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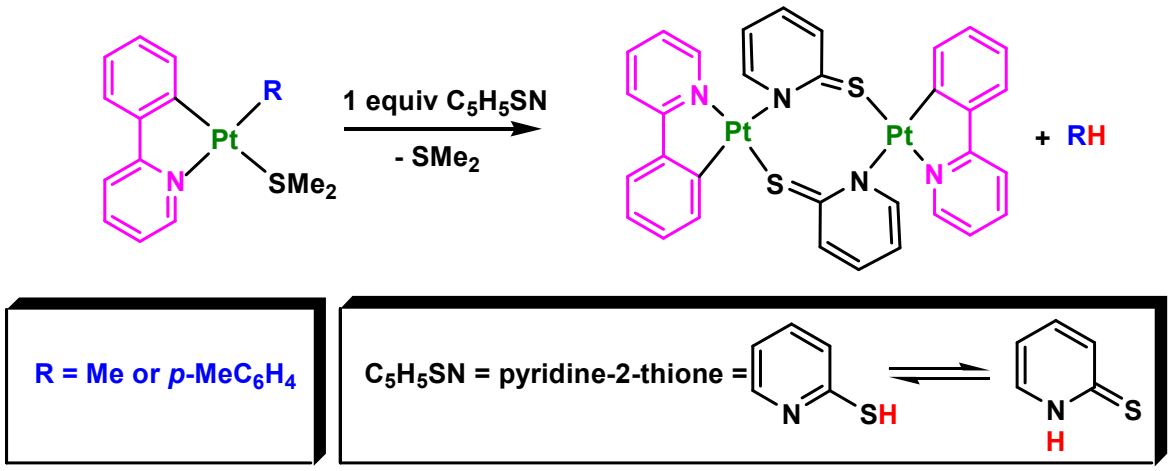
C-H reductive elimination during the reaction of cycloplatinated(II) complexes with pyridine-2-thione: kinetic follow up

Reactions of the cycloplatinated(II) complexes [PtR(ppy)(SMe_2)], **1**, where ppy = deprotonated 2-phenylpyridine and R = Me or *p*-MeC_6H_4, with pyridine-2-thione, C_5H_5SN, were studied were studied by UV-vis and ^1H NMR spectroscopies and on the basis of the data a mechanism is proposed.



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C-H reductive elimination during the reaction of cycloplatinated(II) complexes with pyridine-2-thione: kinetic follow up

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Abstract

Substitution reactions of the labile SMe_2 ligand in the cycloplatinated(II) complexes [PtR(ppy)(SMe_2)], **1**, in which ppy = 2-phenylpyridinate and R = Me, **1a**, or *p*-MeC_6H_4, **1b**, by pyridine-2-thione, C_5H_5SN, were studied. When each of the complexes **1** was treated with 1 equiv C_5H_5SN, existing as a mixture of tautomers thiol (N^SH) and thione (HN^S), a mixture containing the *S*-bound thiol complex [PtR(ppy)(η^1-*S*-S^NH)] (R = Me, **2a**, or R = *p*-MeC_6H_4, **2b**) and the dimeric complex [Pt(ppy)(N^S)]$_2$, **3** (having two bridging deprotonated pyridine-2-thione (N^S) ligands), was observed along with free R-H. This mixture was finally led to pure complex **3** after 3 days. Pure samples of the complexes **2a** and **3** were obtained from the abovementioned **2a+3** mixture by using flash chromatography on silica gel. Kinetics of the reactions were investigated by UV-vis spectroscopy (complexes **1** have a MLCT band in the visible region which was used to easily follow the reactions) and ^{1}H NMR spectroscopy. On the basis of the results, a mechanism was proposed for the related reactions.

1. Introduction

The chemistry of cyclometalated complexes has long been the subject of intense study.[1-4] Among the cyclometalated complexes, cycloplatinated complexes have been attracted a great deal of attention as a result of their highly versatile obvious applications in many fields. [5-8] Monoalkyl cycloplatinated complexes with a solvent or labile ligand have been reported only rarely.[9-16] These complexes reportedly exhibit various reactivities toward fundamental reactions such as oxidative addition and substitution reactions.[17-22]

The rich reactive features of complexes with heterodonor ligands, such as 2-

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diphenylphosphinopyridine ($pyPPh_2$)[21, 23-26] or pyridine-2-thione, C_5H_5SN,[27-38] have been widely studied for application in different aspects. The latter is an unsymmetrical bidentate ligand with a nitrogen donor atom and a sulfur donor atom. Its pK_a values[30] suggest that the parent molecule exists in solution as a mixture containing the thione-thiol tautomers (**Ia** and **Ib** in Figure 1, respectively). This ligand can be deprotonated[27, 31] easily to obtain the thiolate form N^S (C_5H_4SN), indicated as **Ic** in Figure 1.[37] Although the thione–thiol tautomeric equilibrium has been shown generally to favor the thione form, the electronic differentiation associated with the hard nitrogen and soft sulfur donors in this reagent directs its reactivity and coordination behavior when it binds to metal (Figure 2).[37, 39] The reported monomeric platinum(II) complexes containing pyridine-2-thione have been shown to be *S*-bound with pendant pyridyl group,[40] such as *trans*-[Pt(η^1-*S*-$C_5H_4NS)_2(PPh_3)_2$] or N^S chelating, such as [Pt(η^2-*N*,*S*-$C_5H_4NS)(PPh_3)_2]PF_6$,[41] with no related example of the *N*-bound thiol complex.

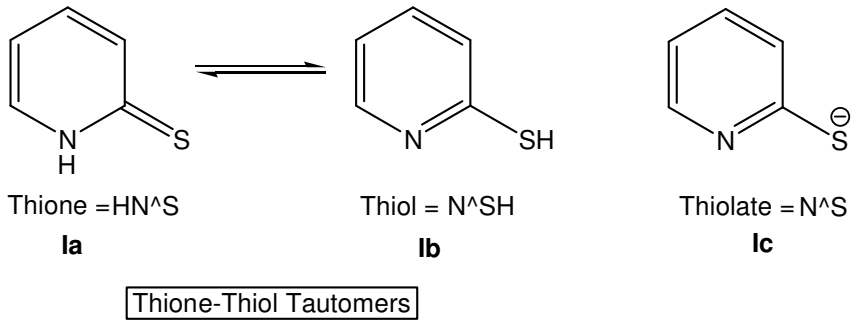

Figure 1

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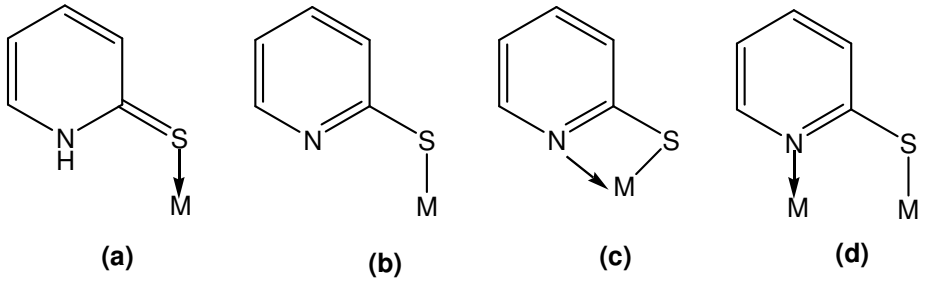

Figure 2. Coordination modes for C_5H_5SN and C_5H_4SN

In the present study, we describe reaction of the cycloplatinated(II) complexes [PtR(ppy)(SMe_2)], **1**, (R = Me; **1a**, R=*p*–MeC_6H_4, **1b**, and ppy = deprotonated 2–phenylpyridine) with pyridine-2-thione (C_5H_5SN) showing that the monodentate *S*-bound complexes [PtR(ppy)(η^1-*S*-S^NH)], **2**, with NH pendant group, are formed along with a dimmeric complex [Pt(ppy)(N^S)]$_2$, **3**, resulting from C-H bond reductive elimination. We have also followed up the kinetics of these reactions by using UV-vis spectroscopy and ^{1}H NMR spectroscopy in different solvents and suggested a mechanism for the related reactions.

2. Experimental Section

The ^{1}H NMR spectra of the complexes were recorded on a Bruker Avance DPX 250 MHz or 400 MHz spectrometer, and TMS (0.00) was used as an external reference. All the chemical shifts and coupling constants are given in units of ppm and Hz, respectively. Kinetic studies were carried out by using a Perkin-Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath. Pyridine-2-thione (C_5H_5SN) was purchased from commercial sources and the starting complexes, [PtMe(ppy)(SMe_2)], **1a**,[10] [Pt(*p*-MeC_6H_4)(ppy)(SMe_2)], **1b**,[10] and

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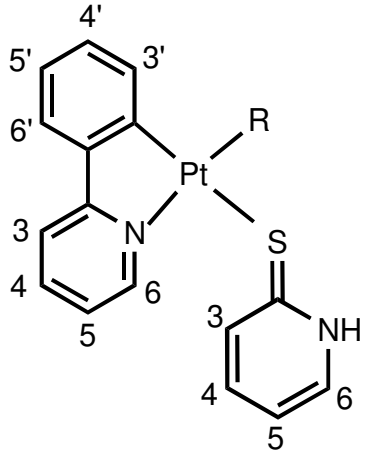
[Pt(ppy)Cl(DMSO)],[42] in which DMSO is dimethylsulphoxide, were prepared as reported. The NMR labeling for ppy and C_5H_5SN ligands are shown in Scheme 1.[43, 44]



Scheme 1. The NMR labeling

2.1 Reaction of [PtMe(ppy)(SMe_2)], 1a, with C_5H_5SN

To a solution of [PtMe(ppy)(SMe_2)], **1a**, (100 mg, 0.23 mmol) in dichloromethane (or benzene) was added 1 equiv pyridine-2-thione (26.1 mg, 0.23 mmol) at room temperature. The mixture was stirred for 2h (or 24 h in benzene) and the solvent was then removed under reduced pressure. The residue was triturated with *n*-hexane to give a pale red solid, which was separated and dried under vacuum. The product was identified as a mixture of [PtMe(ppy)(η^1-*S*-S^NH)], **2a**, and [Pt(ppy)(N^S)]$_2$, **3**, with the ratio **2a/3** being 1/2. Total yield: 76 mg, 69%. Mixture of the compounds **2a** and **3** were separated by flash chromatography with good yields on silica gel eluted with 100:2 CH_2Cl_2/MeOH, to afford pure [PtMe(ppy)(η^1-*S*-S^NH)], **2a**, and [Pt(ppy)(N^S)]$_2$, **3**, identified as follows:

*Identification of the complex **2a***

M.P. 254 °C (decomp.), Anal. Calcd for $C_{17}H_{16}N_2SPt$, C, 41.45; H, 3.38; N, 5.89. Found: C, 41.04; H, 3.06; N, 5.27; ^{1}H NMR in $CDCl_3$; δ 1.86 (s, $^2J_{PtH}$ = 69.9 Hz, Me-Pt, 3H),

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aromatic protons: ppy ligand, 6.80 (m, $^{3}J_{PtH}{}^{3'}$ = 24.5 Hz, $^{3}J_{H}{}^{3'}{}_{H}{}^{4'}$ = 7.0 Hz, CH group adjacent to coordinated C atom, $1H^{3'}{}_{ppy}$), 7.82 (m, $^{3}J_{PtH}{}^{6}$ = 15.8 Hz, $^{3}J_{H}{}^{6}{}_{H}{}^{5}$ = 5.7 Hz, CH group adjacent to coordinated N atom, $1H^{6}{}_{ppy}$), 7.99 (d, $^{3}J_{H}{}^{6}{}_{H}{}^{5}$ = 5.8 Hz, CH group adjacent to coordinated N atom, $H^{6}{}_{spy}$), 8.72 (broad singlet, H atom directly bond to N atom), 6.90-7.81 (other aromatic protons of ppy and S^N groups). ^{1}H NMR data for the complex **2a** in C_6D_6, to be used when monitoring the related reaction in benzene (*vide infra*): δ 2.36 (s, $^{2}J_{PtH}$ = 69.9 Hz, Me-Pt, 3H), aromatic protons: ppy ligand, 7.79 (dd, $^{3}J_{PtH}{}^{3'}$ = 24.5 Hz, $^{3}J_{H}{}^{3'}{}_{H}{}^{4'}$ = 7.4 Hz, $^{4}J_{H}{}^{3'}{}_{H}{}^{5'}$ = 1.1 Hz, CH group adjacent to coordinated C atom, $1H^{3'}{}_{ppy}$), 8.76 (dd, $^{3}J_{PtH}{}^{6}$ = 16.2 Hz, $^{3}J_{H}{}^{6}{}_{H}{}^{5}$ = 5.7 Hz, $^{4}J_{H}{}^{6}{}_{H}{}^{4}$ = 1.8 Hz, CH group adjacent to coordinated N atom, $1H^{6}{}_{ppy}$).

*Identification of the complex **3***

This was identified by comparison of its ^{1}H NMR spectrum with that of the complex **3** prepared by direct method as follows:

The complex **3** has been reported to be synthesized by the reaction of $(Bu_4N)[PtCl_2(ppy)]$ with C_5H_5SN and was only characterized in solid state by single crystal X-ray crystallography [45]. In the present work, [Pt(ppy)Cl(DMSO)] (100 mg, 0.22 mmol) was added to an ethanolic solution of sodium pyridine-2-thiolate, NaC_5H_4NS (see below), under inert atmosphere condition. ^{1}H NMR data in $CDCl_3$, δ 8.09 (d, $^{3}J_{PtH}{}^{6}$ = 19.1 Hz, $^{3}J_{H}{}^{6}{}_{H}{}^{5}$ = 5.6 Hz, CH group adjacent to coordinated N atom, $2H^{6}{}_{ppy}$), 7.47 (d, $^{3}J_{PtH}{}^{3'}$ = 32.8 Hz, $^{3}J_{H}{}^{3'}{}_{H}{}^{4'}$ = 5.7 Hz, CH group adjacent to coordinated C atom, $2H^{3'}{}_{ppy}$), 7.53 (t, 2H), 7.49 (d, 2H), 7.86 (d, $^{3}J_{PtH}{}^{6}$ = 16.2 Hz, $^{3}J_{H}{}^{3}{}_{H}{}^{4}$ = 7.5 Hz, $2H^{6}{}_{N^S}$), 7.13 (t, 4H), 6.91 (t, 4H), 6.74 (t, 2H), 6.71 (t, 2H), 6.43 (t, 2H). Other notes related to complex **3**:

1- Single crystal of dimer **3** was grown in a concentrated benzene solution of the **2a**+**3**

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mixture product obtained from mixing of complex **1a** and C_5H_5SN by slow diffusion of diethylether and its structure was confirmed by single crystal X-ray analysis (see Figure 3).

2- NaC_5H_4NS (as used in direct synthesis of complex **3**, see above) was prepared by dissolving of sodium (6 mg 0.25 mmol) in 10 mL of absolute ethanol following by treatment with pyridine-2-thione (25 mg, 0.22 mmol) to immediately give a red solution that after stirring for 6 h at room temperature a red solid was precipitated which was separated and dried under vacuum. Yield: 73 mg, 74%. This compound gave ^{1}H NMR data similar to the reported data in DMSO-d_6 [45].

3- The complex **3** is not stable in $CDCl_3$ (or CH_2Cl_2) and slowly forms $[Pt(ppy)(N^S)(Cl)]_2$ complex [45], giving ^{1}H NMR data in $CDCl_3$: δ 9.54 (d, $^3J_{PtH^6}$ = 20.8 Hz, $^3J_{H^6H^5}$ = 5.6 Hz, CH group adjacent to coordinated N atom, $2H^6_{ppy}$), 8.15 (d, $^3J_{PtH^{3'}}$ = 28.2 Hz, $^3J_{H^{3'}H^{4'}}$ = 6.2 Hz, CH group adjacent to coordinated C atom, $2H^{3'}_{ppy}$), 7.56 (t, 2H), 7.37 (t, 2H), 7.29 (d, , 2H), 7.17 (t, 4H), 6.97 (t, 4H), 6.90 (t, 2H), 6.71 (t, 2H), 6.77 (t, 2H). These ^{1}H NMR data are similar to those reported for the complex $[Pt(ppy)(N^S)(Cl)]_2$ in DMSO-d_6 [45].

4- When the reaction of $[PtMe(ppy)(SMe_2)]$, **1a**, with pyridine-2-thione in benzene was stirred for 3 days, only dimer **3** as a pure product was formed.

5- ^{1}H NMR data for the complex **3** in C_6D_6: ppy ligand, δ 7.49 (m, $^3J_{H^{3'}H^{4'}}$ = 5.3 Hz, $^4J_{H^{3'}H^{5'}}$ =1.0 Hz, $^3J_{PtH^{3'}}$ = 34.2 Hz, CH group adjacent to coordinated C atom, $1H^{3'}_{ppy}$), 8.09 (m, $^3J_{H^6H^5}$ = 6.0 Hz, $^4J_{H^6H^4}$ = 1.0 Hz, $^3J_{PtH^6}$ = 20.4 Hz, CH group adjacent to coordinated N atom, $1H^6_{ppy}$); 7.84 (d, $^3J_{H^5H^6}$ = 7.8 Hz, br Pt sat, CH group adjacent to coordinated N atom, $1H^6_{N^S}$).

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*Monitoring reaction of **1a** with C_5H_5SN by ^1H NMR spectroscopy*

To a small sample (10 mg, 0.023 mmol) of **1a** dissolved in C_6D_6 (0.75 mL) in a sealed NMR tube, 1 equiv pyridine-2-thione (2.6 mg, 0.023 mmol) was added. NMR spectra of the solution at 27 °C were recorded several times showing gradual conversion to a mixture containing the complexes **2a** and **3** and free CH_4.

2.2 Reaction of [Pt(*p*-MeC$_6$H$_4$)(ppy)(SMe$_2$)], 1b, with C$_5$H$_5$SN

To a solution of [Pt(*p*-MeC_6H_4)(ppy)(SMe_2)], **1b**, (100 mg, 0.19 mmol) in dichloromethane (15 mL) was added 1 equiv pyridine-2-thione (22.1 mg, 0.19 mmol) at room temperature. The mixture was stirred for 5h, the solvent was then removed under reduced pressure and the residue was triturated with n-hexane to give a pale red solid, which was separated and dried under vacuum. The product was identified as a mixture of [Pt(*p*-MeC_6H_4)(ppy)(η^1-*S*-S^NH)], **2b**, and [Pt(ppy)(N^S)]$_2$, **3**, with the ratio **2b/3** being 1/1. Total yield: 68 mg, 65%. Due to low solubility, the compounds formed in this reaction could not be separated and therefore elemental analysis was not useful. ^{1}H NMR data in $CDCl_3$, **2b**: δ 2.29 (s, Me of *p*-tolyl, 3H), aromatic protons: *p*-tolyl ligand, 6.88 (d, $^3J_H{}^m{}_H{}^o$ = 7.6 Hz, 2H^m), 7.17 (d, $^3J_H{}^o{}_H{}^m$ = 7.6 Hz, 2H^o); ppy ligand, 6.41 (d, $^3J_H{}^{3'}{}_H{}^{4'}$ = 7.5 Hz, $^3J_{PtH}{}^{3'}$ = 24.6 Hz, CH group adjacent to coordinated C atom, 1H$^3{}_{ppy'}$), 8.60 (d, $^3J_H{}^6{}_H{}^5$ = 6.8 Hz, $^3J_{PtH}{}^6$ = 16.1, CH group adjacent to coordinated N atom, 1H$^6{}_{ppy}$); η^1-*S*-S^NH ligand, 9.07 (d, $^3J_H{}^3{}_H{}^4$ = 5.6 Hz, 1H^3). **3**: 8.07 (d, $^3J_{PtH}{}^6$ = 19.2 Hz, $^3J_H{}^6{}_H{}^5$ = 5.6 Hz, CH group adjacent to coordinated N atom, 1H$^6{}_{ppy}$), 7.49 (d, $^3J_{PtH}{}^{3'}$ = 32.0 Hz, $^3J_H{}^{3'}{}_H{}^{4'}$ = 5.8 Hz, CH group adjacent to coordinated C atom 1H$^{3'}{}_{ppy}$), 7.89 (d, $^3J_{PtH}{}^6$ = 16.0 Hz, $^3J_H{}^3{}_H{}^4$ = 7.5 Hz, H$^6{}_{N^S}$), 6.50-7.60 (other aromatic protons of ppy and S^N groups).

2.3. Kinetic Study

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In a typical experiment, a solution of complex **1a** in dichloromethane (3 mL, 3 $\times 10^{-4}$ M) in a cuvette was thermostated at 25 °C and a 0.01 molar solution (90 μL) of pyridine-2-thione was added using a microsyringe. After rapid stirring, the absorbance at λ= 500 nm was monitored.

2.4. Theoretical Methods

Geometry optimizations were performed with the program suite Gaussian03 at the DFT/B3LYP level [46]. The effective core potential of Hay and Wadt with a double–ξ valence basis set (LANL2DZ)[47, 48] was chosen to describe Pt and the 6-31G* basis set was used for other atoms. To evaluate and ensure the optimized structures of the molecules, frequency calculations were carried out using analytical second derivatives.

3. Results and discussion

3.1. Synthesis and characterization of the complexes

As shown in Scheme 2, reaction of the Pt(II) starting complexes [PtR(ppy)(SMe_2)], **1**, in which R = Me (**1a**) or *p*-MeC_6H_4 (**1b**) and ppy = deprotonated 2-phenylpyridine, with pyridine-2-thione (C_5H_5SN) in a 1:1 molar ratio, followed by the replacement of the labile ligand SMe_2 to give a mixture containing the *S*-bound thione Pt(II) complex [PtR(ppy)(η^1-*S*-S^NH)], **2**, in which R = Me (**2a**) or *p*-MeC_6H_4 (**2b**), the dimeric complex [Pt(ppy)(N^S)]$_2$, **3**, with two bridging deprotonated pyridine-2-thione (N^S) ligands, and R-H, i.e. CH_4 (in case where R = Me) or MeC_6H_5 (in case where R = *p*-MeC_6H_4). When reaction of **1** with C_5H_5SN is allowed to stir for 3 days in benzene, only **3** along with free R-H are formed.

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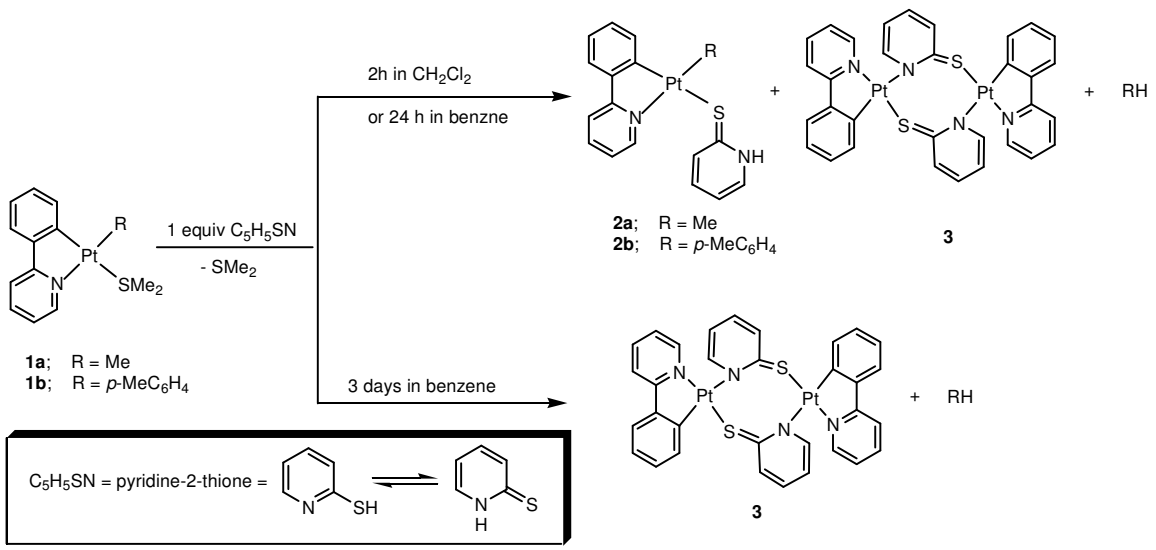

Scheme 2. Reactions studied in this work.

The products were characterized by ^{1}H NMR and X-ray crystallography (for the complex **3**) and full data are collected in the Experimental Section. In the ^{1}H NMR spectrum of complex [PtMe(ppy)(η^{1}-*S*-S^NH)], **2a**, in C_6D_6 at room temperature, the methylplatinum resonance occurred at δ = 2.36 as a singlet which coupled to ^{195}Pt with $^{2}J_{PtH}$ = 69.9 Hz (the value in the range expected for a methylplatinum(II) complex with methyl being *trans* to nitrogen [49-52]). The CH group adjacent to ligating C atom of the ppy ligand, i.e. $H^{3'}$, appeared as a doublet of doublets at δ = 7.79 with $^{3}J_{H^{3'}H^{4'}}$ = 7.4 Hz and $^{4}J_{H^{3'}H^{5'}}$ = 1.1 Hz, and with $^{3}J_{PtH^{3'}}$ = 24.5 Hz, while the hydrogen related to the CH group adjacent to ligating N atom of the ppy ligand, i.e. H^{6}, as expected was appeared further down field as a doublet of doublets at δ = 8.76 with $^{3}J_{H^{6}H^{5}}$ = 5.7 Hz and $^{4}J_{H^{6}H^{4}}$ = 1.8 Hz, and with $^{3}J_{PtH^{6}}$ = 16.2 Hz. The H^{3} proton of the η^{1}-*S*-S^NH ligand appeared as a doublet at δ = 7.92 with $^{3}J_{H^{3}H^{4}}$ = 5.5 Hz, with no observable coupling to Pt center probably due to the related pyridine plane being perpendicular to square geometry of the complex [18]. Notice also that formation of CH_4 is confirmed by the observation of a singlet at 0.16. The complex

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[Pt(ppy)(N^S)]$_2$, **3**, is also characterized with signals due to $H^{3'}{}_{ppy}$, $H^{6}{}_{N^S}$ and $H^{6}{}_{ppy}$ at 7.49 ($^3J_{PtH}{}^{3'}$ = 34.2 Hz), 7.84 (br Pt sat) and 8.09 ($^3J_{PtH}{}^{6}$ = 20.4 Hz) ppm, respectively.

In the ^{1}H NMR spectrum of complex [Pt(*p*-MeC$_6$H$_4$)(ppy)(η^1-*S*-S^NH)], **2b**, in $CDCl_3$ at room temperature, a singlet signal was observed at δ = 2.29 for the methyl group on the *para*-tolyl ligand. The *meta* and *ortho* protons of the *para*-tolyl ligand appeared as two doublets at δ = 6.88 and 7.17, respectively, each with $^3J_H{}^m{}_H{}^o$ = 7.6 Hz. A doublet signal at δ = 6.41 with $^3J_H{}^{3'}{}_H{}^{4'}$ = 7.5 Hz, accompanied by platinum satellites ($^3J_{PtH}{}^{3'}$ = 24.6 Hz), is attributed to hydrogen atom of C-H group adjacent to the coordinated C atom of ppy ligand, i.e. $H^{3'}$. A doublet signal at δ = 8.60 (with $^3J_H{}^6{}_H{}^5$ = 6.8 Hz and $^3J_{PtH}{}^6$ = 16.1 Hz) is assigned to CH group adjacent to coordinated N atom of ppy ligand, i.e. H^6. The H^3 proton of the η^1-*S*-S^NH group appeared as a doublet at δ = 9.07 with $^3J_H{}^3{}_H{}^4$ = 5.6 Hz. The dimer complex, i.e. [Pt(ppy)(N^S)]$_2$, **3**, with similar ^{1}H NMR data as mentioned above (see also Experimental section), was also detected. Besides, formation of R-H (i.e. MeC$_6$H$_5$) is confirmed by the observation of a singlet at 2.31.

The dimeric complex [Pt(ppy)(N^S)]$_2$, **3**, was also prepared by direct route by reaction of the complex [Pt(ppy)Cl(DMSO)] [42] with an ethanolic solution of sodium pyridine-2-thiolate (NaC$_5$H$_4$NS) under inert atmosphere condition and a purified sample of it (as checked by microanalysis) was characterized by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectrum of complex **3** in $CDCl_3$, the CH group adjacent to coordinated N atom of ppy appeared at δ = 8.09 as a doublet ($^3J_H{}^6{}_H{}^5$ = 5.6 Hz) which coupled to ^{195}Pt with $^3J_{PtH}{}^6$ = 19.1 Hz. The resonance of CH group adjacent to coordinated C atom of ppy is occurred at δ = 7.47 as a doublet with Pt satellite ($^3J_{PtH}{}^{3'}$ = 32.8 Hz, $^3J_H{}^{3'}{}_H{}^{4'}$ = 5.7 Hz) and the CH group adjacent to coordinated N atom of N^S chelate was observed at δ = 7.86 as a

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doublet signal ($^{3}J_{H}{}^{3}{}_{H}{}^{4}$ = 7.5 Hz, $^{3}J_{PtH}{}^{6}$ = 16.2 Hz), which confirmed the coordination of N^S as chelate. The complex **3** was also characterized by single-crystal X-ray diffraction analysis as illustrated in Figure 3. [45]

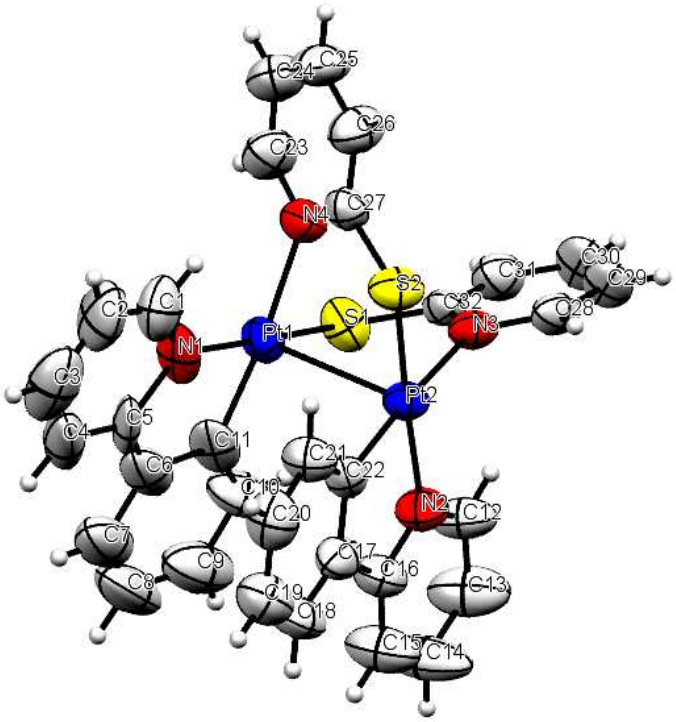

Figure 3. Crystal structure of the complex [Pt(ppy)(N^S)]$_2$, **3**, from crystallization of the product obtained from mixing of complex **1a** and C_5H_5SN. Selected bond distances (Å) and angles (°): Pt2-C22 1.977(11), Pt2-N2 2.064(9), Pt2-N3 2.144(10), Pt2-S2 2.286(3), Pt2-Pt1 2.8513(11), Pt1-C11 1.982(14), Pt1-N1 2.006(11), Pt1-N4 2.170(9), Pt1-S1 2.287(4), S2-C27 1.758(12), S1-C32 1.715(12), C22-Pt2-N2 80.7(4), C22-Pt2-N3 174.2(4), N2-Pt2-N3 93.4(4), C22-Pt2-S2 95.3(3), N2-Pt2-S2 172.8(3), N3-Pt2-S2 90.5(2), C22-Pt2-Pt1 95.6(3), N2-Pt2-Pt1 99.7(3), N3-Pt2-Pt1 85.4(3), S2-Pt2-Pt1 86.57(9), C11-Pt1-N1 81.1(6), C11-Pt1-N4 173.9(5), N1-Pt1-N4 93.6(5), C11-Pt1-S1 95.4(5), N1-Pt1-S1 172.7(4), N4-Pt1-S1 89.6(3), C11-Pt1-Pt2 98.9(4), N1-Pt1-Pt2 100.9(3), N4-Pt1-Pt2 84.9(3), S1-Pt1-Pt2 85.89(9).

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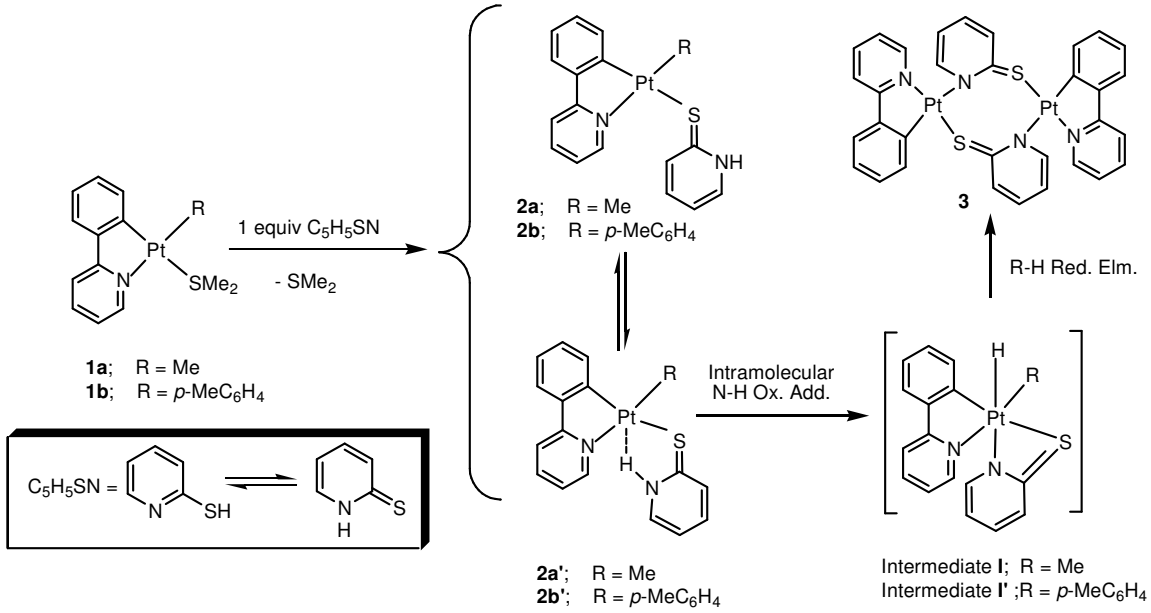
3.2. Kinetics and mechanism of the reactions

On the basis of the data obtained from UV-vis and ^{1}H NMR spectroscopic studies (see below), a mechanism (being depicted in Scheme 3) for reaction of the complex [PtR(ppy)(SMe_2)], **1**, with 1 equiv pyridine-2-thione (C_5H_5SN) is proposed. The reaction is suggested to involve initial displacement of the SMe_2 ligand by C_5H_5SN, during which S donor site of the thione tautomer (HN^S) attacks Pt center of the complex **1** to displace the SMe_2 ligand, giving either the product **2a** (or **2b**) or its isomeric form, **2a**' (or **2b'**), in which the py ring has twisted by 90º as compared to that in **2a** (or **2b**); in the latter case, N-H group has the opportunity to interact with the Pt center to form Pt···H-N hydrogen bonding as confirmed by ^{1}H NMR studies (*vide infra)*. The complex **2a**' (or **2b'**) then performs an intramolecular N-H oxidative addition to form the intermediate **I** (**or I'**) following by CH_3-H (or MeC_6H_5) reductive elimination to give the complex **3**.



Scheme 3. Suggested mechanism for reaction of the complex [PtR(ppy)(SMe_2)], **1**, with pyridine-2-thione.

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3.2.1 Kinetic studies by UV-vis spectroscopy

Reaction kinetics, using UV-vis spectroscopy, of equimolar amounts of the complex [Pt(*p*-MeC_6H_4)(ppy)(SMe_2)], **1b**, and pyridine-2-thione in CH_2Cl_2 solution to form a mixture containing the complexes [Pt(*p*-MeC_6H_4)(ppy)(η^1-*S*-S^NH)], **2b**, and [Pt(ppy)(N^S)]$_2$, **3**, along with the free MeC_6H_5, is typically presented here. A series of spectra recorded during the reaction is shown in Figure 4. On mixing, the characteristic peaks of complex **1b** (MLCT band at 365 nm) and pyridine-2-thione (n-π* at 375 nm) [53, 54] disappeared and a new broad absorption band due the intermediate **2b'** appeared (see Scheme 3). The decay of **2b'** to finally form **3** could be studied by monitoring formation of absorption band of the final product **3** at 500 nm. Typical plots of absorbance at λ = 500 nm versus time are shown in Figure 5.

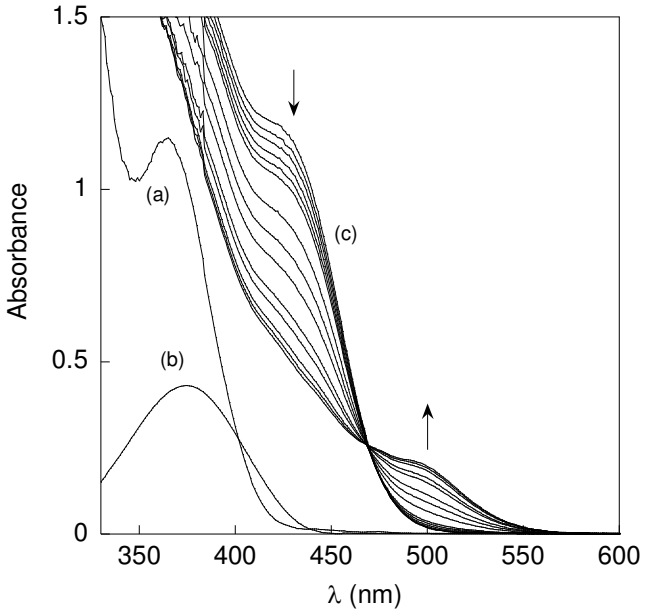

Figure 4. The changes in the UV-vis spectrum during the reaction of [Pt(*p*-MeC_6H_4)(ppy)(SMe_2)], **1b**, with pyridine-2-thione (each 3×10^{-4} M) in CH_2Cl_2 at 25 °C: (a) pure **1b**; (b) pure pyridine-2-thione; (c) spectrum at t = 0; successive spectra recorded at intervals of 1 min.

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The Abs-time data at λ = 500 (i.e. formation of the product **3**) is fitted to the equation $A_t = A + (A_0 - A) \exp(-kt)$, and the calculated rate constants at different temperatures are given in Table 1. The activation parameters were also obtained from measurement at different temperatures using Eyring equation (Figure 6). Rates of the reactions are sensitive to the nature of R ligand and it is lower when the tolyl complex **1b** is involved as compared to the case where the methyl complex **1a** is used. The intermediate **2b'** then performs an intramolecular N-H oxidative addition reaction to form intermediate **I'** (see Scheme 3) following by C-H reductive elimination to form toluene and the dimer complex **3**.

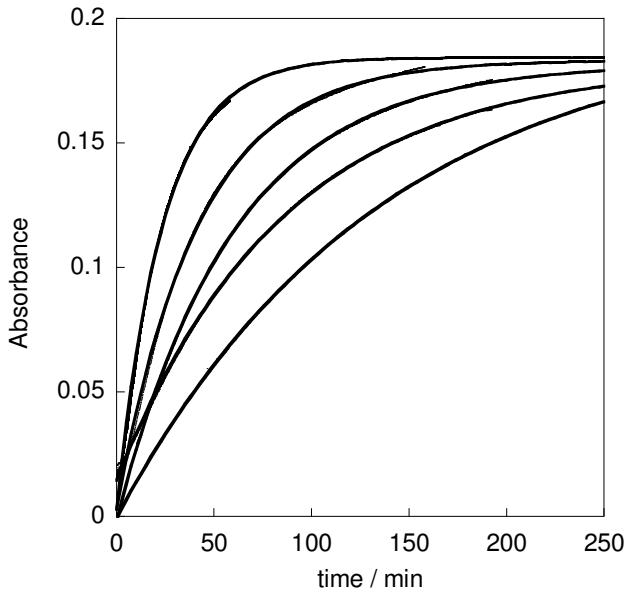

Figure 5. Absorbance (at 500 nm)-time curves for the reaction of [Pt(*p*-MeC_6H_4)(ppy)(SMe_2)], **1b**, with pyridine-2-thione, using 1:1 stoichiometry, in CH_2Cl_2 at temperatures of 15, 20, 25, 30 and 35 °C (temperature increases reading upward).

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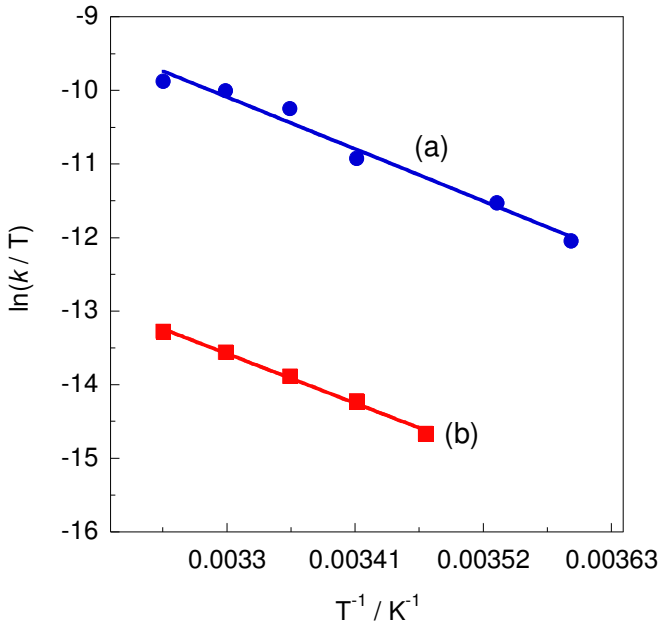

Figure 6. Eyring plots for reductive elimination of R-H and formation of dimer **3** from (a) complex **2a'** (R=Me) and (b) **2b'** (R= *p*-MeC_6H_4) in CH_2Cl_2.

Table 1. Rate constants[a] and activation parameters for R-H reductive elimination from the complexes **2a'** or **2b'** to give dimer **3** in CH_2Cl_2 solution.

R	10^2k/s^{-1} at different temperatures							$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / $JK^{-1}mol^{-1}$
	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C		
Me	0.16	0.28		0.53	1.05[b]	1.14	1.16	53.4 ± 3.9	-105± 13
p-MeC_6H_4			0.012	0.019	0.027	0.039	0.052	50.8 ± 1.9	-142 ± 6

[a] Estimated errors in *k* values are ± 5%. [b] The value in benzene 10^2k = 0.32 s^{-1}.

As is shown in Table 1, $\Delta H^{\ddagger}$ value for methane reductive elimination from the intermediate **I** is 53.4 kJ mol^{-1} being considerably lower than the values of 107.4 and 70 kJ mol^{-1} reported for CH_4 reductive elimination from Pt(IV) complexes [$PtMe_3$(H)(dppe)] (dppe= 1,2-bis(diphenylphosphino)ethane) [55] and [$PtMe(H)(Cl)_2(PMe_3)_2$] [56], respectively.

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This lower energy barrier found for [PtMe(H)(ppy)(S^N)] may be related to higher ring strain, presented in four-membered S^N ring in Pt(IV) intermediate **I**.

3.2.2. Monitoring the reactions by ^{1}H NMR spectroscopy

As can be seen in Figure 7, immediately after addition of pyridine-2-thione to the complex [PtMe(ppy)(SMe_2)], **1a**, at 27 ºC in C_6D_6, the complexes [PtMe(ppy)(η^1-*S*-S^NH)], **2a** and **2a'**, were started to appear. The rate of disappearance of complex **1a** using the ^{1}H NMR signal at δ = 1.55 (due to Me group connected directly to Pt in complex **1a**) was found to be 1.90 (0.10)×10^3 s^{-1}. According to Figure 7, for the complex **2a'**, a singlet signals for Pt-Me protons was observed at δ 2.02 (with $^2J_{PtH}$ = 68.2 Hz) with the liberated SMe_2 appearing at δ 1.72, in comparison with the coordinated SMe_2 ligand of **1a** (at δ 1.85 with $^3J_{PtH}$ = 25.1 Hz). Besides, the presence of a doublet signal, appearing at δ = 10.52 with accompanying ^{195}Pt satellite signals of $^3J_{PtH}$ = 23.3 Hz (assigned for the H^6 of the pyridine-2-thione ring) confirms that the pyridine-2-thione ligand is connected to the Pt center via S atom (which is normally preferred to N atom [41]). The observation of this broad signal at a significantly lower field, in comparison with that for corresponding hydrogen of the free ligand (in thione form, **Ia** in Figure 1, appearing at δ = 7.64 [39]), and with a significant $^3J_{PtH}$ value of 23.3 Hz complies with the formation of Pt···H-N hydrogen bonding; this coupling value is smaller than those usually observed in similar hydrogen bondings which could be attributed to the η^1-*S*-S^NH ligand being rather rigid and thus there is some force on the corresponding hydrogen to locate itself above the platinum coordination plane in order to interact with its $5d_z^2$ orbital.[57]

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The ratio of **2a'** to **1a**, immediately after addition of pyridine-2-thione to **1a**, is close to 1:2. As the time was passing on, the signals due to the starting material **1a** was disappearing while those due to the complex **2a'** were growing and later started to fade away and meanwhile comparatively weak signals due to the complexes **2a** and **3** (being out of the range of Figure 7) were also observed in the first stages. As the reaction was progressed, the complex **2a'** was disappearing while the final complexes **2a** and **3** were forming. As mentioned before, after 3 days the dimer **3** was solely obtained in pure form. Appearance of the corresponding signal for **2a** at δ = 2.36 was used to measure rate of formation of the complex **2a**, which was found to be 1.51(0.05) × 10^{-4} s^{-1}. The rate of formation of CH_4 (at δ = 0.16) which is equal to disappearance of the intermediate **I** and formation of the dimer **3** is measured to be 3.0 × 10^{-3} s^{-1}, very close to value of 3.2 × 10^{-3} s^{-1} obtained from UV-vis study (*vide supra).*

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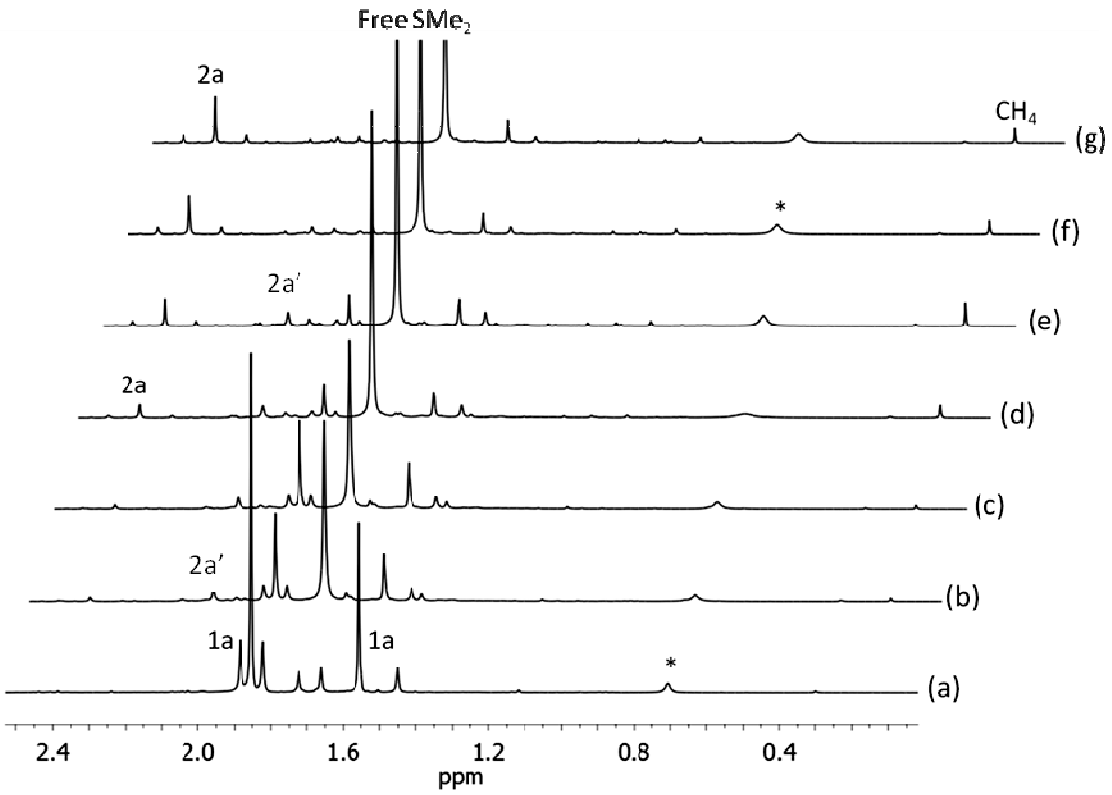

Figure 7. ^{1}H NMR spectra (Me region) of reaction of the complex **1a** with pyridine-2-thione at 27 °C in C_6D_6; (a) pure **1a**, (b) immediately after addition of pyridine-2-thione to **1a**, (c) 5 min after addition, (d) 15 min after addition, (e) 1h after addition, (f) 3h after addition, (g) 5h after addition. Signals with satellites are assigned to the complexes **1a**, **2a'** and **2a**. The peak labeled * is due to water of C_6D_6 solvent.

We suggest that the formation of the complex **3** proceeds through an intramolecular N-H oxidative addition, involving the η^1-*S*-S^NH ligand in **2a**', to the platinum center [58, 59] to form the platinum(IV) hydride intermediate [PtMe(H)(ppy)(S^N)], **I**, followed by reductive elimination of methane to form the complex **3**. Our attempts to observe the intermediate **I** (by following the reaction at low temperatures) were not successful. However, evidence in favor of formation of this hypothesized Pt(IV) complex is the

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methane production, appearing as a singlet signal at δ = 0.16 [60-62]. Formation of the dimeric complex [Pt(ppy)(N^S)]$_2$, **3**, was confirmed by the observation of a doublet signal at δ = 7.84 with $^3J_H{}^6{}_H{}^5$ = 7.6 Hz, due to H^6 of the N^S bridge, that experiences coupling with Pt with the satellites being broad and so the related coupling value was not measurable. Formation of the dimer **3** was also confirmed by X-ray crystal determination of suitable crystal of **3** obtained from crystallization of the mixture. Formation of the product complex [PtMe(ppy)(η^1-*S*-S^NH)], **2a**, in which pyridine-2-thione adopts the thione form [63-66], suggests a pathway including direct substitution of labile SMe_2 by sulfur of thiolate ligand. Same experiment for the reaction of **1a** with pyridine-2-thione was also carried out in CD_2Cl_2 as NMR solvent and found that the reaction in dichloromethane is faster than in benzene (in agreement with data obtained from the UV-vis spectroscopy, see Table 1).

3.3 Geometry optimizations

To get some insights in structures of the synthesized complexes **2** and **3**, calculations in the DFT method were carried out and their geometries were optimized using the B3LYP function. Optimized geometric parameters of the complexes **2** and **3** are given in Table 2 and the DFT-optimized structures for these complexes are shown in Figure 8. The computed structural details are in good agreement with corresponding experimental parameters obtained for the related complexes. Mean error for the bond lengths is 0.026 Å for the complex **3**. One reason for the small bond length discrepancy may be due to differences in the geometrical parameters calculated in the gas phase with those obtained experimentally in the solid state.

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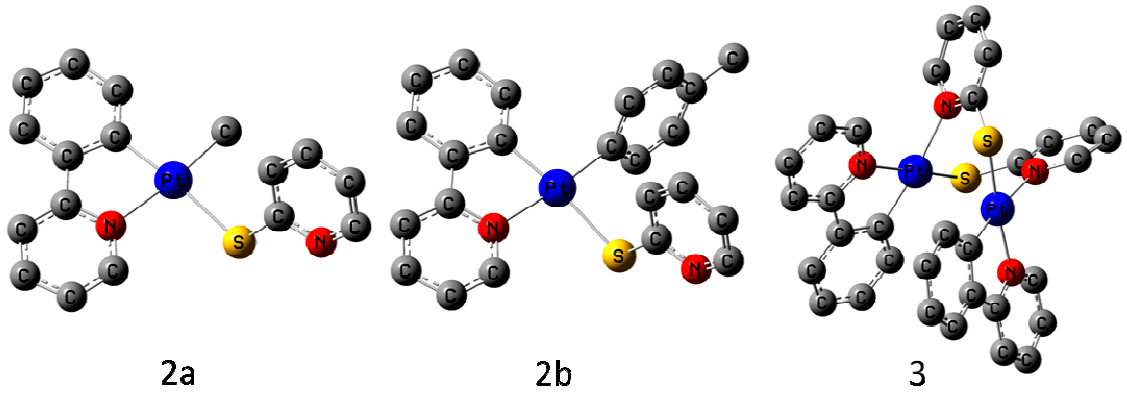

Figure 8. DFT optimized structures of complexes **2** and **3.** The H atoms are omitted for clarity.

The complex **2a** contains a square planar platinum(II) center being connected to the Me group, *ortho* C and N atoms of the ppy ligand and S atom of the S^NH. The two carbon ligating atoms are mutually *cis* in the square-planar structure, as expected, and largest deviation from ideal geometry is the angle N(ppy)-Pt-C(ppy) = 79.7, which is associated with the Pt(ppy) chelate ring. N atom of the S^NH ligand is not coordinated and is positioned opposite to the platinum center. Similar to **2a**, the complex **2b** has also a square-planar stereochemistry at platinum and the *p*-tolyl ligand lies roughly orthogonal to the square plane and to the ppy ligand. The Pt-S (S^NH) distances are 2.514 and 2.521 Å in **2a** and **2b**, respectively. The dimeric complex **3** has a square planar stereochemistry at each Pt center and has a head-to-tail configuration with PtSNPt coordination, in which S atom of one of the SN ligands is in a *cis* arrangement with N atom of the other SN ligand (Figure 8); the coordination geometry around each platinum center is completed by nitrogen and *ortho* C atoms of the ppy ligand. This complex with a head-to-tail arrangement of the two SN ligands has been formulated as containing a Pt–Pt distance of

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3.009 Å which is close to the experimental value of 2.8513(11) Å. This separation is amongst the shortest Pt-Pt interactions observed in binuclear platinum complexes bridged with two ligands.[45] The calculated bond distance Pt–N(N^S) = 2.233 Å is slightly longer than Pt–N(ppy) = 2.093 Å due to a higher *trans* influence of the coordinating C atom of ppy as compared to coordinating S donor atom of N^S. These values are comparable with experimental values of 2.144(10) and 2.064(9) Å for Pt2–N3(N^S) and Pt2-N2(ppy), respectively. The two nitrogen atoms are *cis* disposed to one another (N(ppy)PtN(N^S) = 94.9°), indicating that angles around the Pt center are rather close to the ideal angle of 90°. The experimental values of this bond angle is equal to 93.4(4) °.

Table 2. Selected calculated bond distances (Å) and angles (°) for complexes **2** and **3**.

2a		**2b**		**3**		**3** (exp)
Pt–S(S^NH)	2.514	Pt–S(S^NH)	2.521	Pt2–N3(N^S)	2.233	2.144(10)
Pt–C(Me)	2.064	Pt–C(Ar)	2.024	Pt2-S2(N^S)	2.370	2.286(3)
Pt–N(ppy)	2.193	Pt–N(ppy)	2.190	Pt2-C22(ppy)	2.009	1.977(11)
Pt–C(ppy)	2.012	Pt–C(ppy)	2.165	Pt2-N2(ppy)	2.093	2.064(9)
C(Me)–Pt–S(S^NH)	91.4	C(Ar)–Pt–S(S^NH)	173.4	Pt1–Pt2	3.009	2.8513(11)
S(S^NH)–Pt–N(ppy)	95.0	S(S^NH)–Pt–N(ppy)	94.9	C22(ppy)–Pt2–S2(N^S)	95.0	95.3(3)
N(ppy)–Pt–C(ppy)	79.7	N(ppy)–Pt–C(ppy)	79.6	S2(N^S)–Pt2–N3(N^S)	89.1	90.5(2)
C(ppy)–Pt–C(Me)	93.9	C(ppy)–Pt–C(Ar)	95.4	N2(ppy)–Pt2–N3(N^S)	94.9	93.4(4)

3.4. Energy profile for the product formation

To gain more insights into the species involved in the reaction of complexes **1** with C_5H_5SN (see Scheme 3), DFT calculations were carried out to show structures and energies for the related complexes in CH_2Cl_2 solution (Figures 9 and 10).

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As shown in Figure 9, replacement of labile ligand SMe_2 in the cycloplatinated(II) complex **1a** by pyridine-2-thione (C_5H_5SN) first gives the complex [PtMe(ppy)(η^1-*S*-S^NH)], **2a**, having a NH pendant group, with 33.1 kJmol^{-1} lower in energy with respect to that for **1a**. This step is facilitated by strong *trans*–influence of the metalated C atom of ppy ligand which helps in weakening the Pt–SMe_2 bond. The complex **2a** is obtained in equilibrium with its isomeric form, **2a'**, in which the pyridine ring has twisted by 90º as compared to that in **2a** to form Pt···H-N hydrogen bonding (as confirmed by ^{1}H NMR studies). The complex **2a'** is more stable than **2a** by 14.8 kJmol^{-1}. In the next step, the complex **2a'** attends in an intramolecular N–H oxidative addition reaction to give the organoplatinum(IV) hydride complex [PtHMe(ppy)(N^S)], **I**, followed by reductive elimination of methane to give the dimer **3**. The final product **3** is 139.0 kJmol^{-1} more stable than **1a** complying with the experimental finding.

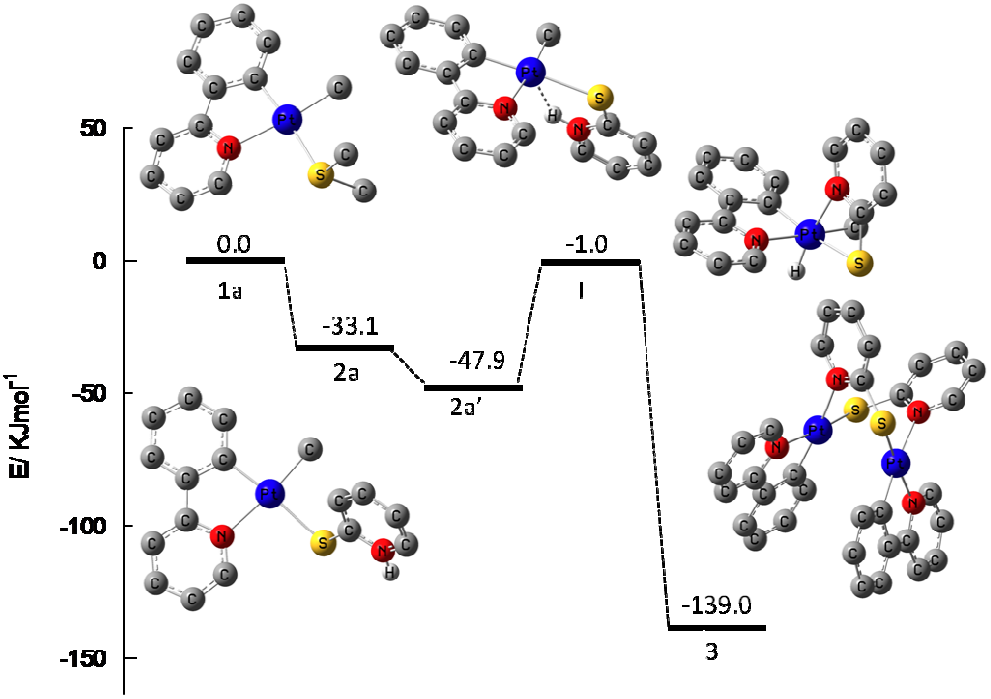

Figure 9. Calculated structures and relative energies of species involved in reaction of the complex **1a** with pyridine-2-thione.

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In the related reaction profile (see Figure 10), the complex **1b** reacts with pyridine-2-thione to form the S-bonded complexes **2b** and **2b'**, which are more stable than **1b** by 29.9 and 43.3 kJmol^{-1}, respectively. Coordination of pyridine-2-thione entering ligand through the N atom is not proposed, because the corresponding isomer [Pt(*p*-MeC$_6$H$_4$)(ppy)(η^1-*N*-N^SH)] was calculated to be 42.4 kJmol^{-1} less stable than **2b'**. Oxidative addition of N–H bond to Pt center of the complex [Pt(*p*-MeC$_6$H$_4$)(ppy)(η^1-*S*-S^NH)], **2b′**, gives the Pt(IV) intermediate complex [PtH(*p*-MeC$_6$H$_4$)(ppy)(N^S)], **I′**, with 12.9 kJmol^{-1} higher in energy than **1b**. At the final step, reductive elimination of toluene gives dimer **3** which is more stable than **1b** by 126.2 kJmol^{-1}.

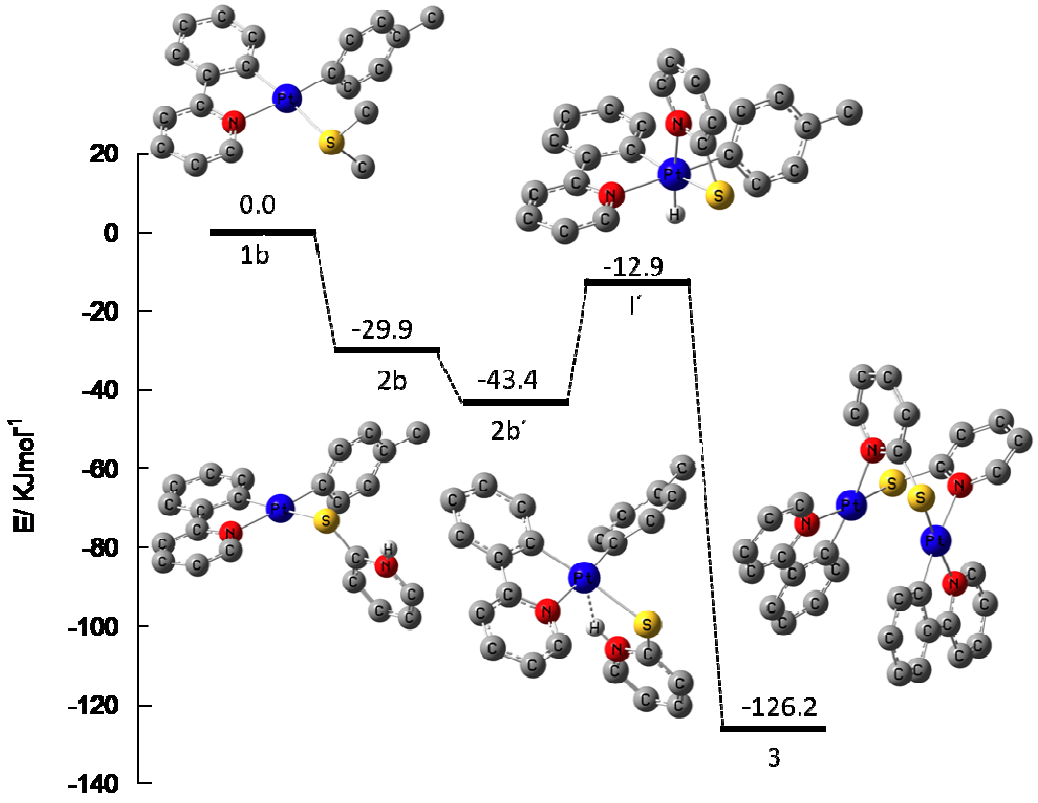

Figure 10. Calculated structures and relative energies of species involved in reaction of the complex **1b** with pyridine-2-thione.

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Conclusion

Reaction of the cycloplatinated(II) complexes [PtR(ppy)(SMe_2)], **1**, with pyridine-2-thione is suggested to proceed via displacement of the labile SMe_2 ligand. In this reaction pyridine-2-thione, which exists as a mixture of tautomers thiol (N^SH) and thione (HN^S), attacks Pt center of the complex **1** from S side of the thione form to give the four coordinated square-planar complex **2a** (or **2b**) and its isomer **2a'** (or **2b'**), with a general formula [PtR(ppy)(η^1-*S*-S^NH)]. DFT calculations show that this behavior is much preferred to the case of attacking from N side of the thiol form. The following points are considered for the reaction:

1- Suggestion in the first step is consistent with the "soft" S atom (from the thione tautomer, HN^S) being preferred to be connected to "soft" Pt(II) center as compared to that for the "hard" nature of N atom (from the thiol tautomer, N^SH).

2- Formation of intramolecular Pt···H-N hydrogen bonding in one of the product isomers of the first step, i.e. the complex [PtR(ppy)(η^1-*S*-S^NH)], **2a'**, (as detected by monitoring the reaction using ^{1}H NMR spectroscopy) is suggested to provide an extra stabilization as compared with the product isomer **2a**.

3- As was determined by UV-vis spectroscopy (see Table 1), R-H reductive elimination from the complex **2a'** or **2b'** to form the dimer complex **3** is significantly faster when R = Me (with $k = 1.05\times10^{-2}$ s^{-1} at 25°C, in CH_2Cl_2) as compared to that when R = *p*-MeC_6H_4 (with $k = 0.027\times10^{-2}$ s^{-1} at 25°C, in CH_2Cl_2). We attributed this to the easier reductive elimination of CH_4 as compare with toluene.

4- The rate of reaction of [PtMe(ppy)(SMe_2)], **1a**, with pyridine-2-thione is significantly faster in CH_2Cl_2 ($k = 1.05\times10^{-2}$ s^{-1} at 25°C) than in benzene ($k = 0.32\times10^{-2}$ s^{-1} at 25°C).

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We attribute this to the possibility that CH_2Cl_2 solvent molecules make the species more stable, by solvation, than when solvent molecules are the less polar benzene.

We finally observed the formation of two complexes, the S bounded complex [PtR(ppy)(η^1-*S*-S^NH)], **2**, and the dimeric complex [Pt(ppy)(N^S)]$_2$, **3**, along with the evolution of free R-H. These observations led us to believe that an intramolecular N-H oxidative addition reaction must have been taken place in the complex [PtR(ppy)(η^1-*S*-S^NH)], **2a'** (or **2b'**), to give the Pt(IV) intermediate complex [PtHR(ppy)(N^S)], **I** (or **I'**), in which the reductive elimination of R-H bond is needed to produce complex **3**.

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