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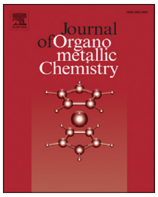

Cycloplatinated(II) complex bearing 2-vinylpyridine and monodentate phosphine ligands: Optical properties and kinetic study

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Dedicated to Professor Elena Lalinde on the occasion of her 60th birthday.

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ABSTRACT

The 2-vinylpyridinate complex [PtMe(Vpy)(DMSO)], **C**, is successfully prepared from dimeric platinum(II) complex *cis,cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$], **B**, in the presence of DMSO and 2-vinylpyridine ligand. The DMSO molecule in complex **C** can be readily substituted by methyldiphenylphosphine (PPh_2Me), allowing synthesis of [PtMe(Vpy)(PPh_2Me)], **1**, which has been fully characterized spectroscopically. Complex **1** is emissive in solid state and solution at room temperature and at 77 K. This complex displays an intense phosphorescence emission (with a significantly long lifetime) which is originated from mixed ^{3}ILCT/^{3}MLCT excited state. Additionally, complex **1** undergoes oxidative addition with alkyl halide (MeI) bearing [$PtMe_2I$(Vpy)(PPh_2Me)], **2**, after 2 h. Kinetic studies suggest that the latter reaction (oxidative addition) proceed by a classical S_N2 mechanism. The rate of oxidative addition reaction at different temperatures is measured and high negative $\Delta S^{\#}$ value is obtained for the reaction which supported the proposed mechanism. On the basis of NMR spectroscopy, when complex **1** reacts with MeI under extended time (5 days), complex **2** gradually converts to a mixture of platinum complexes *trans*-[PtMeI(PPh_2Me)$_2$], **3**, [{$PtMe_2$(Vpy)}$_2$(μ-I)$_2$], **4**, and a free ligand *Z*/*E*-[C_8H_9N], **5**, based on the carbon–carbon bond coupling.

1. Introduction

Growing interest in organometallic complexes containing cyclometalated ligands [1–3] is conditioned by their highly versatile applications in myriad of fields such as biology [4–8], organic synthesis [9–11], catalysts [12–14] and optoelectronic materials [15–19] with useful potential application in organic light-emitting diode (OLED) devices [20–25] or molecular sensors [26–29]. In the midst of these cyclometalated compounds, mono alkyl or mono aryl cycloplatinated complexes bearing a labile leaving group such as SMe_2 [30–32], DMSO [27,32–34], CH_3COCH_3 [35] have been extensively studied on account of their different reactivities toward fundamental organometallic reactions [36–46].

Several C^N cyclometalating ligands have been utilized in the above mentioned cycloplatinated complexes as these ligands provide a five-membered chelate which induces chemical stability to metal complexes (Scheme 1). 2-vinylpyridinate ligand (**V** in Scheme 1) [47–49] is a new type of ligand in cycloplatination and the chemistry of such complexes is undiscovered against 2-phenylpyridinate and/or benzoquinolate complexes (**I** and **II**, respectively, in Scheme 1) [2,50,51]. In such ligand, platinum metal center is bound to the β carbon atom in the vinyl group instead of to aromatic ring through a vinylic C–H bond activation [48].

The present study introduce a new method for preparation of 2-vinylpyridinate complex [PtMe(Vpy)(DMSO)], **C** [48], from dimeric methyl platinum complex **B** in high yield [52,53]. In addition, the possibility of substitution reaction of the DMSO solvent with a phosphine ligand (L = PPh_2Me) is investigated. Characterization, photophysical behavior and systematic temperature dependence kinetic study involving oxidative addition reaction of MeI with the new corresponding phosphine complex [PtMe(Vpy)(PPh_2Me)], **1**, are also studied. Our results moreover indicate that Pt(IV) complex [$PtMe_2I$(Vpy)(PPh_2Me)], **2**, is not stable in solution and is converted to a mixture of compounds.

2. Result and discussion

Among various platinum precursors, monomeric or dimeric organoplatinum(II) derivatives containing labile leaving groups

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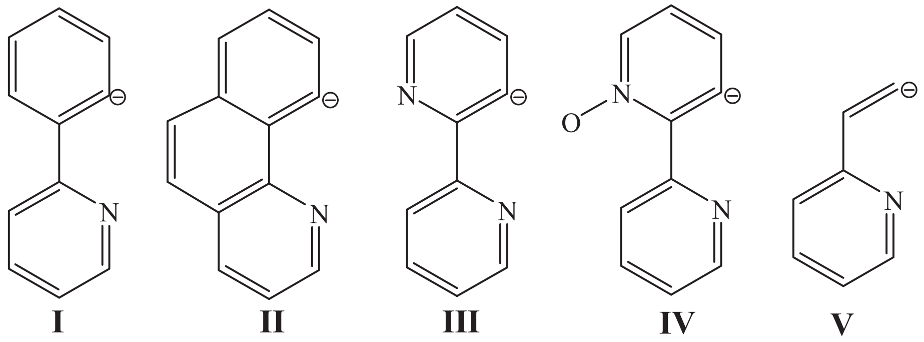


Scheme 1. Different cyclometalating ligands.

with general formula *cis*-[PtMe$_2$(DMSO)$_2$], **A** [54–56], or *cis*,*cis*-[Me$_2$Pt(μ-SMe$_2$)$_2$PtMe$_2$], **B** [52,53,57], respectively, are convenient and notable starting materials for C—H bond activation. Using these precursors, different neutral methyl cycloplatinated(II) complexes [PtMe(C^N)S], in which S = DMSO or SMe$_2$ and C^N = different deprotonated cyclometalating ligands such as 2-phenylpyridine (ppy) [30,32,58], 7,8-benzoquinoline (bzq) [37,59,60], rollover of 2,2′-bypiridyne (N′-bpy-H), have been prepared [34,40,42].

Recently, 2-vinylpyridine (VpyH) [33,48,61–64] has been used in cyclometalation reaction with precursor **A** in different reaction conditions and yielded complex [PtMe(Vpy)(DMSO)], **C** [48], (Scheme 2). In this study, in an attempt, the complex **B** was used as starting material to obtain complex **C** (Scheme 3).

A new promising way was suggested for preparation of the complex [PtMe(Vpy)(DMSO)], **C**, from the dimeric complex **B** (Scheme 3). Complex **B** was dissolved in acetone, and then DMSO (4.5 equiv.) was added and then the mixture was stirred for 1 h at room temperature. VpyH ligand (2.2 equiv.) was then added to the *in situ* formed complex **A** mixture (isolated compound was characterized by ^{1}H NMR, Fig. S1) and the resulting mixture was refluxed for 18 h. After removing the solvent, complex **C** was isolated as a yellow solid (confirmed by ^{1}H NMR [48], Fig. S2). This new synthetic route alleviated the difficulty in preparation of complex **A** from [PtCl$_2$(DMSO)$_2$] and SnMe$_4$ (toxic and flammable) because this reaction requires harsh reaction condition and complex **A** was obtained in a low yield [54,56].

3. Ligand substitution

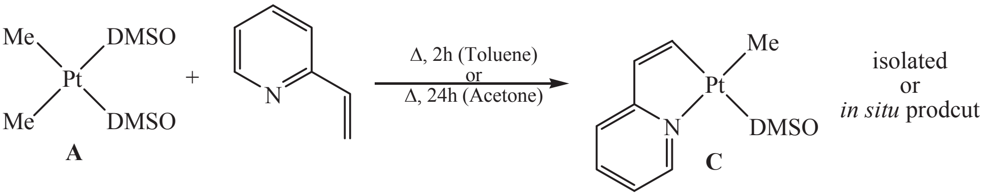
In complex **C**, carbon (C$^\beta$) of 2-vinylpyridinate ligand has a higher *trans* influence in respect with other cyclometalating ligands like ppy [32] or N′-bpy-H [34] which is caused by the lower inductive effect of vinyl substituent compared with phenyl group in the later ligands. Therefore, DMSO is considered as a good leaving group and it can be readily substituted in reaction with two electron donors like phosphine ligand [48]. Reaction of complex **C** (isolated or *in situ* formed) with the phosphorous nucleophile (L = PPh$_2$Me) in a 1:1.2 ratio gave the corresponding complex [PtMe(Vpy)(PPh$_2$Me)], **1**, as presented in Scheme 4. This complex was isolated as a stable orange solid and characterized by ^{1}H and ^{31}P {^{1}H} NMR spectroscopy (Figs. S3 and S4, respectively). In the ^{1}H NMR spectrum of **1**, the MePt resonance appeared as a doublet with platinum satellite at $\delta = 0.98$ ppm ($^2J_{\text{PtH}} = 84.3$ Hz), due to coupling with phosphorus and platinum center. The signal was observed as a doublet accompanied with platinum satellite at $\delta = 2.03$ ppm can be attributed to Me group bound to phosphorus atom and this resonance has a low coupling constant with ^{195}Pt ($^3J_{\text{PtH}} = 23.1$ Hz). ^{31}P {^{1}H} NMR confirms only one phosphorus was bound to platinum center and this phosphorus donor atom was indicated as singlet with platinum satellite at $\delta = 13.0$ ppm ($^1J_{\text{PtP}} = 1976$ Hz). This value of coupling constant between platinum and phosphorus was ascribable to the phosphorus coordinated *trans* to a group having strong *trans* influence [37,39].

4. Photophysical properties

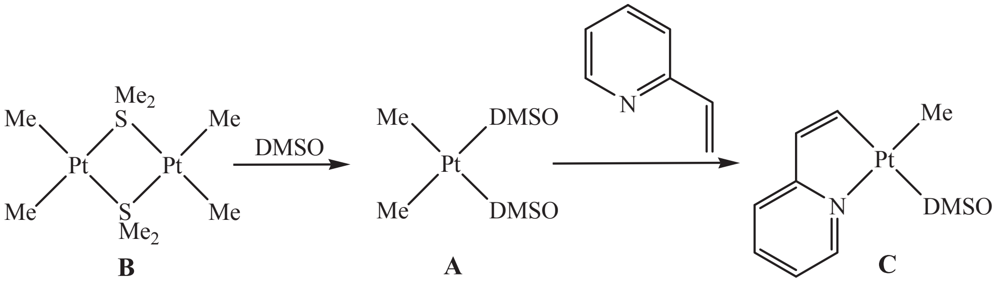
Complex **1** is stable and soluble in organic solvents such as acetone or dichloromethane (CH$_2$Cl$_2$). Photophysical properties of **1** was explored in solid state and fluid solution for obtaining the absorption and luminescence spectra.

4.1. Absorption spectra

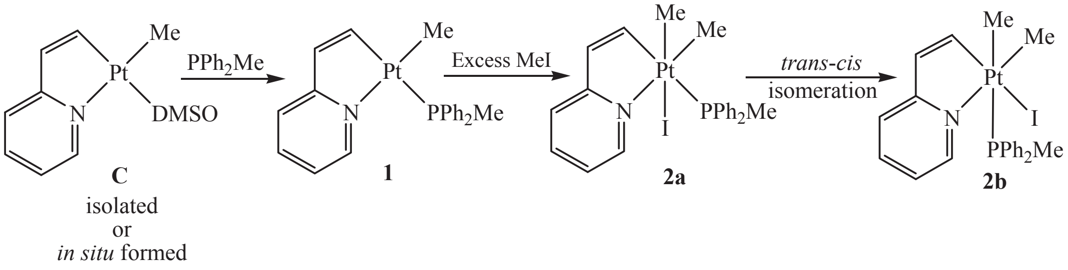
The UV–vis absorption spectrum of **1** shows various bands with different energy positions at room temperature (Fig. 1). The more intense transitions are in range of 230–340 nm with high extinction coefficients ($\varepsilon > 10^4$ M^{-1} cm^{-1}) which can be attributed to spin-allowed π-π^* intraligand transitions (^{1}IL) [64]. According to the previous assignments [35,51], less intense transitions ($\varepsilon > 10^3$ M^{-1} cm^{-1}) at 395 nm and 418 nm are assigned to a mixture of ^{1}IL and/or ^{1}MLCT (metal to ligand charge transfer). These lower energy bands demonstrate a notable solvatochromatic property, shifting to higher energies in acetone solvent (*ca.* 10 nm) as compared with CH$_2$Cl$_2$ (see kinetic study section), indicating that



Scheme 2. Synthetic route for preparation of complex **C**.



Scheme 3. New method for preparation of complex **C**.



Scheme 4. The route for preparation of platinum(IV) complex.

the transitions have a certain degree of charge transfer character [31].

4.2. Emission spectra

Upon photoexcitation, **1** is intensely emissive at 298 K and exhibits similar emission profile in solution and solid state. It displays a structured emission band with a maximum at 550 nm accompanied with the feature of vibronic progression spacing *ca.* 1400 cm^{-1}, which is characteristic of the cyclometalated ligands (Fig. 1) [31]. The structured emission profile and long luminescent lifetimes at room temperature (10.1 μs, in solid state), which are characteristics of triplet states. Furthermore, the intensity of this orange emission diminishes in presence of O_2 molecule (Fig. S5) since oxygen acts as a powerful quencher of the long-lived triplet excited state [65]. Therefore, **1** exhibits a normal phosphorescence and this can be assigned to a typical mixed spin-forbidden ^{3}ILCT/^{3}MLCT excited state. While the temperature is lowered to 77 K, the preliminary orange emission of **1** becomes more intense and it is similar to emission profile which was observed at 298 K (Fig. S6). Also, by cooling the temperature, the luminescence band shifts to the blue (~10 nm). This hypsochromic shift could be assigned to the increased rigidity in the glassy state, which has usually been defined as rigidochromism [66].

5. Oxidative addition reactions and kinetic study

Reaction of electron rich **1** with excess MeI yielded a mixture of *trans* and *cis* platinum(IV) after 2 h, concomitant with a color change to pale yellow (Scheme 4). As it is well established from other reports [37,40–42,46], due to the restriction of 2-vinylpyridine cyclometalated ring and high *trans* influence of methyl groups, only two isomers can be formed and others may be ignored [41]. In this case, *trans* isomer **2a** was formed very fast as a kinetic isomer and progressively it changed to *cis* isomer **2b** (thermodynamic isomer). On the basis of NMR characterization, ^{31}P {^{1}H} showed two resonances as singlet with platinum satellite at $\delta = -22.0$ ($^1J_{PtP} = 1252$ Hz) and -22.9 ($^1J_{PtP} = 1127$ Hz) ppm for **2a** and **2b**, respectively (Fig. S7). In the aliphatic region of ^{1}H spectrum of complex **2**, four PtMe signals appeared as doublet with platinum coupling (Fig. 2 and Fig. S8) and two deshielded doublet resonances with low Pt coupling were assigned to PPh_2Me protons. Integration of these peaks were used to estimate the isomer ratios (*trans*: *cis* = 2:1) (Fig. S8). In *trans* isomer **2a**, signals at 0.50 ($^2J_{PtH} = 70.1$ Hz), 1.17 ($^2J_{PtH} = 69.0$ Hz) for PtMe and 2.39 ppm ($^3J_{PtH} = 11.7$ Hz) for PPh_2Me ligand, whereas in the *cis* isomer **2b**, resonances at 0.92 ($^2J_{PtH} = 59.1$ Hz), 1.56 ($^2J_{PtH} = 69.3$ Hz) for PtMe and 2.19 ppm ($^3J_{PtH} = 11.7$ Hz) for PPh_2Me ligand.

Additionally, kinetics and mechanism studies of oxidative addition of MeI to the cycloplatinated(II) complexes, such as **1**, is known to be very slow [37,40,44,46,67]. Generally, this kinetic investigation is followed by pseudo-first-order conditions and UV–vis absorption spectroscopy is used to measure the rate of reaction. **1** exhibited an intense MLCT band in visible region as responsible for its orange color (see Photophysical properties section). The fade away of this band (MLCT) at $\lambda = 387$ nm (in acetone) by addition of excess MeI ($[MeI]_0 >> [$Pt complex **1**$]$) under pseudo first order kinetic conditions was selected to monitor this reaction (Fig. 3). By fitting of absorbance *versus* time plot (Fig. 3) in the monophasic first order equation (Eq. (1)), in which A_t = absorption at time t, A_0 = initial absorption and A_∞ = infinity absorption, pseudo-first order rate constants (k_{obs}) were calculated.

$$A_t = (A_0 - A_\infty)\exp(-k_{obs}t) + A_\infty. \tag{1}$$

Plots of k_{obs} against MeI concentration was linear with no intercepts (no solvolytic or no sign of any involvement of dissociative pathway) and slope of each line gave the second order rate constant (k_2) (Fig. 4). The same method was used for different temperatures and activation parameters were obtained from the Eyring equation (Fig. S9 and Eq. (2)), in which T = temperature in Kelvin unit, k_B = Boltzmann constant, h = Planck constant, R = universal gas constant, $\Delta S^\#$ = entropy and $\Delta H^\#$ = enthalpy of activation, and the results are collected in Table 1.

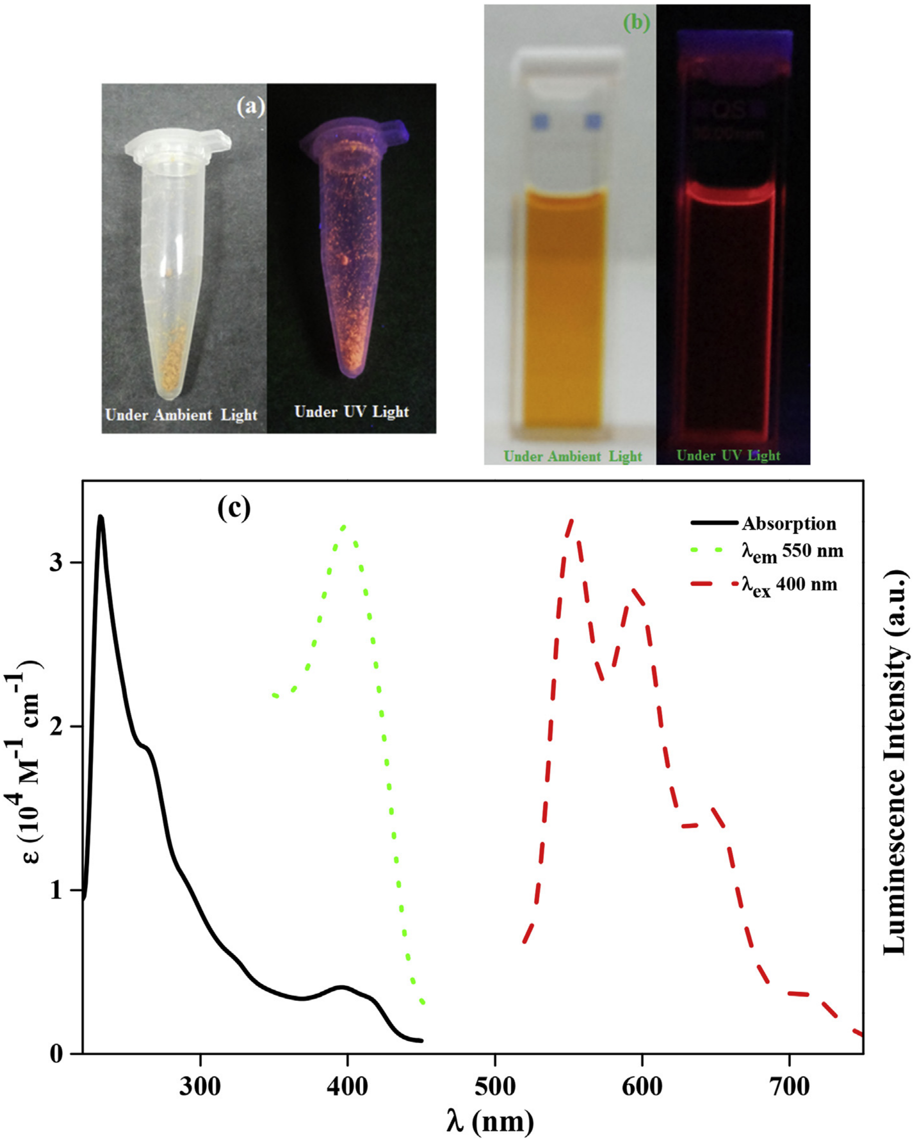


Fig. 1. Photographs showing the luminescence color change under UV light irradiation (365 nm) a) in solid state; b) in CH_2Cl_2 solution; c) Absorption (solid line), excitation (dotted line) and emission (dashed line) spectral of complex **1** in CH_2Cl_2 solution (5×10^{-5} M) at 298 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \qquad (2)$$

This reaction was followed as a simple second order rate law (Eq. (3)), 1st order in both the corresponding **1** and MeI.

$$-d[\text{complex } \mathbf{1}]/dt = k_2[\text{complex } \mathbf{1}][\text{MeI}] \qquad (3)$$

These observations and highly negative $\Delta S^{\#}$ value suggested that a typical of oxidative addition was involved and reaction started with the nucleophilic attack of the cycloplatinated complex **1** at MeI in an S_N2 fashion [37,40,41].

To gain further insight into effect of 2-vinylpyridinate ligand on the rate of oxidative addition reaction, the complex $[PtMe(tpy)(PPh_2Me)]$ [37] (tpy = 2-(*p*-tolyl)pyridinate) was selected. Interestingly, rate constants of reaction between MeI and complex $[PtMe(tpy)(PPh_2Me)]$ is smaller than those of **1** (Table 1). This observation may be due to inductive effect of phenyl group which is incorporating in tpy ligand and it made the tpy to be slightly electronegative (weaker donor) than Vpy. Therefore, it reduces electron density on platinum center and subsequently the rate constants, complying with the larger coupling constant between platinum and phosphorus in tpy complex ($^1J_{PtP}$ = 2042 Hz) [37] than complex **1** ($^1J_{PtP}$ = 1976 Hz).

In order to obtain pure *cis* isomer **2b**, reaction mixture of *trans*-*cis* was stirred for 5 days at room temperature. Interestingly, extending reaction time resulted in formation of monomeric platinum(II) complex *trans*-$[PtMeI(PPh_2Me)_2]$, **3** [53,68], the binuclear platinum(IV) complex $[\{PtMe_2(Vpy)\}_2(\mu\text{-}I)_2]$, **4** [30,69,70], and a free ligand *Z*/*E*-$[C_8H_9N]$, **5** [71,72], 2-propenyl-pyridine (Scheme 5). It is to be noted that **3** and ligand **5** were characterized by comparing their ^1H and/or ^{31}P $\{^1H\}$ NMR spectra with those of the authentic samples used to characterize products (Figs. 5 and 6).

^1H NMR spectrum was invaluable in the structural characterization of the products (Fig. 5). A triplet with satellite as coupling by platinum center and two equivalent phosphorus (δ = −0.02 ppm, $^2J_{PtH}$ = 78.3 Hz and $^3J_{PH}$ = 6.9 Hz) could be attributed to PtMe group

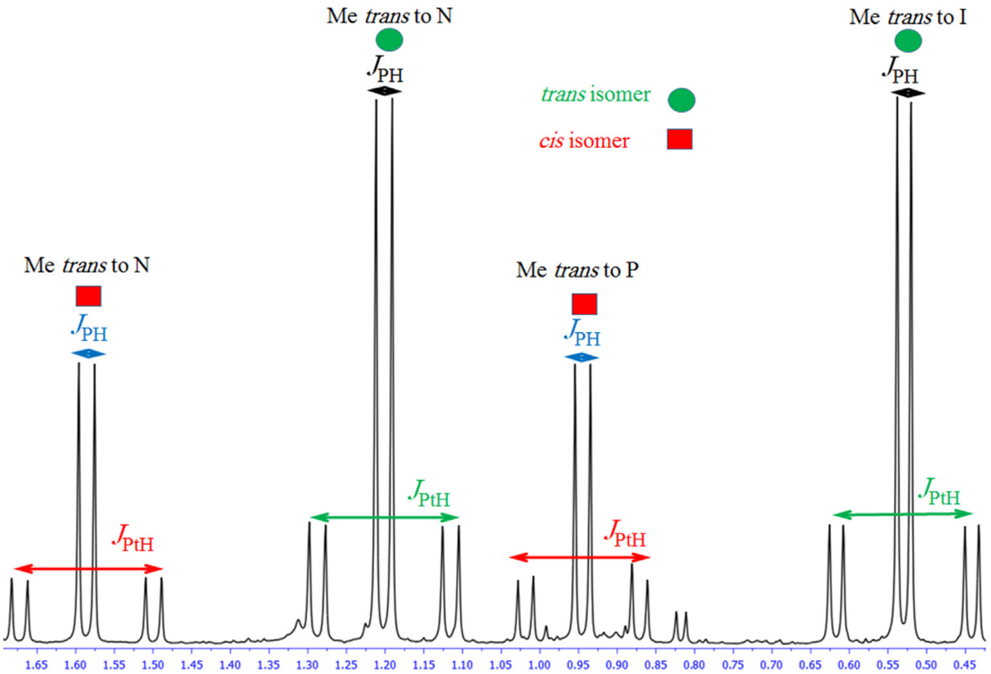


Fig. 2. ^{1}H NMR spectrum of PtMe region in the mixture of *trans* and *cis* isomer of complex **2** in Acetone-d_6.

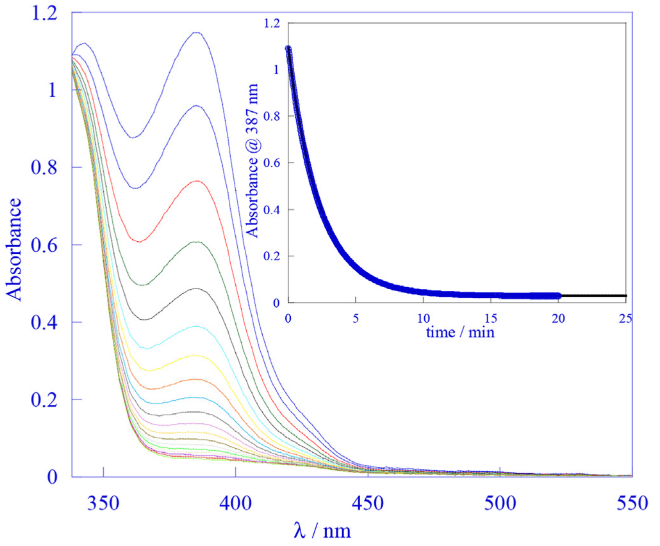


Fig. 3. Changes in the absorbance spectra of complex [PtMe(Vpy)(PPh$_2$Me)], **1**, with an excess of MeI in acetone at T = 20 °C as function of wavelength; successive spectra recorded at intervals of 45 s. Inset is the variation of absorbance at λ = 387 nm over time.

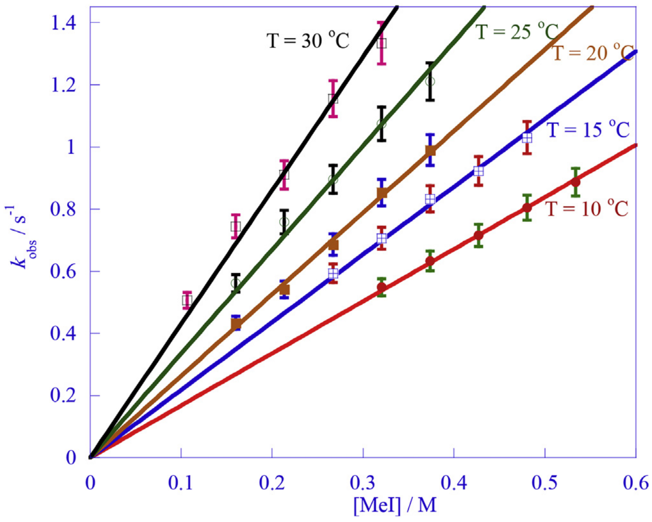


Fig. 4. Plots of first-order rate constants (k_{obs}/s^{-1}) for the reaction of [PtMe(Vpy)(PPh$_2$Me)], **1**, with MeI in acetone at different temperatures *versus* [MeI] (R^2 (R-squared) = 0.99836, 0.99614, 0.99757, 0.99198, 0.9915 for T = 10, 15, 20, 25 and 30 °C, respectively).

in complex **3** [68]. Meanwhile, another triplet resonance at $\delta = 2.51$ with significantly lower value of platinum coupling constant ($^3J_{PtH} = 31.0$ Hz and $^2J_{PH} = 6.6$ Hz), which appeared as a second order AA′XX′ spin system through coupling between H and P atoms, could be assigned to Me group in PPh$_2$Me in **3** [68]. For the methyl groups on the Pt(IV) centers in the complex **4**, two singlet signals with platinum satellite at $\delta = 1.08$ ($^2J_{PtH} = 74.5$ Hz, MePt *trans* to I) and $\delta = 1.91$ ($^2J_{PtH} = 71.7$ Hz, MePt *trans* to N) were observed. Besides, there is a resolved coupling between ^{195}Pt nucleus and H^6 proton of the py ring of 2-vinylpyridinate ligand ($\delta = 9.81$ ppm, $^3J_{HH} = 4.8$ Hz, $^3J_{PtH} = 13.1$ Hz), indicating that Vpy ligand was bonded to the platinum center *via* nitrogen in complex **4**. It is worth mentioning that the formation of the compound **5** proceeded through a C–C bond formation between a Me group and C$^\beta$ of Vpy ligand rather than the coupling reaction between two Me groups for formation of ethane (the signal not observed in NMR spectrum) [73,74]. This was confirmed by presence of two doublet of doublet signals [71], appearing at $\delta = 1.97$ with $J_{HH} = 7.2$, 1.5 Hz (assigned to isomer *Z*) and $\delta = 1.85$ with $J_{HH} = 6.8$, 1.2 Hz (assigned to isomer *E*) and these isomers were in different ratio (*Z*:*E* = 6:1).

In complex **2b**, the “soft” Pt-C$^\beta$ bond of the 2-vinylpyridinate chelate is *trans* to a “soft” iodine ligand which labilize the later bond. Therefore, they exhibit antisymbiotic behavior [75]. Inversely, the PtMe group which is positioned *trans* to the nitrogen

Table 1
Second-order rate constants[a] and activation parameters[b] for reaction of [PtMe(Vpy)(PPh$_2$Me)], **1**, and [PtMe(tpy)(PPh$_2$Me)][c] with MeI in acetone.

Complex	$10^2\ k_2$/L mol^{-1} s^{-1} at different temperatures					$\Delta H^{\#}$/kJ mol^{-1}	$\Delta S^{\#}$/JK^{-1}mol^{-1}
	10 °C	15 °C	20 °C	25 °C	30 °C		
1	2.80	3.63	4.38	5.57	7.16	30.5 ± 0.1	−166 ± 1
[PtMe(tpy)(PPh$_2$Me)]	2.38	3.05	3.82	4.91	6.14	31.4 ± 0.1	−165 ± 1

[a] Estimated errors in k_2 values are ±3%.
[b] Activation parameters were calculated from the temperature dependence of the second-order rate constant in the usual way using Eyring equation (Eq. (2)).
[c] From Ref. [37].

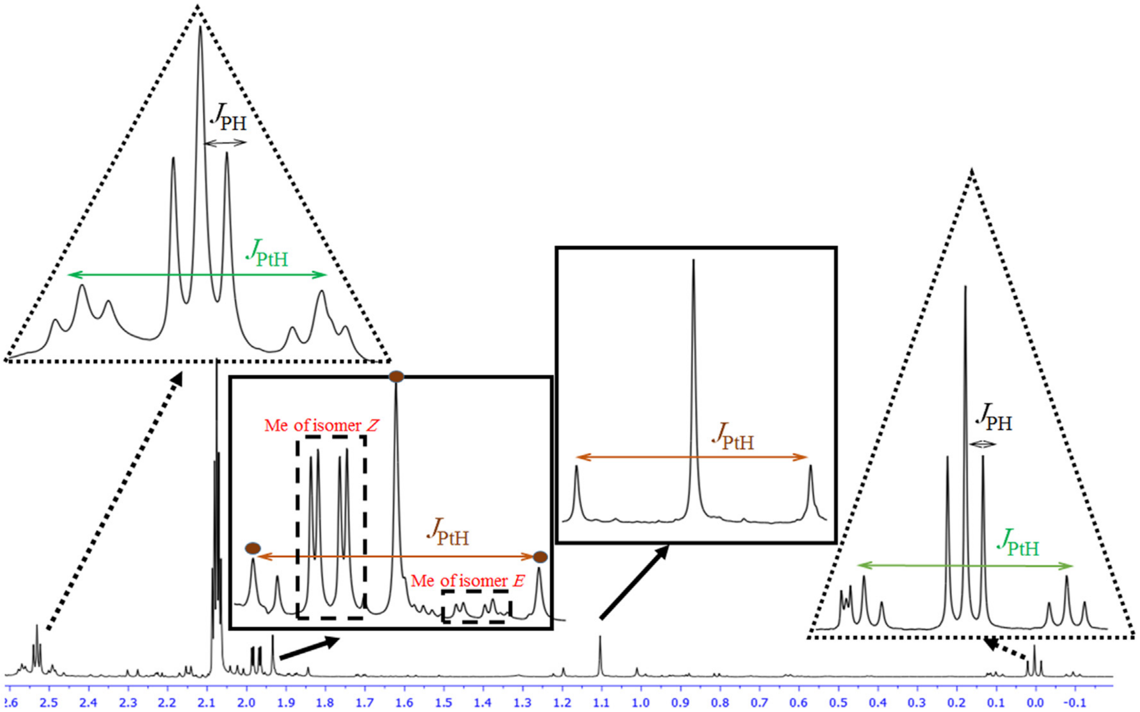


Fig. 5. ^{1}H NMR spectrum of reaction of complex [PtMe(Vpy)(PPh$_2$Me)], **1**, with MeI after 5 days in Acetone-d_6, Aliphatic region. Dotted line (….) signals for complex **3**, Solid line (—) signals for complex **4** and Dashed line (---) signals for compound **5**.

donor of 2-vinylpyridinate ligand (N is considerably harder than iodine ligand) [76] did not exhibit such behavior. This concept suggested that Pt-C$^\beta$ bond is more bowed to be involved in C–C bond coupling reaction rather than the PtMe ligand [43].

The reaction of complex **1** with excess MeI was monitored using ^{31}P {^{1}H} NMR spectroscopy in Acetone-d_6 in an NMR tube at 25 °C (Fig. 6). Immediately after the addition of MeI, singlet resonance for **1** disappeared and two singlet signals with platinum satellite at $\delta = -22.0$ and -22.9 in different ratio were detectable in shielded region which could be assigned to *trans* **2a** and *cis* **2b** isomers, respectively. Over time, signals of *trans* isomer **2a** gradually started to fade away while the signal of *cis* isomer **2b** was growing. As this reaction progressed, the signal with large Pt coupling constant appearing at $\delta = 9.4$ ($^1J_{PtP} = 2950$ Hz) [68] could be assigned to **3**, which is in Pt(II) region, and the resonance of *cis* isomer **2b** disappeared slowly. As aforementioned, after 5 days **3** was merely obtained that is containing the phosphine ligand.

These observations from NMR spectra suggested that we cannot prepare a pure *cis* isomer **2b** and it is converted to a mixture of products (Scheme 5). Therefore, for describing a proper mechanism on this transformation reaction, based on our preliminary studies and similar previous reports like reaction of [PtMe(bpy-H)(L)], in which L = PPh$_3$ [42], PPh$_2$Me [40], PMe$_3$ [48], with MeI yielded in different geometrical Pt(IV) isomer as a stable complex in solution. These would suggest that this reaction completely depended on the nature of cyclometalating and phosphine ligands. In this circumstance for extending the role of cyclometalating ligand, [PtMe(tpy)(PPh$_2$Me)] [37] was selected as a complex with different cyclometalated ligand and its reaction with excess of MeI was followed up by NMR spectroscopy. The kinetically isomer changed very fast to *cis* isomer and thermodynamically isomer was very stable in solution by elapse of time and did not change to any new product(s) (Fig. S10).

Moreover, changes in the absorbance spectra of the reaction mixture was followed up by UV–vis spectroscopy during 5 days. The result showed that when MeI was added to **1**, the absorbance decreased quickly and Pt(IV) was formed, and over time the absorbance did not display any changes and similar plot (like Fig. 3) was obtained. Therefore, we were not able to track formation of new compounds from platinum(IV) complex **2** and study the mechanism, because newly formed products did not exhibit any absorption in visible region [68,71].

Further studies on similar 2-vinylpyridinate complexes with different phosphine ligands like PPh$_3$ and PPhMe$_2$ are currently in progress for the understanding of the role of the phosphine ligand as well as the formed *trans* isomer in this reaction for a better mechanism assumption.

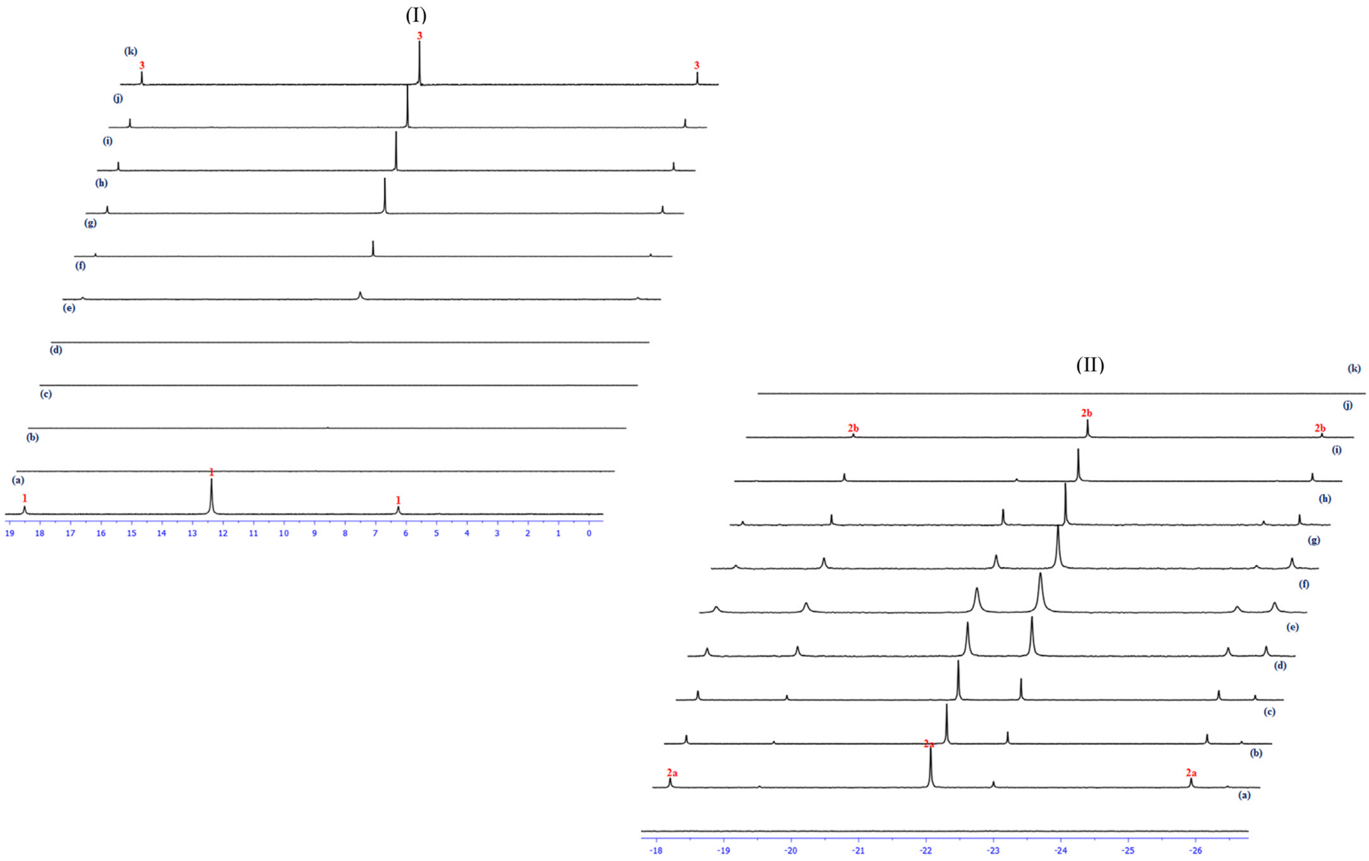
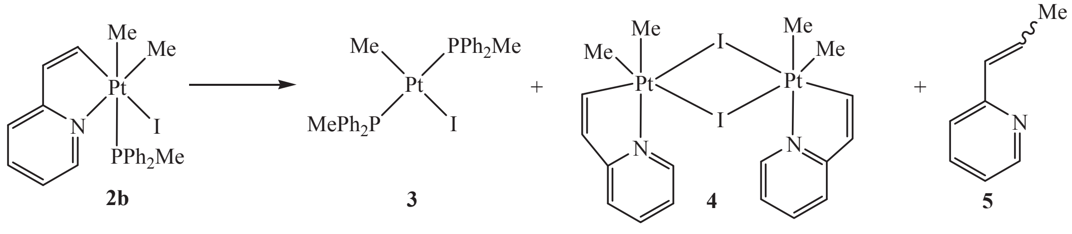


Fig. 6. The reaction of complex [PtMe(Vpy)(PPh$_2$Me)], **1**, with an excess of MeI (30 folds) as monitored by ^{31}P {^{1}H} NMR spectroscopy in Acetone-d_6 at room temperature. (I): Pt(II) region. (II): Pt(IV) region. (a) pure complex **1**, (b) immediately, (c) 30 min (d) 2 h, (e) 6 h, (f) 12 h, (g) 1 day, (h) 2 days, (i) 3 days, (j) 4 days and (k) 5 days after addition of excess MeI. The signal assignments are depicted.



Scheme 5. Transformation of complex **2b** by passing of time.

6. Conclusion

Herein, cycloplatinated(II) complex **C** has been synthesized through dimeric methyl platinum complex **B** in existence of DMSO, when 2-vinylpyridine was used as the cyclometalating ligand. On the other hand, this labile leaving group (DMSO) was allowed to be replaced by a phosphine ligand (PPh$_2$Me) for preparation of novel emissive complex [PtMe(Vpy) (PPh$_2$Me)], **1**. Complex **1** exhibited a low energy absorption band around 400 nm tentatively attributed to transitions having mixed configurations (^{1}LC/^{1}MLCT). Upon photoexcitation at 298 K and 77 K in this wavelength, **1** exhibited an intense orange emission profile with the lifetime being in order of μs. This emission is arising from spin forbidden triplet state with mixing origin (^{3}LC/^{3}MLCT). By reaction of **1** with excess MeI this band disappeared quickly and this was used to readily follow kinetics of formation of corresponding cycloplatinated(IV) complex [PtMe$_2$I(Vpy)(PPh$_2$Me)], **2**. According to our kinetic data, the oxidative addition reaction followed a second order kinetic, first order in each reagent and occurred by a typical S$_N$2 mechanism. The stability of **2** was checked with NMR spectroscopy (up to 5 days) and we found that this complex is converted to a mixture of compounds exhibiting C–C bond coupling. Furthermore, preliminary results indicated that this transformation depends on the cyclometalated ligand and nature of phosphine ligand [77].

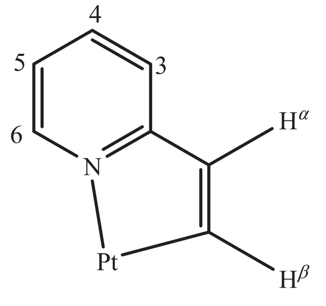
7. Experimental

All NMR spectra (^{1}H and ^{31}P{^{1}H}) were recorded on a Brucker Avance DPX 400 MHz instrument and are referenced to the residual peak of the solvent, *i.e.* CDCl$_3$ or CD$_3$COCD$_3$, the chemical shifts (δ) being reported as ppm and coupling constants (*J*) expressed in Hz. The microanalyses were performed using a vario EL CHNS elemental analyzer. Mass spectra were recorded on an Agilent 7000 triple quad spectrometer. Kinetic studies were carried out by using an Ultrospec 4000 Pro, UV–Vis spectrometer with temperature control using a Pharmacia Biotech constant-temperature bath. Excitation and emission spectra were obtained on Varian Cary Eclips instrument and/or PerkinElmer LS45 fluorescence spectrometer with the lifetimes measured in phosphorimeter mode. 2-vinylpyridine (VpyH) and methyldiphenylphosphine (PPh_2Me) were purchased from Acros and Aldrich, respectively. The starting materials *cis*-[$Pt(Me)_2(DMSO)_2$], **A** [54–56], *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$], **B** [52,53,57], [PtMe(Vpy)(DMSO)], **C** [48,78], [$PtMe(tpy)(PPh_2Me)$] [37] and [$PtMe_2I(tpy)(PPh_2Me)$] [37] were prepared according to known procedures. The NMR labeling for the Vpy ligand for clarifying the chemical shift assignments is shown in Scheme 6. For complex **C**, ^1H NMR data in CD_3COCD_3: δ 0.68 (s, $^2J_{PtH} = 83.4$ Hz, 3H, PtMe), 3.12 (s, $^3J_{PtH} = 17.1$ Hz, 6H, Me of DMSO), 6.92 (d, $^3J_{HH} = 8.8$ Hz, $^3J_{PtH} = 107.6$ Hz, 1H, H^{α} Vpy ligand), 7.17–7.20 (m, 1H, H^5 Vpy ligand), 7.28 (d, $^3J_{HH} = 7.8$ Hz, 1H, H^3 Vpy ligand), 7.43 (d, $^3J_{HH} = 8.8$ Hz, $^2J_{PtH} = 170.2$ Hz, 1H, H^{β} Vpy Ligand), 7.86 (td, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.6$ Hz, 1H, H^4 Vpy ligand), 9.37 (d, $^3J_{HH} = 5.6$ Hz, $^3J_{PtH} = 12.3$ Hz, 1H, H^6 Vpy ligand).

7.1. Synthesis of complexes

7.1.1. [$PtMe(Vpy)(PPh_2Me)$], **1**

7.1.1.1. Method I. To a solution of *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$], **B**, (100 mg, 0.174 mmol) in acetone (15 mL) was added DMSO (55.7 μL, 0.783 mmol, 4.5 equiv.) under an Ar atmosphere and reaction mixture stirred for 1 h. Then, 2-vinylpyridine (41.3 μL, 0.383 mmol, 2.2 equiv.) was added to the solution and refluxed for 18 h, then heating was turned off and the PPh_2Me (77.8 μL, 0.418 mmol, 2.4 equiv.) added. The solution was stirred for 1 h, then concentrated to a small volume (2 mL) and treated with *n*-hexane (5 mL). The formed precipitate was filtered off, washed with *n*-hexane to give the product as an orange solid. The precipitate was dried in vacuum. Yield: 87%, mp = 120 °C (decomp.). Anal. Calcd. For $C_{21}H_{22}NPPt$; C, 49.02; H, 4.31; N, 2.72. Found: C, 49.30; H, 4.02; N, 2.84. Mass data: *m/z* 513.1 $[M]^+$; 499.1 $[M\text{-}Me]^+$. NMR data in CD_3COCD_3: δ (^1H) 0.84 (d, $^3J_{PH} = 8.2$, $^2J_{PtH} = 85.05$ Hz, 3H, PtMe), 2.04 (d, $^2J_{PH} = 7.8$, $^3J_{PtH} = 23.1$ Hz, 3H, Me group of the PPh_2Me ligand, this signal has overlap with CD_3COCD_2H NMR solvent), 6.59 (t, $^3J_{HH} = 7.1$ Hz, 1H, H^5 Vpy ligand), 7.21 (d, $^3J_{HH} = 8.1$ Hz, 1H, H^3 Vpy ligand), 7.25 (dd, $^3J_{HH} = 9.3$ Hz, $^4J_{PH} = 15.1$ Hz, $^3J_{PtH} = 90.1$ Hz, 1H, H^{α} Vpy ligand), 7.46–7.50 (m, overlapping 7H, ArH Vpy and PPh_2Me ligands), 7.67 (dd, $^3J_{HH} = 9.1$ Hz, $^3J_{PH} = 7.7$ Hz, $^2J_{PtH} = 159.5$ Hz, 1H, H^{β} Vpy Ligand), 7.70–7.76 (m, overlapping 5H, ArH Vpy and PPh_2Me ligands); δ (^{31}P) 12.4 (s, $^1J_{PtP} = 1981$ Hz, 1P of PPh_2Me ligand). NMR data in $CDCl_3$: δ (^1H) 0.98 (d, $^3J_{PH} = 8.6$, $^2J_{PtH} = 84.3$ Hz, 3H, PtMe), 2.03 (d, $^2J_{PH} = 7.6$, $^3J_{PtH} = 23.1$ Hz, 3H, Me group of the PPh_2Me ligand), 6.45 (t, $^3J_{HH} = 7.2$ Hz, 1H, H^5 Vpy ligand), 7.10 (d, $^3J_{HH} = 8.0$ Hz, 1H, H^3 Vpy), 7.36 (dd, $^3J_{HH} = 9.4$ Hz, $^4J_{PH} = 14.9$ Hz, $^3J_{PtH} = 90.5$ Hz, 1H, H^{α} Vpy ligand), 7.38–7.46 (m, overlapping 7H, ArH Vpy and PPh_2Me ligands), 7.51 (t, $^3J_{HH} = 8.0$ Hz, 1H, H^4 Vpy ligand), 7.70–7.76 (m, overlapping 4H, ArH Vpy and PPh_2Me ligands), 7.67 (t, $^3J_{HH} = 8.9$ Hz, $^2J_{PtH} = 159.2$ Hz, 1H, H^{β} Vpy Ligand); δ (^{31}P) 13.0 (s, $^1J_{PtP} = 1976$ Hz, 1P of PPh_2Me ligand).



Scheme 6. Representation of Vpy ligand with position labeling.

7.1.1.2. Method II. PPh_2Me (57 μL, 0.306 mmol, 1.2 equiv.) was added to a solution of [PtMe(Vpy) (DMSO)], **C**, (100 mg, 0.255 mmol) in acetone (20 mL) under an Ar atmosphere. The mixture was stirred at room temperature for 1 h. The deep orange solution was evaporated and concentrated to a small volume (2 mL), and *n*-haxene was added (5 mL) to give an orange solid identified as **1**. The solid was dried in vacuum.

7.1.2. [$PtMe_2I(Vpy)(PPh_2Me)$], **2**

At room temperature, to a solution of [$PtMe(Vpy)(PPh_2Me)$], **1**, (60 mg, 0.117 mmol) in acetone (10 mL) was added 220 μL (excess, 30 folds) of MeI. The solution was stirred for 2 h at room temperature, then diethyl ether was added to give a precipitate which was filtered, washed with diethyl ether to give the product as a pale yellow solid identified as **2** (*cis* and *trans* mixture). The product was dried in vacuum. Yield: 73%, mp = 110 °C. Anal. Calcd. For $C_{22}H_{25}INPPt$; C, 40.26; H, 3.84; N, 2.13. Found: C, 40.09; H, 3.69; N, 2.20. Mass data: *m/z* 657.1 $[M]^+$; 530.3 $[M\text{–}I]^+$. NMR data in CD_3COCD_3: (*trans* isomer, **2a**) δ (^1H) 0.50 (d, $^3J_{PH} = 7.2$, $^2J_{PtH} = 70.1$ Hz, 3H, Me ligand *trans* to I, PtMe), 1.17 (d, $^3J_{PH} = 8.4$, $^2J_{PtH} = 69.0$ Hz, 3H, Me ligand *trans* to N, PtMe), 2.39 (d, $^2J_{PH} = 8.7$, $^3J_{PtH} = 11.7$ Hz, 3H, Me group of the PPh_2Me ligand), 8.35 (d, $^3J_{HH} = 5.0$ Hz, $^3J_{PtH} = 14.5$ Hz, 1H, H^6 Vpy ligand), 6.65–8.10 (overlapping multiplets, ArH Vpy and PPh_2Me ligands for both *trans* and *cis* isomer); δ (^{31}P) −22.0 (s, $^1J_{PtP} = 1252$ Hz, 1P of PPh_2Me ligand). (*cis* isomer, **2b**) δ (^1H) 0.92 (d, $^3J_{PH} = 7.9$, $^2J_{PtH} = 59.1$ Hz, 3H, Me ligand *trans* to P, PtMe), 1.56 (d, $^3J_{PH} = 8.2$, $^2J_{PtH} = 69.3$ Hz, 3H, Me ligand *trans* to N, PtMe), 2.19 (d, $^2J_{PH} = 9.0$, $^3J_{PtH} = 11.7$ Hz, 3H, Me group of the PPh_2Me ligand), 9.04 (d, $^3J_{HH} = 5.1$ Hz, $^3J_{PtH} = 14.9$ Hz, 1H, H^6 Vpy ligand), 6.65–8.10 (overlapping multiplets, ArH Vpy and PPh_2Me ligands for both *trans* and *cis* isomer); δ (^{31}P) −22.9 (s, $^1J_{PtP} = 1127$ Hz, 1P of PPh_2Me ligand).

If stirring was prolonged for 5 days at room temperature and then solvent was removed, and the resulting residue was dried to form a yellowish solid as a mixture of **3**, **4** and **5** in 2:1:2 ratios (Scheme 5). Selected NMR result for this mixture in CD_3COCD_3: (Complex **3**) δ (^1H) −0.02 (t, $^3J_{PH} = 6.9$ Hz, $^2J_{PtH} = 78.3$ Hz, 3H, PtMe), 2.51 (t, $^2J_{PH} = 6.6$ Hz, $^3J_{PtH} = 31.0$ Hz, 6H, Me group of the PPh_2Me ligands); δ (^{31}P) 9.4 (s, $^1J_{PtP} = 2950$ Hz, 2P of PPh_2Me ligands). (Complex **4**) δ (^1H) 1.08 (s, $^2J_{PtH} = 74.5$ Hz, 6H, Me *trans* to I, PtMe), 1.91 (s, $^2J_{PtH} = 71.7$ Hz, 6H, Me *trans* to N, PtMe), 9.81 (d, $^3J_{HH} = 4.8$ Hz, $^3J_{PtH} = 13.1$ Hz, 2H, H^6 Vpy ligands). (Compound **5**) δ (^1H) 1.85 (dd, $J_{HH} = 6.8$, 1.2 Hz, 3H, (% 15), Me (isomer *E*)), 1.97 (dd, $J_{HH} = 7.2$, 1.5 Hz, 3H, (% 85), Me (isomer *Z*)), 9.05 (d, $^3J_{HH} = 4.6$ Hz, 1H (15%), pyridine H^6 (*E*)), 9.22 (d, $^3J_{HH} = 4.6$ Hz, 1H (85%), pyridine H^6 (*E*)).

7.2. Kinetic study

A solution of complex [$PtMe(Vpy)(PPh_2Me)$], **1**, in acetone (3 mL, 5×10^{-4} M) in a cuvette was thermostated at 20 °C and a known excess of MeI (15 μL, 160 folds) was added using a microsyringe. After rapid stirring, the absorbance at $\lambda = 387$ nm was collected with time. The absorbance-time curves were analyzed by pseudo first order method (Eq. (1)). The same method was used at other temperatures (10, 15, 25, and 30 °C) and activation parameters ($\Delta S^{\#}$ and $\Delta H^{\#}$) were obtained from the Eyring equation [79] (Eq. (2)) and the full data are collected in Table 1.

7.2.1. Reaction of [PtMe(Vpy)(PPh$_2$Me)], 1, with MeI

This reaction was monitored by ^{31}P NMR spectroscopy at room temperature in an NMR tube. To a solution of [PtMe(Vpy)(PPh$_2$Me)], **1**, (10 mg) in CD$_3$COCD$_3$ (0.5 mL), an excess of MeI (30 μL, 30 folds) was added. The NMR spectra were recorded several times at during about 120 h until the mixture was converted to *trans*-[PtMeI(PPh$_2$Me)$_2$], **3**, in solution.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.12.005.

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