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Palladium complexes of pyrrole-2-aldehyde thiosemicarbazone: Synthesis, structure and spectral properties

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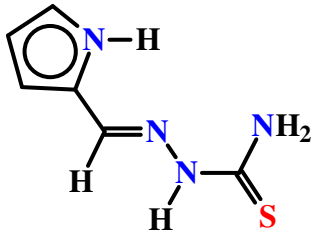
Abstract. Reaction of pyrrole-2-aldehyde thiosemicarbazone (abbreviated as $\mathbf{H_2L}$, where H_2 stands for the two potentially dissociable protons) with $[Pd(PPh_3)_2Cl_2]$ in ethanol in the presence of NEt_3 afforded two complexes, $[Pd(PPh_3)(HL_{NS})Cl]$ and $[Pd(PPh_3)(L_{NNS})]$, where the thiosemicarbazone ligand is coordinated to the metal centre respectively as monoanionic N,S-donor (depicted by HL_{NS}) and dianionic N,N,S-donor (depicted by L_{NNS}). Similar reaction with $Na_2[PdCl_4]$ afforded a bis-complex, $[Pd(HL_{NS})_2]$. Crystal structures of all the three complexes have been determined. With reference to the structure of the uncoordinated thiosemicarbazone ($\mathbf{H_2L}$), the N,S-coordination mode observed in $[Pd(PPh_3)(HL_{NS})Cl]$ and $[Pd(HL_{NS})_2]$ is associated with a geometrical change around the imine bond. While the N,N,S-mode of binding observed in $[Pd(PPh_3)(L_{NNS})]$ takes place without any such geometrical change. All three complexes display intense absorptions in the visible and ultraviolet regions, which have been analyzed by TDDFT method.

Keywords. Pyrrole-2-aldehyde thiosemicarbazone; palladium complexes; N,S- and N,N,S-coordination modes; crystal structures; spectral properties.

1. Introduction

There has been considerable interest in the chemistry of thiosemicarbazone complexes of the transition metal ions,[1] which is largely due to their bioinorganic relevance and medicinal applications.[2] Systematic studies on the binding of thiosemicarbazone ligands to transition metal ions are of considerable importance in this respect. However, we have been exploring the chemistry of platinum metal complexes of the thiosemicarbazones,[3] mainly because of the variable binding mode displayed by these ligands in their complexes, and the present work has emerged out of this exploration. For the present study pyrrole-2-aldehyde thiosemicarbazone has been chosen as the ligand and palladium as the metal centre. The selected thiosemicarbazone has two potentially dissociable protons, *viz.* the hydazinic N-H proton and the pyrrole N-H proton, and hence it is abbreviated as H_2L, where H_2 stands for these two acidic hydrogens. This ligand has several potential donor sites, *viz.* four nitrogens, each of different type, and a sulfur, all of which may, in principle, participate in coordination to a metal centre. Thus, coordination chemistry of this selected ligand is of particular interest. It may be relevant to mention here that the chosen thiosemicarbazone ligand, as well as its coordination chemistry, appears to have received very little attention.[4] Two different palladium compounds, *viz.* $[Pd(PPh_3)_2Cl_2]$ and $Na_2[PdCl_4]$, with demonstrated ability to incorporate new ligands via displacement of pre-coordinated ligands,[3b–d,j] have been utilized in this study as the sources of palladium. Reactions of pyrrole-2-aldehyde thiosemicarbazone with these palladium compounds have afforded three complexes, in which the thiosemicarbazone ligand has been found to display two different modes of coordination. Herein we describe the chemistry of these three complexes, with special reference to their formation, structure and spectral properties.



H_2L

*For correspondence

2. Experimental

2.1 *Materials*

Palladium chloride was obtained from Arora Matthey, Kolkata, India. The $[Pd(PPh_3)_2Cl_2]$ and $Na_2[PdCl_4]$ complexes were prepared by following reported procedures.[5] Pyrrole-2-aldehyde and thiosemicarbazide were procured respectively from Spectrochem, Mumbai, India and SRL, Mumbai, India. Pyrrole-2-aldehyde thiosemicarbazone (H_2L) was prepared by condensing equimolar amounts of pyrrole-2-aldehyde and thiosemicarbazide in ethanol. All other chemicals and solvents were reagent grade commercial materials and were used as received.

2.2 *Syntheses of the complexes*

2.2a *$[Pd(PPh_3)(HL_{NS})Cl]$ and $[Pd(PPh_3)(L_{NNS})]$*: To a solution of pyrrole-2-aldehyde thiosemicarbazone (24 mg, 0.14 mmol) in hot ethanol (30 mL) triethylamine (14 mg, 0.14 mmol) was added followed by $[Pd(PPh_3)_2Cl_2]$ (100 mg, 0.14 mmol). The mixture was heated at reflux for 5 h to yield an orange solution. The solvent was evaporated and the solid mass, thus obtained, was subjected to purification by thin layer chromatography on a silica plate. With acetonitrile:benzene (1:10) as the eluant, an orange band separated as the major band, followed by a minor yellow band. Extraction of these bands, followed by evaporation of the extracts yielded $[Pd(PPh_3)(HL_{NS})Cl]$ and $[Pd(PPh_3)(L_{NNS})]$ respectively as orange and yellow crystalline solids.

2.2b *$[Pd(PPh_3)(HL_{NS})Cl]$*: Yield: 43%. Analysis: Calc for $C_{24}H_{22}N_4SClPPd$: C, 50.45; H, 3.85; N, 9.81%. Found: C, 51.01; H, 3.81; N, 9.85%. ^{1}H NMR:[1] 4.62 (NH_2); 5.66 (H); 5.80 (H); 6.50 (H); 7.40–7.79 (PPh_3 + H)*; 11.09 (H). IR:[2] 1598(vs), 1563(vs), 1520(vs), 1480(s), 1435(vs), 1487(vs), 1338(s), 1333(w), 1301(s), 1277(w), 1240(s), 1214(w), 1181(w), 1159(w), 1097(s), 1071(w), 1040(s), 1033(vw), 998(w), 922(vw), 888(w), 828(w), 801(s), 743(vs), 708(s), 694(vs), 678(w), 618(w), 604(w), 534(vs), 510(s) and 498(w) cm^{-1}.

2.2c *$[Pd(PPh_3)(L_{NNS})]$*: Yield: 17%. Analysis: Calc for $C_{24}H_{21}N_4SPPd$: C, 53.89; H, 3.93; N, 10.48%. Found: C, 53.73; H, 3.89; N, 10.42%. ^{1}H NMR: 4.72 (NH_2); 6.26 (H); 6.73 (H); 7.01 (H); 7.40–7.78 (PPh_3); 8.41(H). IR: 1603(vs), 1537(vs), 1520(w), 1480(s), 1435(vs), 1401(s), 1338(w), 1318(vs), 1288(w), 1238(vw), 1184(w), 1160(s), 1105(vw), 1059(s), 1096(w), 1073(vs), 1037(vs), 1027(vw), 1000(s), 961(w), 927(w), 883(s), 827(s), 766(s), 745(s), 707(s), 693(s), 648(s), 618(w), 609(s), 568(s), 534(vs), 516(vw) and 496(s) cm^{-1}.

2.2d *$[Pd(HL_{NS})_2]$*: To a solution of pyrrole-2-aldehyde thiosemicarbazone (114 mg, 0.68 mmol) in hot ethanol (30 mL) triethylamine (69 mg, 0.68 mmol) was added followed by $Na_2[PdCl_4]$ (100 mg, 0.34 mmol). The mixture was heated at reflux for 5 h to yield an orange solution. The solvent was evaporated and the solid mass, thus obtained, was subjected to purification by thin layer chromatography on a silica plate. With acetonitrile:benzene (1:3) as the eluant, an orange band separated, which was extracted with acetonitrile, and evaporation of this extract yielded complex $[Pd(HL_{NS})_2]$ as a microcrystalline solid. Yield: 79%. Analysis: Calc for $C_{12}H_{14}N_8S_2Pd$: C, 32.69; H, 3.18; N, 25.43%. Found: C, 32.58; H, 3.21; N, 25.46%. ^{1}H NMR: 6.03 (H); 6.65 (H); 6.94 (NH_2); 7.03 (H); 7.11 (H); 11.64 (H). IR: 1599(vs), 1527(vs), 1483(w), 1446(s), 1404(vw), 1338(vw), 1310(s), 1289(vw), 1239(w), 1143(w), 1111(s), 1096(s), 1073(vs), 1033(s), 885(s), 829(s), 749(vs), 686(w), 648(s), 616(w), 609(vw), 568(vw), 550(vw), 514(vw) and 502(vw) cm^{-1}.

2.3 *Physical measurements*

Microanalyses (C, H, N) were done using a Heraeus Carlo Erba 1108 elemental analyzer. ^{1}H NMR spectra in $CDCl_3$ solutions were obtained on a Bruker Avance 300 NMR spectrometer using TMS as the internal standard. IR spectra were obtained on a Perkin-Elmer Spectrum Two spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a JASCO V-630 spectrophotometer. Geometry optimization by density functional theory (DFT) method and electronic spectral analysis by TDDFT calculation were performed using the Gaussian 03 (B3LYP/SDD-6-31G) package.[6]

2.4 *X-ray crystallographic analysis*

Single crystals of complexes $[Pd(PPh_3)(HL_{NS})Cl]$, $[Pd(PPh_3)(L_{NNS})]$ and $[Pd(HL_{NS})_2]$ were obtained by slow evaporation of solvent from solutions of the

[1] Chemical shifts are given in ppm and overlapping signals are marked with an asterisk.

[2] Meanings of the short forms within parentheses are: vs = very strong, s = strong, w = weak and vw = very weak.

Table 1. Crystallographic data for the complexes.

	$[Pd(PPh_3)(HL_{NS})Cl]$	$[Pd(PPh_3)(L_{NNS})]$	$[Pd(HL_{NS})_2]$
Empirical formula	$C_{24}H_{22}N_4PSClPd$	$C_{24}H_{21}N_4PSPd$	$C_{12}H_{14}N_8S_2Pd{\cdot}CH_3CN$
Formula weight	571.37	534.91	481.4
Crystal system	orthorhombic	triclinic	monoclinic
Space group	Pbca	$P\bar{1}$	C2/c
a (Å)	16.0817(4)	10.3219(1)	27.944(6)
b (Å)	15.9825(4)	14.9715(2)	5.5854(13)
c (Å)	18.8427(5)	24.3777(3)	15.854(4)
α (°)	90	100.883(1)	90
β (°)	90	99.527(1)	124.5700
γ (°)	90	107.204(1)	90
V (Å^3)	4843.1(2)	3434.12(8)	2037.6(8)
Z	8	6	4
D_{calcd}/mg m^{-3}	1.567	1.552	1.569
$F(000)$	2304	1620	1056
Crystal size (mm)	0.17 × 0.12 × 0.10	0.19 × 0.15 × 0.11	0.31 × 0.17 × 0.11
T (K)	273	273	293
μ(mm^{-1})	1.049	0.991	1.142
Collected reflections	38357	64243	8222
R_{int}	0.032	0.043	0.072
Independent reflections	5754	17951	1808
$R1$[a]	0.0277	0.0452	0.1200
$wR2$[b]	0.0952	0.1529	0.3082
GOF[c]	0.85	0.93	1.27

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$
[b]$wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$
[c]$GOF = [\Sigma[w(F_o^2-F_c^2)^2]/(M-N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

respective complexes in acetonitrile. Selected crystal data and data collection parameters are given in table 1. Data were collected on a Bruker SMART CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). X-ray data reduction, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs.[7] The structures were solved by the direct methods.

3. Results and Discussion

3.1 *Synthesis and structure*

Reaction of pyrrole-2-aldehyde thiosemicarbazone (H_2L) was first carried out with $[Pd(PPh_3)_2Cl_2]$, which proceeded smoothly in refluxing ethanol in the presence of triethylamine to afford two complexes, an orange complex as the major product and a yellow complex as the minor product. Preliminary characterizations (microanalysis, IR and ^{1}H NMR) indicated the presence of a thiosemicarbazone ligand and a triphenylphosphine in both the complexes. For an unambiguous characterization of these complexes, with particular reference to coordination mode of the thiosemicarbazone ligand in them, structures of both the complexes were determined by X-ray crystallography. Structure of the orange complex is shown in figure 1, and

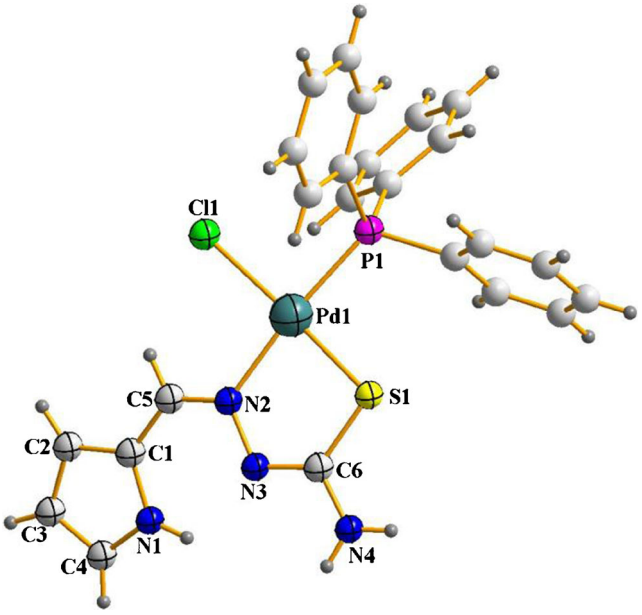
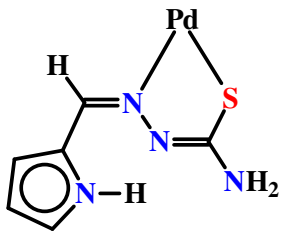


Figure 1. Crystal structure of $[Pd(PPh_3)(HL_{NS})Cl]$.

Table 2. Selected bond lengths (Å) and bond angles (°) for the complexes.

		$[Pd(PPh_3)(HL_{NS})Cl]$	
		bond lengths (Å)	
Pd(1)-Cl(1)	2.3611(8)	N(2)-N(3)	1.395(3)
Pd(1)-P(1)	2.2560(6)	N(3)-C(6)	1.294(4)
Pd(1)-S(1)	2.2406(7)	C(6)-S(1)	1.744(3)
Pd(1)-N(2)	2.088(2)	C(6)-N(4)	1.353(4)
		C(5)-N(2)	1.290(3)
		bond angles (°)	
P(1)-Pd(1)-N(2)	173.18(6)	S(1)-Pd(1)-N(2)	83.42(6)
S(1)-Pd(1)-Cl(1)	176.57(3)		
		$[Pd(PPh_3)(L_{NNS})]$	
		bond lengths (Å)	
Pd(1)-P(1)	2.2404(11)	N(2)-N(3)	1.385(5)
Pd(1)-S(1)	2.2570(12)	N(3)-C(6)	1.317(6)
Pd(1)-N(1)	2.045(4)	C(6)-S(1)	1.747(5)
Pd(1)-N(2)	2.004(3)	C(6)-N(4)	1.353(6)
		C(5)-N(2)	1.295(6)
		bond angles (°)	
P(1)-Pd(1)-N(2)	176.47(9)	N(1)-Pd(1)-N(2)	80.77(16)
S(1)-Pd(1)-N(1)	164.25(13)	S(1)-Pd(1)-N(2)	83.49(10)
		$[Pd(HL_{NS})_2]$	
		bond lengths (Å)	
Pd(1)-S(1)	2.293(2)	N(2)-N(3)	1.385(10)
Pd(1)-N(2)	2.013(8)	N(3)-C(6)	1.306(12)
		C(6)-S(1)	1.744(9)
		C(6)-N(4)	1.366(10)
		C(5)-N(2)	1.314(13)
		bond angles (°)	
N(2)-Pd(1)-N(2a)	180.00	S(1)-Pd(1)-N(2)	82.4(2)
S(1)-Pd(1)-S(1a)	180.00		

selected bond distances and angles are listed in table 2. The structure shows that the thiosemicarbazone ligand is coordinated to palladium, via dissociation of the hydazinic N-H proton, in the bidentate N,S-mode (**I**) forming a five-membered chelate ring. A triphenylphosphine and a chloride are also coordinated to the metal centre, where the chloride is *trans* to the coordinated sulfur and the phosphorus is *trans* to the coordinated nitrogen. In view of the composition of this orange complex, it will be henceforth referred to as $[Pd(PPh_3)(HL_{NS})Cl]$, where HL_{NS} depicts the mono de-protonated thiosemicarbazone ligand coordinated to palladium in the N,S-mode (**I**). Palladium is thus nested in an NSPCl core in this complex, which is distorted significantly from ideal square-planar geometry, as manifested in the bond parameters around the metal centre. The Pd-N, Pd-P, Pd-S and Pd-Cl distances (table 2) are normal, as observed in structurally characterized complexes of palladium containing these bonds.[3b–d,j] It is interesting to note here that, with reference to structure of the uncoordinated pyrrole-2-aldehyde thiosemicarbazone,[4b] which is similar to that shown in the line-drawing of H_2L (*vide supra*), this five-membered chelate ring formation is associated with a restricted rotation around the pre-existing C=N bond, due to which disposition of the pyrrole ring, as well as of the azomethine proton, has changed. Though such rotation is well experienced during formation of bezaldehyde thiosemicarbazone complexes,[3c,j] it was, to our knowledge hitherto unknown for complexes of pyrrole-2-aldehyde thiosemicarbazone.



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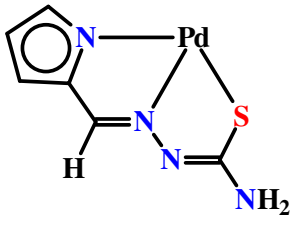


II

Structure of the yellow complex is shown in figure 2. The structure reveals that in forming this complex, pyrrole-2-aldehyde thiosemicarbazone has utilized the pyrrole-nitrogen in addition to the two other donor sites, *viz*. the imine-nitrogen and the thiolate-sulfur, and is coordinated to the metal centre in the tridentate N,N,S-mode (**II**) forming two adjacent five-membered chelate rings. The fourth coordination site on palladium is occupied by a triphenylphosphine. Hence, based on the composition of this yellow complex, it is formulated as $[Pd(PPh_3)(L_{NNS})]$, where L_{NNS} indicates the doubly de-protonated thiosemicarbazone ligand coordinated to palladium in the N,N,S-mode (**II**). Report of a slightly different method yielding the same complex as the sole product exists in the literature,[4a] and the bond parameters in $[Pd(PPh_3)(L_{NNS})]$ (table 2) are found to compare well with the reported values.

Formation of $[Pd(PPh_3)(HL_{NS})Cl]$ and $[Pd(PPh_3)(L_{NNS})]$, from a rather simple reaction between pyrrole-2-aldehyde thiosemicarbazone and $[Pd(PPh_3)_2Cl_2]$, has been quite intriguing. Some speculated sequences behind formation of these two complexes from a single reaction, which seem probable, are illustrated in scheme 1. The synthetic reaction is believed to proceed through two different routes. In one route, in the initial step the imine-nitrogen of the thiosemicarbazone seems to bind to the metal centre in $[Pd(PPh_3)_2Cl_2]$, via displacing a PPh_3, to generate an intermediate **A-1**. Elimination HCl, involving the S-H proton and the proximal metal-bound chloride in **A-1**, takes place in the next step generating a second intermediate **A-2**. This brings the pyrrole N-H close to the remaining Pd-Cl fragment, and elimination of a second equivalent of HCl leads to binding of the anionic pyrrole-nitrogen to the metal centre yielding $[Pd(PPh_3)(L_{NNS})]$ as the final product. In the other route, an intermediate **B** seems to form in the first step, which is an isomer of **A-1** differing only in disposition of the pyrrole and azomethine proton. The same **B** may also form from **A-1** via a rotation about the pre-existing C=N bond. Elimination of HCl from **B**, as in the second step of the first route, affords $[Pd(PPh_3)(HL_{NS})Cl]$ as the end product.

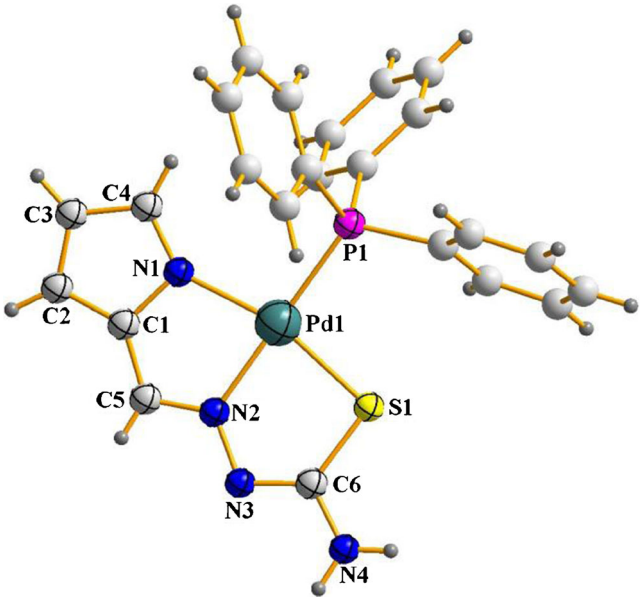
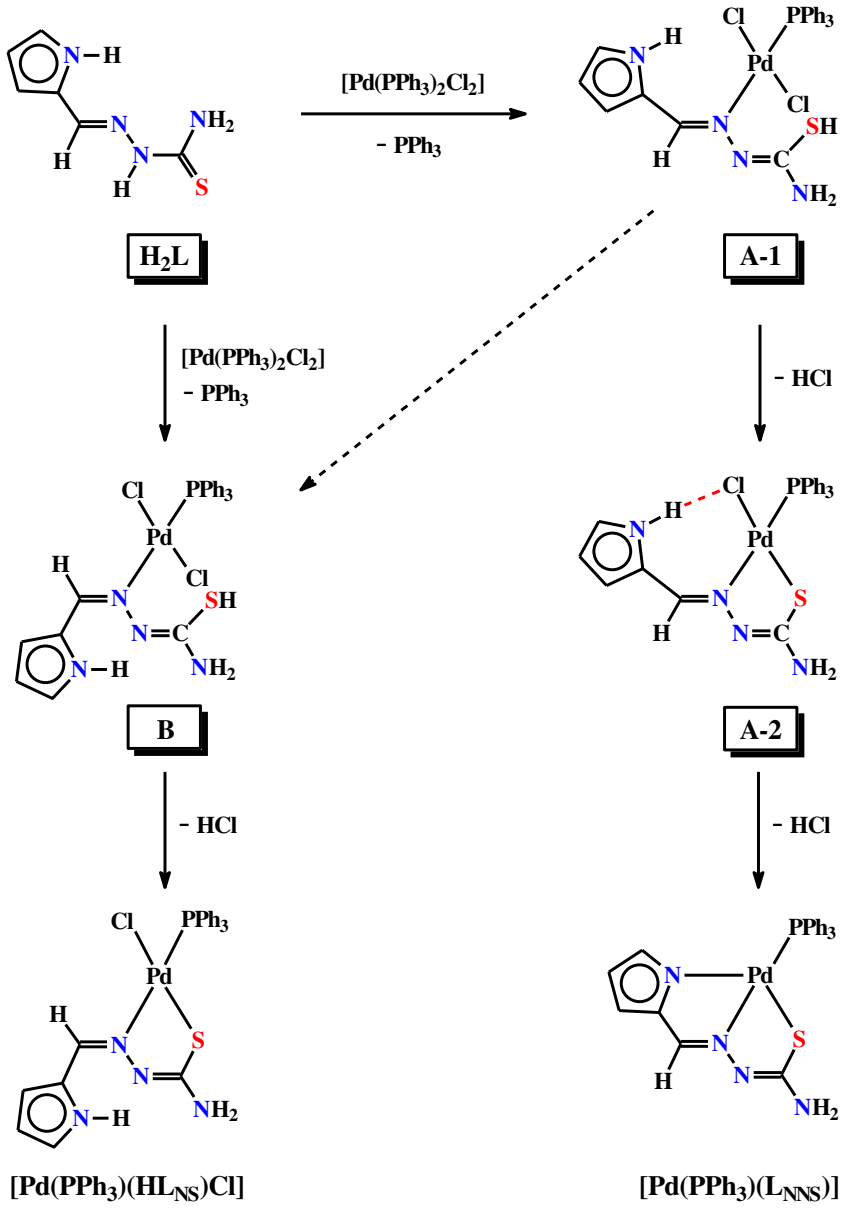


Figure 2. Crystal structure of $[Pd(PPh_3)(L_{NNS})]$.

The observed higher yield of $[Pd(PPh_3)(HL_{NS})Cl]$, which was associated with a conformational change of the thiosemicarbazone, than $[Pd(PPh_3)(L_{NNS})]$, where no such conformational change took place, was quite intriguing. Though the exact driving force behind this observation is not completely understood yet, steric bulk of the triphenylphosphines in the starting $[Pd(PPh_3)_2Cl_2]$ complex seems to be one of the possible reasons. To check this, reaction of the pyrrole-2-aldehyde thiosemicarbazone was also carried out with another palladium starting material, *viz*. $Na_2[PdCl_4]$, which does not have any bulky ligand. From this reaction an orange complex was obtained as the sole product in good yield.[3] Preliminary characterizations indicated it to be a homoleptic bis-complex**,** which was further authenticated by its structure determination by X-ray crystallography. The structure (figure 3) shows that both the thiosemicarbazone ligands are coordinated to palladium in the bidentate N,S-mode (**I**). The two coordinated nitrogens are *trans* and so are the two sulfurs. Based on the binding mode of the thiosemicarbazone ligand in this bis-complex, it will henceforth be referred to as $[Pd(HL_{NS})_2]$. Formation of the same five-membered chelate ring (**I**) by pyrrole-2-aldehyde thiosemicarbazone, upon its reaction with both $[Pd(PPh_3)_2Cl_2]$ and $Na_2[PdCl_4]$, clearly indicates that steric bulk of the PPh_3 ligand in the former palladium starting material is not the main reason behind the observed geometrical change about the pre-existing imine bond of the thiosemicarbazone. It may be relevant to mention here that formation of complexes of similar types by benzaldehyde thiosemicarbazones upon their reactions with $[Pd(PPh_3)_2Cl_2]$ and $Na_2[PdCl_4]$, displaying five-membered N-S chelate formation involving similar geometrical change, was observed by us before.[3c,k] The bond parameters found in $[Pd(HL_{NS})_2]$ (table 2) compare well with those found in the $Pd(HL_{NS})$ fragment of $[Pd(PPh_3)(HL_{NS})Cl]$.

[3]Upon using an equimolar quantity of $Na_2[PdCl_4]$ and $\mathbf{H_2L}$, the same $[Pd(HL_{NS})_2]$ complex is obtained in about 30% yield (based on palladium).



Scheme 1. Probable steps behind formation of $[Pd(PPh_3)(HL_{NS})Cl]$ and $[Pd(PPh_3)(L_{NNS})]$.

3.2 *^{1}H NMR spectra*

^{1}H NMR spectra of $[Pd(PPh_3)(HL_{NS})Cl]$ and $[Pd(PPh_3)(L_{NNS})]$ were recorded in $CDCl_3$ solutions, while spectrum of $[Pd(HL_{NS})_2]$ was recorded in DMSO-d_6 solution. Spectral data are presented in the experimental section. Majority of the expected signals could be clearly identified in all the three complexes. For example, in $[Pd(PPh_3)(HL_{NS})Cl]$, phenyl protons of the PPh_3 ligand showed broad signals within 7.40–7.79 ppm. From the coordinated thiosemicarbazone the NH_2 and pyrrole-NH signals were observed at 4.62 ppm and 11.09 ppm respectively, and out of the remaining four signals three were distinctly observed at 5.66, 5.80 and 6.50 ppm, while the fourth one could not be identified due to its overlap with the broad peaks arising from the PPh_3 ligand. Spectral features of $[Pd(PPh_3)(L_{NNS})]$ were found to be qualitatively similar to those observed in $[Pd(PPh_3)(HL_{NS})Cl]$, except signal for the pyrrole N-H was missing in the former indicating coordination of the anionic pyrrole-nitrogen to palladium. In $[Pd(HL_{NS})_2]$, all the six expected signals were clearly observed within 6.03–11.64 ppm.

3.3 *IR spectra*

Infrared spectra of all the complexes show many bands of different intensities in the 1600–400 cm^{-1} region. Spectral data of each individual complex are presented

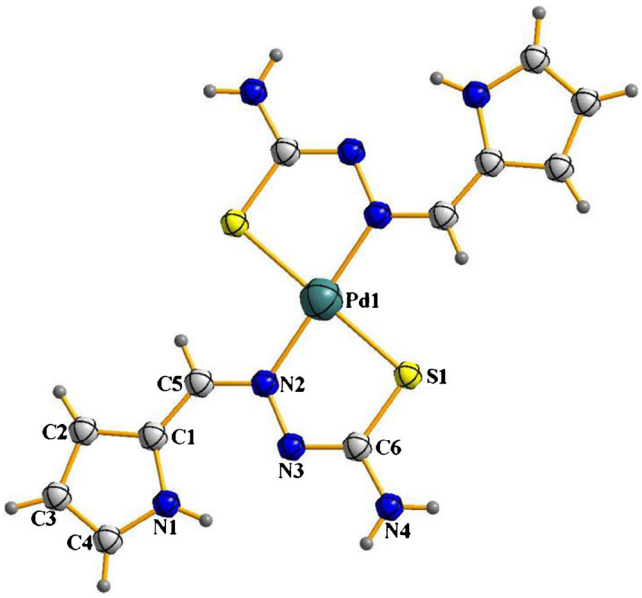


Figure 3. Crystal structure of $[Pd(HL_{NS})_2]$.

Table 3. Electronic spectral data of the complexes.

Complexs	Electronic spectral data[a] λ_{max} (nm) (ε/$M^{-1}cm^{-1}$)
$[Pd(PPh_3)(HL_{NS})Cl]$	439 (2910), 368 (2090)
$[Pd(PPh_3)(L_{NNS})]$	430 (330), 368 (2800)
$[Pd(HL_{NS})_2]$	468 (470), 381 (1760)

[a]In dichloromethane solution.

in the experimental section. In the infrared spectra of $[Pd(PPh_3)(HL_{NS})Cl]$ and $[Pd(PPh_3)(L_{NNS})]$, three strong bands near 534, 694 and 744 cm^{-1} were observed due to the coordinated PPh_3 ligand. In comparison with the spectrum of $[Pd(PPh_3)_2Cl_2]$, several new bands (such as: bands near 1598, 1523, 1485, 1338, 1240, 1072, 1033, 887, 828, 617, 606 and 500 cm^{-1}) could be identified in both of these spectra, which are attributable to the coordinated thiosemicarbazone ligands. Except absence of the three bands due to the PPh_3 ligands and small shifts in the positions of the remaining bands, infrared spectrum of $[Pd(HL_{NS})_2]$ was found to be similar to that of $[Pd(PPh_3)(HL_{NS})Cl]$. Infrared spectral data of the complexes are therefore in well accordance with their compositions.

3.4 *Electronic absorption spectra*

$[Pd(PPh_3)(HL_{NS})Cl]$ and $[Pd(PPh_3)(L_{NNS})]$ are readily soluble in alcohol, acetone, dichloromethane, chloroform, acetonitrile, etc., producing orange and yellow solutions, respectively. However, $[Pd(HL_{NS})_2]$ is found to be insoluble in dichloromethane and chloroform, but soluble in the other solvents producing orange solution. Electronic spectra of all the complexes were recorded in acetonitrile solution. Spectral data are presented in table 3. Each complex showed several intense absorptions in the visible and ultraviolet regions. To have an insight into the nature of these absorptions, TDDFT calculations were being performed on all three palladium complexes using the Gaussian 03 package.[6] Phenyl rings of the triphenylphosphines in $[Pd(PPh_3)(HL_{NS})Cl]$ and $[Pd(PPh_3)(L_{NNS})]$ were replaced by hydrogens for simplifying the calculation. The results of the TDDFT calculations for $[Pd(PH_3)(HL_{NS})Cl]$ are presented in table 4, and those for $[Pd(PH_3)(L_{NNS})]$ and $[Pd(HL_{NS})_2]$ are deposited in table S1 and table S2 respectively. Contour plots of some selected molecular orbitals for $[Pd(PH_3)(HL_{NS})Cl]$ are shown in figure 4 and those for $[Pd(PH_3)(L_{NNS})]$ and $[Pd(HL_{NS})_2]$ are deposited as figure S1 and figure S2 respectively. The results obtained are found to be more or less similar for all three complexes, and hence only the case of $[Pd(PH_3)(HL_{NS})Cl]$ is discussed here. The lowest energy absorption at 439 nm is attributable to a combination of H-2 → L, H-5 → L and H-7 → L transitions, and based on the nature of these participating orbitals

Table 4. Main calculated optical transition for $[Pd(PH_3)(HL_{NS})Cl]$ with composition in terms of molecular orbital contribution of the transition, vertical excitation energies, and oscillator strength in acetonitrile solvent.

Excited state	Composition	CI	E (eV)	Oscillator strength (f)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1	H-7 → L	−0.14126	2.9875	0.0810	415.01	ILCT/LLCT/MLCT/LMCT	439
	H-5 → L	−0.16030				ILCT/LLCT/MLCT/LMCT	
	H-2 → L	0.62410				ILCT/LLCT/MLCT/LMCT	
2	H-11 → L	0.22186	3.5107	0.0560	353.16	ILCT/LLCT/MLCT/LMCT	368
	H-7 → L	−0.13112				ILCT/LLCT/MLCT/LMCT	
	H-5 → L	0.60444				ILCT/LLCT/MLCT/LMCT	
	H-2 → L	0.13669				ILCT/LLCT/MLCT/LMCT	

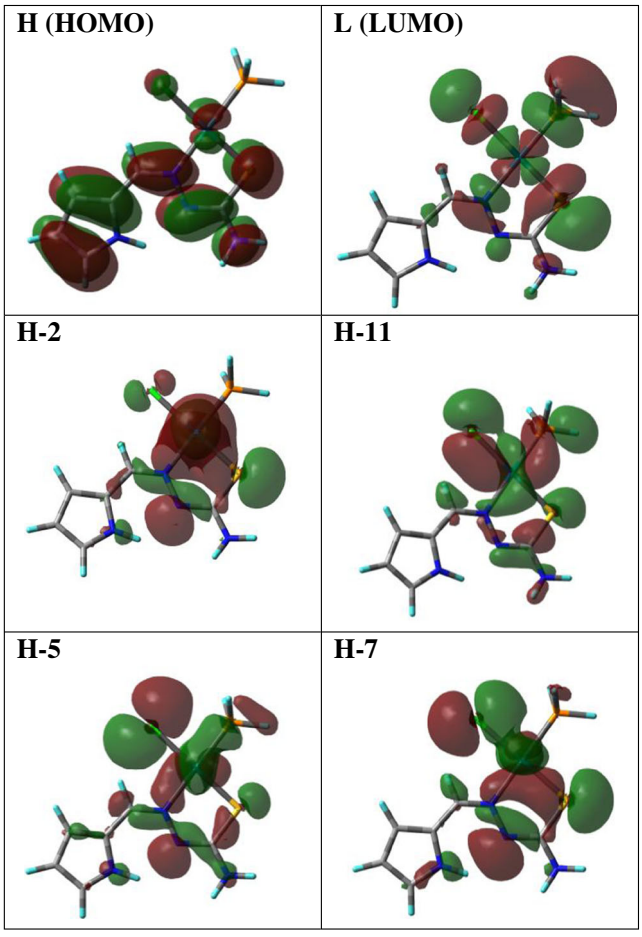


Figure 4. Contour plot of selected molecular orbitals of $[Pd(PPh_3)(HL_{NS})Cl]$.

the same is assignable to a mixture of ILCT, LLCT, MLCT and LMCT transitions. The next absorption at 368 nm is found to be a combination of H-2 → L, H-5 → L, H-7 → L and H-11 → L transitions, and is attributable to an admixture of ILCT, LLCT, MLCT and LMCT transitions.

4. Conclusions

The present study demonstrates that the pyrrole-2-aldehyde thiosemicarbazone (**H_2L**) can readily bind to palladium and displays a rather uncommon N,S-mode of binding (**I**) involving a restricted rotation around the imine bond, as well as a N,N,S-mode of coordination (**II**) without any such rotation.

Supplementary Information

CCDC 989560-989562 contain the supplementary crystallographic data for this paper. Results of TDDFT calculations of $[Pd(PPh_3)(L_{NNS})]$ (table S1) and $[Pd(HL_{NS})_2]$ (table S2), contour plots of selected molecular orbitals of $[Pd(PPh_3)(L_{NNS})]$ (figure S1) and $[Pd(HL_{NS})_2]$ (figure S2) are available as supplementary information.

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