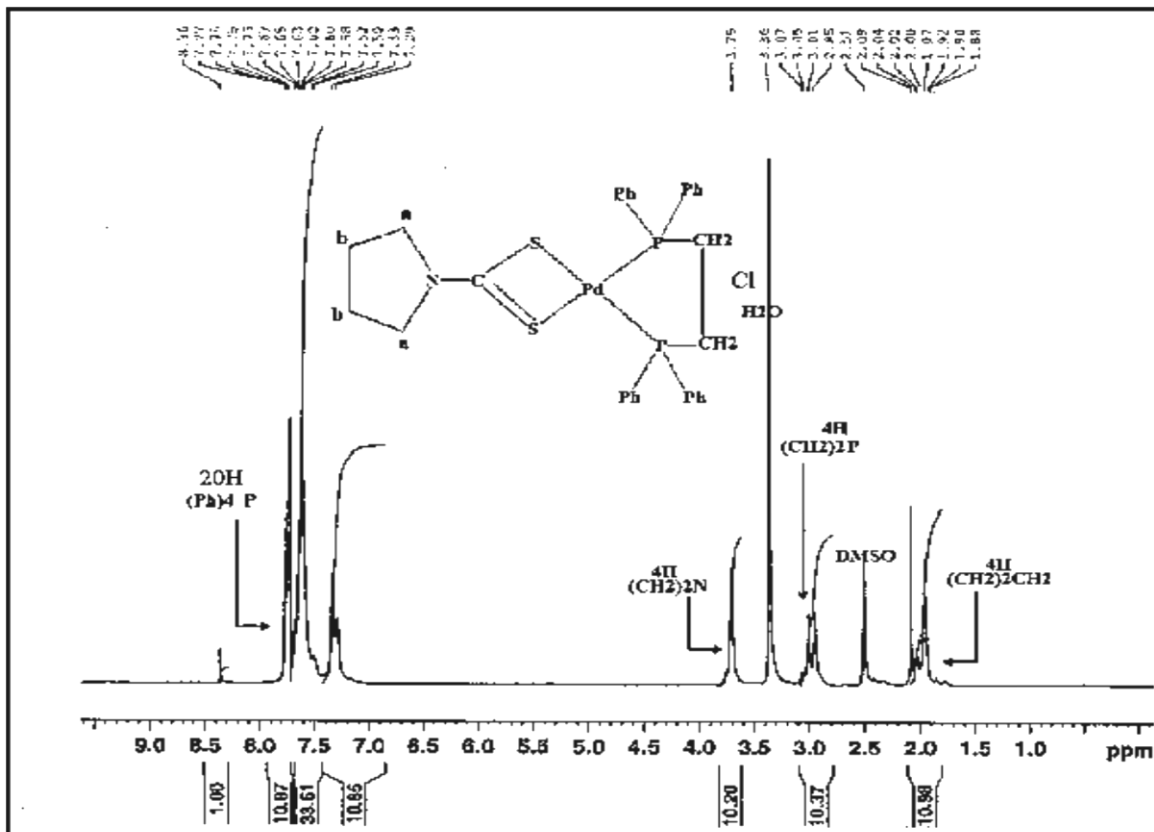


Fig.(2): 1H NMR spectra of the $[Pd(PDTC)(dppe)]Cl$.

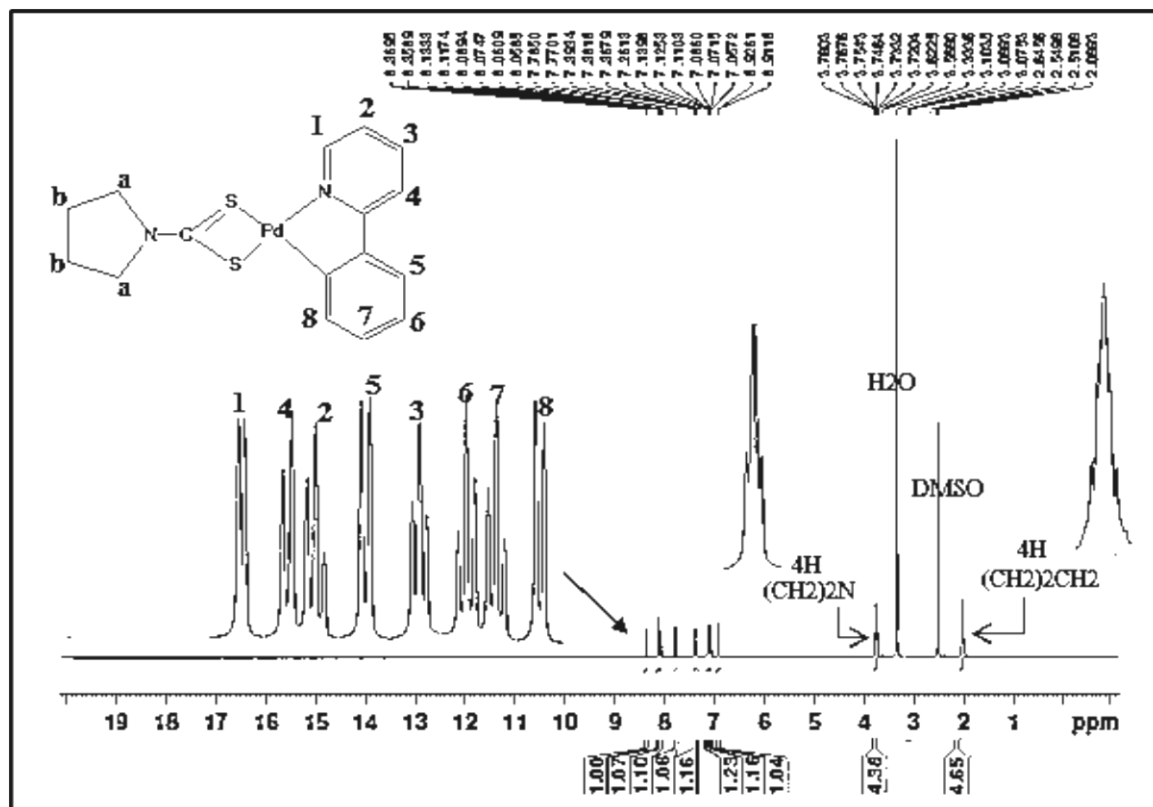


Fig.(3): 1H NMR spectra of the $[Pd(PDTC)(ppy)]$.

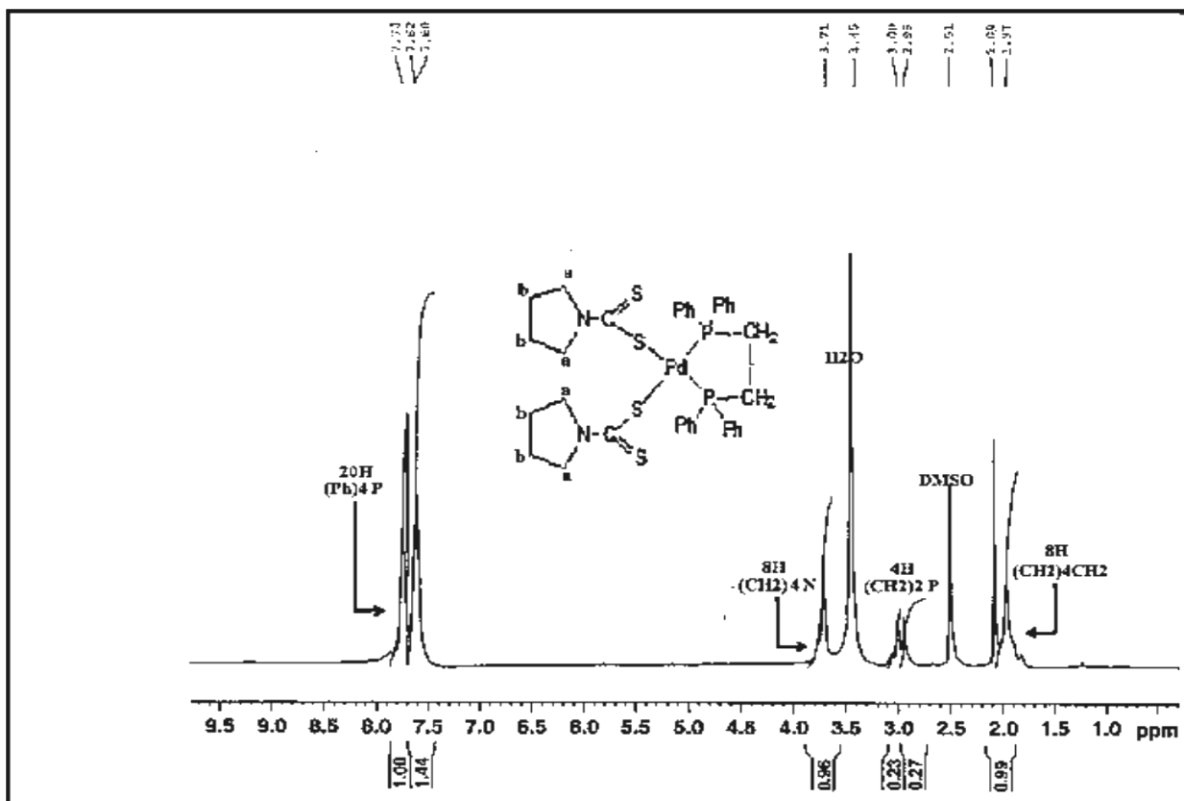


Fig.(4): ¹H NMR spectra of the $[Pd(PDTC)_2(dppe)]$.

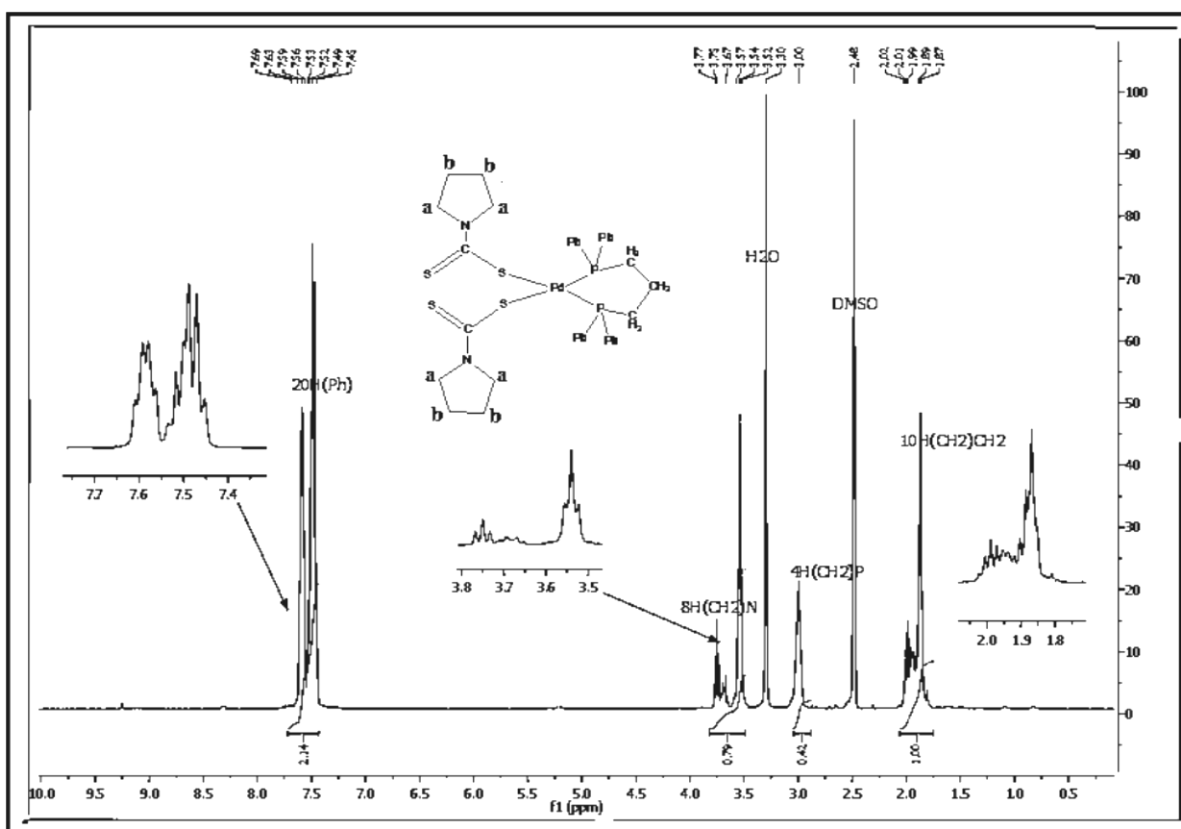


Fig. (5): ¹H NMR spectra of the $[Pd(PDTC)_2(dppp)]$.

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