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Palladium(II) and Platinum(II) complexes containing the mixed ligands N-phenyl-N-(2-pyridyl or 2-methylpyridyl) thiourea and diphosphines $Ph_2P(CH_2)_nPPh_2$ (n=1-4)

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ABSTRACT

Palladium(II) and platinum(II) complexes containing mixed ligands N-phenyl-N-(2-pyridyl) thiourea (AH) or N-phenyl-N-(2-methylpyridyl) thiourea (BH) and the diphosphine $Ph_2P(H_2)_nPPh_2$ (n = 1-4) have been prepared and characterized by elemental analysis, magnetic susceptibility, molar conductance and i.r. spectral data. ^1H n.m.r. data have been used to characterize the prepared ligands while ^{31}P-{^1H} n.m.r. data have been applied to characterize the produced isomers.

Key words: Palladium, Platinum, Phosphines, Thiourea ligand complexes.

INTRODUCTION

Transition metal complexes of thiourea derivatives have been an active area of some recent research[1-5]. The biological activity of such complexes has been screened for various biological actions[6-7]. The Platinum complexes have been used as antitumor agents in chemotherapy for some types of cancer[8,9]. A novel series of platinum(II) complexes have been reported recently[6,8] for potentials use as chemotherapeutic agents to prepare complexes that are not structurally analogous to cis-platin $[Pt(NH_3)_2Cl_2]$ in an attempt to develop new platinum(II) based antitumor drugs with much lower side effects[1]. Research were focused on preparation of a series of platinum(II) thiourea derivative complexes in which both the leaving ligand and the non-leaving groups attached to platinum(II) center were varied[8]. Variation of the amine attached to the thiocarbonyl functionality and other substituents attached to the amine group could influence the lipophilicity / hydrophilicity and electronic properties of the complexes and thus also affect the liability of the leaving group which could control the reactivity and biological activity of the complexes.

As part of our interest in development of bifunctional antitumor agents we are studying the incorporation of the two active ligands heterocyclic thiones and phosphines in the same complexes[10-12]. Furthermore we incorporate two metal centers in the same complexes[13-14].

In the present paper we report the synthesis and characterization of some palladium(II) and platinum(II) complexes of some substituted thiourea. Furthermore we report some mixed ligand complexes of substituted thiourea and diphosphines.

EXPERIMENTAL

General

The ^{1}H- and ^{31}P-{^{1}H} n.m.r. spectra were performed in the laboratories of Prof. Dirk Stienborn, Martin-Luther-Universität, Halle-Wittenberg, Germany. I.r. spectra were recorded on a shimadzu FT-IR 8400 spectrophotometer in the 200-4000 cm^{-1} rang using CsI discs. Elemental analyses were carried out on a CHN analyzer type 1106 (Carlo-Erba). Magnetic measurements were recorded on a Brucker BM6 instrument at room temperature using the Faraday method. Conductivity measurements were made on a conductivity meter type Hana EC 214. Melting points were measured on an electrothermal 9300 melting point apparatus.

Starting materials

The compounds Na_2PdCl_4, K_2PtCl_4, dppm, dppe, dppb, 2-amiopyridine, 2-aminomethylpyridine and Phenyl isothiocyanate were commercial products and used as supplied.

N-Phenyl-N-(2-pyridyl) thiourea (AH)

Phenyl isothiocyanate (3.8 cm^3, 33.2 mmole) was added to a solution of 2-aminopyridine (3.12 g, 33.2 mmole) in C_6H_6 (10 cm^3). The mixture was heated under reflux for 1.5 h. then cool in an ice bath. The resulting white solid was filtered off washed with C_6H_6 and recrystalized from EtOH.

N-Phenyl-N-(2- methyl pyridyl) thiourea (BH)

This compound was prepared and isolated by a method similar to that used for the preparation of N-Phenyl-N-(2-pyridyl) thiourea (AH).

Preparation of complexes

[PdCl$_2$(AH)$_2$] (1)

A solution of Na_2PdCl_4(0.09 g, 0.43 mmol) in Me_2CO (5 cm^3) was added to a warm solution of the ligand (AH) (0.2 g, 0.87 mmol) in Me_2CO (5 cm^3). The mixture was stirred at room temperature for 3 h. The yellow-orange solid which formed was filtered off, washed with H_2O and dried under vacuum.

[PdCl$_2$(BH)$_2$] (19)

This complexes was prepared and isolated by a method similar to that used for [PdCl$_2$(AH)$_2$] .

[Pd(A)$_2$] (2)

A solution of Na_2PdCl_4 (0.09 g, 0.43 mmol) in EtOH (5 cm^3) was added to a warm solution of a sodium salt of the ligand AH, prepared by mixing a solution of the AH (0.2 g, 0.87 mmol) in EtOH (5 cm^3) with a solution of NaOH in EtOH (0.87 mmol).The mixture was stirred for 1.5 h.. The yellow solid which formed was filtered off, washed with H_2O and dried under vacuum.

Complex[14] was prepared and isolated by a similar method.

[Pd(A)$_2$(dppm)]$_2$ (3)

A warm solution of dppm (0.11 g, 0.21 mmol) in $CHCl_3$ (3 cm^3) was added to a warm solution of [Pd(A)$_2$](2) (0.12 g, 0.21 mmol) in $CHCl_3$ (5 cm^3). The resulting red solution was stirred for 1.5 h., solvent was then evaporated, hexane (5 cm^3) was added and the mixture was stirred for 3 h. The red solid which formed was filtered off and dried under vacuum.

The following complexes were prepared and isolated by a similar method[4-6, 9-12] and[15 -18].

[PtCl$_2$(AH)$_2$] (7)

A solution of K_2PtCl_4 (0.13 g, 0.33 mmol) in H_2O (3 cm^3) was added to a solution of the ligand AH (0.015 g, 0.65 mmol) in EtOH (5 cm^3). The mixture was stirred for 1.5 h. The resulting orange solid was filtered off, washed with H_2O and dried under vacuum.

Complex[13] was prepared and isolated by a similar method.

[Pt(A)$_2$] (8)

A solution of K_2PtCl_4 (0.18 g, 0.44 mmol) in H_2O (3 cm^3) was added to a solution of the sodium salt of the ligand AH, prepared by mixing a solution of AH (0.2 g, 0.87 mmol) in EtOH (5 cm^3)with a solution of NaOH (0.87 mmol) in EtOH (8.7 cm^3).The mixture was stirred for 1.5h.. The yellow solid which formed was filtered off, washed several time with H_2O and dried under vacuum.

Complex[20] was prepared and isolated by a similar method.

$[Pt(B)_2(dppm)]_2$ (21)

A warm solution of dppm (0.11 g, 0.22 mmol) in $CHCl_3$ (3 cm^3) was added to a warm solution of $[Pt(B)_2]$ (20) (0.15 g, 0.22 mmol) in EtOH (5 cm^3). The mixture was stirred for 1.5h, solvent was then evaporated to dryness. Hexane (5 cm^3) was added and the mixture was stirred for 2h. The resulting pale-yellow solid was filtered off and dried under vacuum.

The following complexes were prepared and isolated by a similar method[22-24].

RESULTS AND DISCUSSION

Ligand synthesis and characterization

The ligands were prepared by the reaction of amino-substituted heterocyclic with phenylisothiocyanate in benzene solvent. The ligands were purified by recrystalisation from ethanol and characterized by elemental analysis, ^1H n.m.r. and i.r. spectroscopy. The analytical and spectroscopic data are consistent with the proposed structures given in Fig. 1.

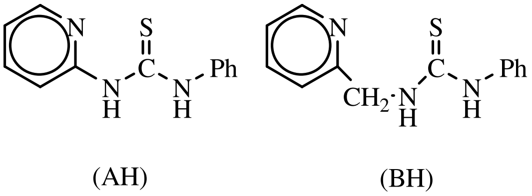

Fig. 1. The structural formula of the ligands (AH) and (BH)

The assignment of the ^1H n.m.r. spectra of the ligands were in general straight forward Table 3. A notable feature of the spectra is the observation of separate resonances for the amine protons attached to the phenyl and the heterocyclic substituents, within the 8.3 – 13.8 p.p.m. range. The methylene signal of the ligands BH appeared as a doublet at δH 4.82 p.p.m. with $^3J(HH)$, 3.6 Hz due to coupling to the NH proton.

The i.r. spectra of the prepared ligands (AH) and (BH) (Table 2) showed weak to strong bands at ca. 1532, 1427, 995, 772 and 1530, 1435, 995, 761 cm^{-1} which may be assigned to the thioamide vibrational bands I, II, III and IV respectively[15]. The spectra also showed two bands within the 3169 to 3339 cm^{-1} range assigned to $\nu(NH)$ [1, 16]. Other identification data are given in the Tables.

Synthesis of complexes

Treatment of Na_2PdCl_4 or K_2PtCl_4 with the ligands LH (LH = AH or BH) gave complexes of the type $[MX_2(LH)_2]$ (M = Pd trans or Pt cis). The ligands LH behave as monodentate neutral ligands coordinated through the nitrogen atom of the pyridine ring for AH or the NH group attached to the methylene group in BH ligand, Treatment with the sodium salts of the ligands NaL gave the chelated complexes $[ML_2]$. The anionic ligands L behave as bidentate chelates bonded to metal through the nitrogen atom of the pyridine ring and the thiourea sulfur atom.

Treatment of the chelated complexes $[ML_2]$ with the diphosphines $Ph_2P(CH_2)_nPPh_2$; (n = 1 – 4) gave complexes of the type $[ML_2(diphos)]_2$, (n = 1) or $[ML_2(diphos)]$ (n = 2 – 4). The anionic ligands behave as monodentate coordinated to metal through either the thio – sulfur atom or the nitrogen of the amide group as evident from the n.m.r. data Table 3.

Characterization of complexes

The complexes were identified by elemental analysis, i.r. spectra, magnetic susceptibility, conductivity measurements and some of them by $^{31}P\text{-}\{^1H\}$ n.m.r. spectra and their data are listed in Tables 1-3. The magnetic susceptibility measurements for the prepared complexes indicate that all of them are diamagnetic have square planar arrangement. The molar conductivity of the complexes in $CHCl_3$ is low enough to suggest that they are non–electrolytes[17]. The infrared spectra of the prepared compounds showed the usual four thioamide bands required by the presence of the substituted thiourea ligands[15] as well as the characteristic NH streaching vibrations[1,16] (Table 2). The shifts observed for these bands due to coordination in combination with the lack of one í(NH) band signify the S-or N-coordination of the anionic substituted thiourea ligands.

Table 1: Colour, yield, m.p., elemental analysis, magnetic moment and conductivities for complexes (1-24)

Seq.	Complex	Colour	Yield (%)	m. p. (°C)	Found (calc) (%)			μ_{eff} (B.M.)	Λ_M ($\Omega^{-1}cm^2 mol^{-1}$) $CHCl_3$
					C	H	N		
	AH	white	71	172-174	66.7(66.9)	5.1(5.2)	12.8(13.0)		
	BH	white	74	117-118	68.2(68.1)	5.9(5.7)	12.5(12.2)		
1.	$[PdCl_2(AH)_2]$	orange	67	196-197	47.4(47.4)	3.9(3.7)	9.1(9.2)	0.7	0.0
2.	$[Pd(A)_2]$	yellow	73	210-212	56.0(53.9)	3.6(3.8)	10.2(10.5)	0.6	0.0
3.	$[Pd(A)_2(dppm)]_2$	red	68	107-108	63.9(64.0)	4.7(4.6)	5.9(6.1)	1.2	3.5
4.	$[Pd(A)_2(dppe)]$	yellow	86	133-134	64.4(64.3)	4.7(4.8)	6.2(6.0)	1.2	0.4
5.	$[Pd(A)_2(dppp)]$	yellow	90	57-58	64.9(64.7)	5.0(4.9)	5.8(5.9)	1.0	0.4
6.	$[Pd(A)_2(dppb)]$	pale-yellow	85	64-65	65.0(65.0)	5.1(5.0)	6.0(5.8)	1.2	0.6
7.	$[PtCl_2(AH)_2]$	yellow	89	156-157	41.5(41.4)	3.2(3.2)	8.2(8.0)	0.7	0.0
8.	$[Pt(A)_2]$	yellow	86	179-180	46.1(46.2)	3.4(3.2)	9.1(9.0)	1.0	0.0
9.	$[Pt(A)_2(dppm)]$	pale-yellow	88	152-153	58.6(58.4)	4.2(4.2)	5.8(5.6)	1.1	0.2
10.	$[Pt(A)_2(dppe)]$	pale-yellow	83	139-140	58.7(58.8)	4.1(4.3)	5.4(5.5)	1.0	0.0
11.	$[Pt(A)_2(dppp)]$	pale-yellow	82	130-131	59.0(59.1)	4.6(4.5)	5.6(5.4)	1.1	0.3
12.	$[Pt(A)_2(dppb)]$	pale-yellow	80	85-86	59.7(59.5)	4.4(4.6)	5.2(5.3)	1.2	1.2
13.	$[PdCl_2(BH)_2]$	green-blue	82	110-111	49.1(49.1)	4.3(4.1)	8.9(8.8)	0.9	2.0
14.	$[Pd(B)_2]$	brown	90	135-136	55.7(55.5)	4.1(4.3)	10.2(10.0)	0.6	0.0
15.	$[Pd(B)_2(dppm)]$	brown	70	78-79	64.8(65.7)	4.9(4.9)	6.2(5.9)	1.1	3.1
16.	$[Pd(B)_2(dppe)]$	green-blue	74	69-70	65.1(65.0)	5.3(5.0)	5.9(5.8)	1.0	1.4
17.	$[Pd(B)_2(dppp)]$	green	81	74-75	65.4(65.3)	5.4(5.0)	5.8(5.7)	1.3	0.7
18.	$[Pd(B)_2(dppb)]$	blue	82	72-73	66.2(66.0)	5.5(5.2)	5.7(5.6)	1.1	2.3
19.	$[PtCl_2(BH)_2]$	blue	78	187-188	43.2(43.1)	3.4(3.6)	7.5(7.7)	0.7	0.0
20.	$[Pt(B)_2]$	yellow	89	92-93	58.0(47.9)	3.9(3.7)	8.8(8.6)	0.9	0.6
21.	$[Pt(B)_2(dppm)]$	yellow	80	76-77	59.4(59.1)	4.6(4.5)	5.5(5.4)	1.3	1.5
22.	$[Pt(B)_2(dppe)]$	green	82	61-62	59.3(59.5)	4.5(4.6)	5.2(5.3)	1.1	1.0
23.	$[Pt(B)_2(dppp)]$	brown	87	80-81	59.9(59.8)	4.9(4.7)	5.2(5.3)	1.3	2.5
24.	$[Pt(B)_2(dppb)]$	brown	87	66	60.5(60.6)	5.5(5.7)	5.4(5.1)	1.3	2.3

Reaction of AH with Na_2PdCl_4 gave trans-$[PdCl_2(AH)_2]$(1). I.r. spectrum showed a strong band at 325 cm^{-1} due to ν(Pd – Cl) in a trans-arrangement. The spectrum also showed ν(NH) at 3176 and 3220 cm^{-1} at the same position as those appeared for free ligand which suggest a non-coordination of the NH groups. The spectrum showed a medium band at 511 cm^{-1} which might be due to ν(Pd-N) [14]. ^{1}H n.m.r. spectrum showed two signals at δH 13.8 and 10.9 p.p.m. due to the pyridyl NH and Phenyl NH protons respectively. These are at the same positions as those for the free ligand which suggest that the two NH groups are not participitating in coordination. From these data it can be concluded that AH ligand coordinated to palladium through the nitrogen of the pyridine ring [18]. The platinum complex cis - $[PtCl_2(AH)_2]$ (8) showed a spectral data similar to that of the palladium analogous except that far i.r. showed two medium intensity bands at 280 and 324 cm^{-1} which suggest a cis – arrangement.

Treatment of BH with Na_2PdCl_4 or K_2PtCl_4 gave $[MCl_2(BH)_2]$ {M = Pd (13) trans; M = Pt (19) cis}. Far i.r. spectra showed a single strong band at 320 cm^{-1} and two medium intensity bands at 290 and 320 cm^{-1} respectively. I.r. spectra showed the í(NH) bands at 3211 and 3373 cm^{-1} for the palladium complex (13) and 3213 and 3377 cm^{-1} for the platinum complex (19). These bands are shifted from that of the free ligand (3169 and 3339 cm^{-1}). These data suggest that BH ligand have probably coordinated to palladium or platinum through the NH group attached to the methylene rather than the pyridine nitrogen.

Reaction of sodium salt of the ligands AH or BH with Na_2PdCl_4 or K_2PtCl_4 gave $[M(A)_2]$ or $[M(B)_2]$ {M = Pd (2) or Pt (8)} as evidence from i.r. and other data. The i.r. spectra showed disappearance of the ν(M - Cl) bands in the far i.r. region and the ν(NH) bands due to the NH group attached to the pyridine ring which were at 3176, 3170, 3211 and 3213 cm^{-1} respectively. While the second í(NH) band was shifted (Table 2). The spectra showed two other bands due to ν(M – N) and ν(M – S). All these data suggest a chelate behavior of the anionic ligands A^- and B^-.

Treatment of $[Pd(A)_2]$ with the diphosphine $Ph_2PCH_2PPh_2$ (dppm) gave a red complex. On the basis of elemental analysis and other identification data (Table 1–3) the complex was formulated as the dinuclear complex $[Pd_2(A)_4(\mu\text{-dppm})_2]$ (3). Thus ^{31}P-{^{1}H} n.m.r. spectrum of the product showed a singlet at δP = 26.0 p.p.m. The positive chemical shift value indicates that dppm behave as a bidentate bridging ligand[19,20].

Although reaction of $[Pd(A)_2]$ with one mole equivalent of dppm gave a single product, the binuclear complex $[Pd_2(A)_4(\mu\text{-dppm})_2]$ (3), reaction with two mole equivalents of dppm gave three types of complexes, the dinuclear complex (3) and two mononuclear $[Pd(A)_2(\eta^1\text{–dppm})_2]$, the N-and S-bonded in the ratio 1 : 2 : 1 respectively (Fig. 2) in addition to some unreacted dppm as evidence from ^{31}P-{^{1}H} n.m.r. spectrum of the reaction products. ^{31}P–{^{1}H} n.m.r. spectrum of the reaction product showed a singlet at δP = 26.0 p.p.m. assigned to the dinuclear palladium complex (3) and two sets

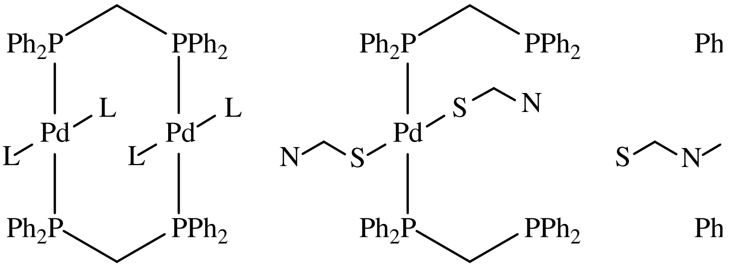

Fig. 2: The produced complexes from reaction of $[Pd(A)_2]$ with 2dppm.

Table 2: I.r. spectral data [a] cm^{-1} of the ligands and complexes (1–24)

Complex	Thioamide bands				Others					
	I	II	III	IV	ν(N-H)	ν(M-N)	ν(M-S)	ν(M-Cl)	ν(C-H)$_{aromatic}$	ν(C-H)$_{aliphatic}$
AH	1532m	1427m	995w	772m	3218w, 3174w				3037w	
BH	1530s	1435w	995w	761m	3339m, 3169s				3030w	2989m
1.	1548m	1434m	1004w	777s	3220w, 3176w	511m	439w	325s	3033w	
2.	1562w	1452w	997w	795s	3330m	509m	445w		3035w	
3.	1548m	1433m	995w	777m	3220w	509m			3047w	2937w
4.	1548m	1427m	993w	750s	3220w	526vs	445w		3047w	2916w
5.	1560m	1431m	995w	748m	3228w	511s	410w		3053w	2931w
6.	1560m	1434m	995w	746m	3232w	511m			3053w	2933w
7.	1555s	1440w	1029w	775s	3215w, 3170w	513w	440w	324s, 280s	3031w	
8.	1562m	1433w	1020m	769s	3117w	505w			3053w	
9.	1556m	1427s	990w	773m	3220w	507s			3047w	2920w
10.	1556m	1429m	995w	770w	3220w	530s	440w		3045w	2912w
11.	1544m	1429m	995w	777w	3220w	511s	437w		3047m	2929w
12.	1562m	1431m	995w	784w	3224m	507s	425w		3053	2927w
13.	1562s	1442w	1000w	759s	3373w, 3211m	497m		320s	3056	2940w
14.	1569m	1487m	1030w	754s	3263w	505m	435m		3056	2923w
15.	1546s	1490m	997m	742s	3272w	505m	430w		3053m	2925w
16.	1546s	1492m	997m	750s	3269w	530s			3055m	2910w
17.	1550s	1496m	998m	748s	3255w	513s			3054m	2923m
18.	1550s	1490m	997m	750s	3398w	509s			3055m	2931m
19.	1564m	1492m	999w	765s	3377w, 3213w	507m		320s, 290s	3035w	2939w
20.	1548m	1490m	997m	765s	3240w	501m	445m		3055	2927m
21.	1566m	1490m	997m	744s	3257w	505m			3053m	2921m
22.	1544s	1494m	999m	750s	3259w		464m		3053m	2925m
23.	1548s	1492m	1031m	750s	3259w	509s			3053m	2925m
24.	1548s	1492m	997m	750s	3282w	509s			3054m	2931m

[a] For i.r. data; w; weak; m, medium; s, strong.

Table 3: ^{1}H- and ^{31}P- n.m.r. data (δp.p.m. and J Hz) for some the prepared complexes [a]

Compound	Sequ.	Amine Protons	Phenyl and Pyridine Protons				
		δH		δP	$^2J(P_A$-$P_X)$	J(Pt-P)	Comments
N-Ph-N(2-Py) thiourea	AH	13.8 10.9	7.2-8.3				
N-Ph-N(2-MePy) thiourea	BH	9.9 4.8[b] 8.3	7.1-8.54				
trans-$[PdCl_2(AH)_2]$	(1)	13.8 10.9	7.0-9.0				
$[Pd(A)_2(dppm)]_2$	(3)			26.0			
$[Pd(A)_2(\eta^1$-$dppm)_2]$[c]				P_A 41.1 P_X -26.8	76		A ligand is N- bonded
				P_A 30.6 P_X -27.3	68		A ligand is S- bonded
$[Pd(A)_2(dppe)]$	(4)			P_A 56.8 P_X 50.0	d		
$[Pt(A)_2(dppe)]$	(10)			P_A 42.9	d	3283	B ligand is N- bonded
				P_X 39.3		3142	B ligand is S-bonded
$[Pt(B)_2(dppe)]$	(22)			48.1		2337	B ligand is S-bonded

[a] Measured in $CDCl_3$ downfield 85 % H_3PO_4.

[b] Methylene Protons, ^3J (HH) = 3.6 Hz .

[c] Resulted from reaction of $[Pd(A)_2]$ with two mole equivalent dppm.

[d] $J(P_AP_X)$ was unresolved due to broadness of signals.

of AX spin systems in the ratio 2 : 1 at $\delta P_A = 41.1$, $\delta P_X = -26.84$ p.p.m., $^2J(P_AP_X) = 76$ Hz and $\delta P_A = 30.6$, $\delta P_X = -27.3$ p.p.m., $^2J(P_AP_X) = 68.0$ Hz, assigned to two linkage isomers trans-[Pd(A)$_2$(ç^1-dppm)$_2$] the N– and S– bonded isomers. The positive chemical shift values $\delta P_A = 41.1$ and 30.58 p.p.m. refer to the coordinated phosphorus atoms, while the negative chemical shift values δP = –26.8 and –27.3. p.p.m. which are similar to that for the free dppm (-22.0 p.p.m.) refer to the uncoordinated phosphorus atoms of dppm [17]. From chemical shift values (δP) of the coordinated end of dppm, we assigned these to the N– and S– bonded linkage isomers respectively[21], (Fig. 2).

We believe that the presence of the mononuclear and binuclear complexes together with free dppm may suggest the presence of the following equilibrium [17],

$$2[Pd(A)_2(\eta^1\text{-dppm})_2] \square\ \square\square\ [Pd(A)_2(\mu\text{-dppm})]_2 + 2dppm.$$

Reaction of $[M(A)_2]$(M = Pd or Pt) with dppe gave complexes of the type $[M(A)_2(dppe)]$. ^{31}P-{1H} n.m.r. spectra of the products showed an AX spin splitting system for the palladium at $\delta P_A = 56.8$, $\delta P_X = 50.0$ p.p.m. and an AX spin splitting system associated with platinum satellites for the platinum complex at $\delta P_A = 42.9$ p.p.m., $J(Pt - P_A) = 3283$ Hz, $\delta P_X = 39.3$ p.p.m., J(Pt – P) = 3142 Hz. From the J(Pt – P) values it can be suggested that P_A with greater J(Pt - P) value is trans to nitrogen atoms while P_X with low J(Pt - P) value is trans to sulfur atom. I.r. data (Table 2) support this conclusion.

Although reaction of $[Pt(A)_2]$ with dppe gave the N–, S–bonded isomer, reaction of $[Pt(B)_2]$ with dppe gave the S,S-bonded isomer as evident from ^{31}P-{^1H}n.m.r.. The spectra showed a single peak at $\delta P=48.1$ associated with platinum satellites J(Pt–P) = 2337H_2. The low J(Pt–P) value suggest that the trans atom is sulfur[12]. I.r. showed a medium band at 464cm^{-1} which way be assigned to ν(M–S). Identication data for the other complexes are given in the Tables 1-3.

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