Phenylpyrazolate cycloplatinated(II) complexes: kinetics of oxidation to Pt(IV) complexes

Asma Nahaei,^a Asma Rasekh,^a Mehdi Rashidi,^{a} Fatemeh Niroomand Hosseini^b
and S. Masoud Nabavizadeh^{a*}*

^aDepartment of Chemistry, College of Sciences, Shiraz University, Shiraz 71467-13565, Iran,

^bDepartment of Chemistry, Shiraz Branch, Islamic Azad University, Shiraz, 71993–37635,
Iran

* Corresponding authors. Tel.: +98 713 613 7110; fax: +98 713 646 0788. E-mail addresses:
rashidi@chem.susc.ac.ir (M. R), nabavi@chem.susc.ac.ir (S.M.N.)

Abstract

The cycloplatinated(II) complex $[\text{PtMe}(\text{phpz})(\text{DMSO})]$, **1**, in which DMSO is dimethylsulphoxide and phpz is 1-phenylpyrazolate was synthesized by reaction of phpzH (1-phenylpyrazole) with the known complex $[\text{PtMe}_2(\text{DMSO})_2]$. The C^N cycloplatinated(II) complexes $[\text{PtMe}(\text{phpz})(\text{L})]$, **2**, where $\text{L} = \text{PPh}_3$ (**2a**), PPh_2Me (**2b**) and P(OPh)_3 (**2c**), were synthesized by reaction of the complex **1** with the appropriate P donor ligands L. Reaction of the Pt(II) complexes **2** with MeI gave the cycloplatinated(IV) complexes $[\text{PtMe}_2\text{I}(\text{C}^{\wedge}\text{N})(\text{L})]$, where $\text{L} = \text{PPh}_3$ (**3a**), PPh_2Me (**3b**) and P(OPh)_3 (**3c**). All the complexes were fully characterized using NMR spectroscopy and the Pt(II) complex **2a** and the Pt(IV) complex **3a**, both containing PPh_3 ligand, were further determined by X-ray crystallography. The cycloplatinated(II) complexes **2** have a metal-to-ligand charge-transfer band, which was used to easily follow the kinetics of their reactions with MeI. Rates of the reactions at different temperatures were measured and the large negative $\Delta S^\ddagger$ values were found in each reaction. The data were consistent with an associative $\text{S}_{\text{N}}2$ mechanism. The reactivity of Pt(II) complexes **2** towards oxidative addition was also theoretically investigated using DFT calculations, which were in agreement with experimental findings.

Keywords: Cyclometalated complexes; Platinum; Kinetic; Mechanism; Oxidative addition; DFT calculation

1. Introduction

Organoplatinum(II) complexes of formula $[\text{PtMe}_2(\text{D})_2]$, in which D is a weakly bound donor ligand such as SMe_2 or dimethylsulfoxide, are important reagents in studies of C-H bond activation [1, 2] and their cycloplatinated(II) derivatives $[\text{PtMe}(\text{D})(\text{C}^{\wedge}\text{N})]$ and $[\text{PtMe}(\text{C}^{\wedge}\text{N})(\text{L})]$, where $\text{C}^{\wedge}\text{N}$ is a chelating carbon-nitrogen donor ligand such as 2-

phenylpyridinate or benzo[h]quinolate and L is a phosphorous donor ligand, are among the most reactive substrates for oxidative addition reactions [3-8]. In oxidative addition reaction, there are significant differences in reactivity between different C^N containing complexes in which C^N is a 5-membered chelate ring [3]. The complexes [PtMe(C^N)(L)] react with alkyl halides (RX) to give platinum(IV) complexes, such as [PtMe₂I(C^N)(L)] (where RX = MeI), by oxidative addition and these reactions have been used to prepare a wide range of organoplatinum(IV) complexes,[3, 4, 9] as well as in fundamental studies of reactivity and mechanism in oxidative addition reactions [10]. Most of the abovementioned studies have used 2-phenylpyridinate as component of the chelate ligand, C^N. When 1-phenylpyrazole is used as cyclometalation reagent (HC^N), the platinum(II) complexes [Pt(C^N)(N^{CH})Cl][11], [Pt(C^N)₂][12] and [Pt(C^N)(acac)][13] (acac = acetylacetonato) are reported to yield; note that no such complexes containing a P-donor ligand have so far been reported. These and similar cyclometalated complexes have since been used in photophysical studies [14, 15]. Herein, we report the first series of complexes of type [PtMe(C^N)(L)], where C^N = 1-phenylpyrazolate and L = PPh₃, PPh₂Me and P(OPh)₃, and study their reactivities towards oxidative addition reactions with MeI.

2. Experimental section

2.1. General remarks

The ¹H and ³¹P NMR spectra were recorded on a Bruker Avance DRX 250 or 400 MHz spectrometer in CDCl₃ as solvent. The operating frequencies and references, respectively, are shown in parentheses as follows: ¹H (250 or 400 MHz, TMS) and ³¹P (162 MHz, 85% H₃PO₄). The chemical shifts and coupling constants are in 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. The precursor compound $[\text{PtMe}_2(\text{DMSO})_2]$ [16] was prepared according to reported procedure.

2.2. Synthesis of the complexes

$[\text{PtMe}(\text{phpz})(\text{DMSO})]$, **1**

1-Phenylpyrazole (71.5 μL , 5.2 mmol) was added dropwise *via* syringe to a solution of $[\text{PtMe}_2(\text{DMSO})_2]$ (200 mg, 0.52 mmol) in acetone (50 mL) at room temperature. The reaction mixture was refluxed at 70 $^{\circ}\text{C}$, during which a pale-gray precipitate began to form. After 6 h, the mixture was cooled to room temperature and the solvent was evaporated to give the product as a pale-gray solid which was washed with diethyl ether and n-hexane and dried under vacuum. Yield: 200 mg, 87%. mp.=130 $^{\circ}\text{C}$ (decomp.). Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{OPtS}$; C, 33.4; H, 3.7; N, 6.5; S, 7.4. Found: C, 33.4; H, 3.4; N, 6.8; S, 7.8. ^1H NMR in CDCl_3 : δ 0.70 (s, $^2J_{\text{PtH}} = 83.8$ Hz, 3H, PtMe), 3.20 ($^3J_{\text{PtH}} = 18.8$ Hz, 6H, Me of DMSO), 6.50-8.31 [overlapping multiplets, other aromatic protons].

$[\text{PtMe}(\text{phpz})(\text{PPh}_3)]$, **2a**

PPh_3 (78 mg, 0.30 mmol) was added to a solution of $[\text{PtMe}(\text{phpz})(\text{DMSO})]$ (126 mg, 0.29 mmol) in acetone (25 mL) and a white precipitate rapidly appeared. The mixture was stirred at room temperature for 2h. After removal of the solvent, the solid was washed with n-hexane to give the product as a white solid. Yield: 161 mg, 90%. Mp = 228 $^{\circ}\text{C}$ (decomp.). Anal. Calcd for $\text{C}_{28}\text{H}_{25}\text{N}_2\text{PPt}$: C, 54.6; H, 4.1; N, 4.6; Found: C, 54.4; H, 3.9; N, 4.7. NMR data in CDCl_3 : δ (^1H) = 0.79 (d, $^3J_{\text{PtH}} = 7.7$ Hz, $^2J_{\text{PtH}} = 85.1$ Hz, 3H, MePt), 6.14 (br. d, $^3J_{\text{HH}} \approx 11.2$ Hz, $^3J_{\text{PtH}} =$ not measured, CH group adjacent to the coordinated C atom), other parts of aromatic region: 7.11 – 8.09 ppm (6H, H of ppz ligand); δ (^{31}P) = 27.8 (s, $^1J_{\text{PtP}} = 2309$ Hz, 1P of PPh_3).

The following complexes were made similarly using the appropriate phosphine ligand:

[PtMe(phpz)(PPh₂Me)], 2b; Yield: 92%. Mp = 187 °C (decomp.). Anal. Calcd for C₂₃H₂₃N₂Pt; C, 49.90; H, 4.15; N, 5.06. Found: C, 49.82; H, 3.84; N, 5.15. NMR data in CDCl₃: δ (¹H) 0.73 (d, ³J_{PH} = 7.5 Hz, ²J_{PtH} = 85.6 Hz, 3H, MePt), 1.97 (d, ²J_{PH} = 8.0 Hz, ³J_{PtH} = 26.7 Hz, 3H, Me of PPh₂Me). Regions between 5.70-8.15 ppm assigned as aromatic protons of phpz and Ph groups; δ (³¹P) = 10.3 (s, ¹J_{PtP} = 2242 Hz, 1P of PPh₂Me).

[PtMe(phpz)(P(OPh)₃)], 2c; Yield: 43%. Mp = 134 °C. Anal. Calcd for C₂₈H₂₅N₂PtO₃: C, 41.84; H, 4.60; N, 4.96; Found: C, 41.65; H, 4.50; N, 4.54. NMR data in CDCl₃: δ (¹H) = 0.74 (d, ³J_{PH} = 7.2 Hz, ²J_{PtH} = 86.0 Hz, 3H, MePt), aromatic protons: 6.43-8.06; δ (³¹P) = 113.5 (s, ¹J_{PtP} = 3985 Hz, 1P, P of P(OPh)₃).

[PtMe₂I(phpz)(PPh₃)], 3a

An excess of MeI (22 μ L) was added to a solution of complex [PtMe(phpz-H)(PPh₃)], **2a**, (20 mg, 0.03 mmol) in 20 mL of dichloromethane at room temperature. The mixture was stirred for 24 h, and then the solvent was removed. The residue was treated with diethyl ether to form the product as a white precipitate which was dried under vacuum. Yield: 18 mg, 73%. Mp = 172 °C (decomp.). Anal. Calcd for C₂₉H₂₈N₂IPt: C, 46.0; H, 3.7; N, 3.7; Found: C, 46.0; H, 3.5; N, 4.5. NMR data in CDCl₃: δ (¹H) 1.19 (d, ³J_{PH} = 7.5 Hz, ²J_{PtH} = 60.3 Hz, 3H, PtMe *trans* to P), 1.57 (d, ³J_{PH} = 7.8 Hz, ²J_{PtH} = 73.0 Hz, 3H, PtMe *trans* to N), δ aromatic protons: 6.27-8.28; δ (³¹P) = -9.8 (s, ¹J_{PtP} = 952 Hz, 1P of PPh₃).

The complex **[PtMe₂I(phpz)(PPh₂Me)], 3b** was made similarly using the Pt(II) complex **2b**; Yield: 88%. Mp = 150 °C (decomp.). Calcd for C₂₄H₂₆N₂IPt; C, 41.50; H, 3.74. N, 4.03. Found: C, 41.39; H, 4.01, N, 4.22. NMR data in CDCl₃: major isomer, δ (¹H) = 1.43 (d, ³J_{PH} = 7.7 Hz, ²J_{PtH} = 70.7 Hz, 3H, Me *trans* to N), 0.57 (d, ³J_{PH} = 7.7 Hz, ²J_{PtH} = 69.0 Hz, 3H, Me *trans* to P). 2.45 (d, ²J_{PH} = 9.7 Hz, ³J_{PtH} = 13.2 Hz, 3H, Me of PPh₂Me), 6.28-8.17 ppm assigned as aromatic protons of Ph and phpz groups; δ (³¹P) = -21.6 (s, ¹J_{PtP} = 1433 Hz, 1P, P of PPh₂Me. Minor isomer, in which I ligand is *trans* to Me: 1.06 (d, ³J_{PH} = 7.8 Hz, ²J_{PtH} =

59.5 Hz, 3H, Me *trans* to I), 1.46 (d, $^3J_{\text{PH}} = 8.0$ Hz, $^2J_{\text{PtH}} = 72.5$ Hz, 3H, Me *trans* to N), 1.90 (d, $^2J_{\text{PH}} = 8.4$ Hz, $^3J_{\text{PtH}} = 10.3$ Hz, 3H, Me of PPh₂Me), 6.28-8.17 ppm assigned as aromatic protons of Ph and phpz groups. $\delta(^{31}\text{P}) = -25.0$ (s, $^1J_{\text{PtP}} = 1035$ Hz, 1P, P of PPh₂Me).

[PtMe₂I(phpz)(P(OPh)₃)], **3b**.

An excess of MeI (30 μL) was added to a solution of complex [PtMe(phpz)(P(OPh)₃)], **2c**, (10mg, 0.015 mmol) in 20 mL of acetone at room temperature. The mixture was allowed to stir at this condition for 5d, and then the solvent was removed by evaporation. The residue was treated with diethyl ether to form a white precipitate, and the product was dried under vacuum. Yield: 83%, m.p. = 132 °C. Anal. Calcd for C₂₉H₂₈N₂PPtO₃: C, 43.28; H, 3.48; N, 3.48; Found: C, 42.80; H, 3.43; N, 3.25. NMR data in CDCl₃: $\delta(^1\text{H}) = 1.17$ (d, $^3J_{\text{PH}} = 12.4$ Hz, $^2J_{\text{PtH}} = 58.7$ Hz, 3H, PtMe *trans* to P), 1.85 (d, $^3J_{\text{PH}} = 10.5$ Hz, $^2J_{\text{PtH}} = 71.3$ Hz, 3H, PtMe *trans* to N); $\delta(^{31}\text{P}) = 73.0$ (s, $^1J_{\text{PtP}} = 1837$ Hz, P of P(OPh)₃).

2.3. Kinetic Measurements

The kinetic rate constants were determined using UV-visible spectroscopy by monitoring the change in absorbance. A linear relationship between absorbance, *Abs*, and concentration, *C*, confirmed the validity of the Beer-Lambert law ($Abs = \epsilon bC$ with b = path length = 1 cm) for the complexes **2a-2b** at experimental wavelengths. All kinetic measurements were monitored under pseudo first-order conditions with MeI concentrations 100-5000 times the concentration of the Pt(II) complexes. At least five different concentrations within this range were used. The concentration of Pt(II) complexes were 3×10^{-4} M. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the reaction in chloroform were obtained from kinetic experiments performed at five temperatures between 15 and 40 °C. The stability of Pt(II) complexes **2a-2b** were tested in chloroform by means of overlay UV-vis spectra for at least 10 h. ^1H NMR spectra of the complexes **2a-2b** after 24 h in solution of CDCl₃ confirmed also stability of

platinum complexes. Pseudo first-order rate constants, k_{obs} , were calculated by fitting of the kinetic data to the first-order equation $Abs_t = Abs_{\infty} + (Abs_{\infty} - Abs_0) \exp(-k_{\text{obs}}t)$. The experimentally determined pseudo first-order rate constants were converted to second-order rate constants, k_2 , by determining the slope of the linear plots of k_{obs} against the concentration of the MeI at corresponding temperature according to equation $k_{\text{obs}} = k_2 [\text{MeI}]$. The activation parameters were determined from the Eyring equation $\ln(k_2/T) = \ln(k_B/h) - \Delta H^\ddagger/RT + \Delta S^\ddagger/R$ with $\Delta H^\ddagger$ = activation enthalpy, $\Delta S^\ddagger$ = activation entropy, k_2 = rate constant, k_B = Boltzmann's constant, T = temperature, h = Planck's constant, and R = gas constant.

2.3. Crystallography

Single crystals of the complexes $[\text{PtMe}(\text{phpz})(\text{PPh}_3)]$, **2a**, and $[\text{PtMe}_2\text{I}(\text{phpz})(\text{PPh}_3)]$, **3a**, were grown from a concentrated CH_2Cl_2 solution by slow diffusion of *n*-pentane. Single crystal X-ray data for the complexes are collected at 298(2) K on STOE IPDS 2T diffractometer (Mo $K\alpha$ = 0.71073 Å). The cell parameters were retrieved using X-AREA [17] software and refined using X-AREA on all observed reflections. Absorption corrections were applied using MULABS [18, 19]. All the structures were solved by direct methods and refined by full-matrix least squares on F^2 for all data using SHELXTL software [20]. Crystal data, data collection, and structure refinement details are listed in Table 1. CCDC- 1411043 and 1411044 contain the supplementary crystallographic data for these compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data, data collection and structure refinement details for the complexes [PtMe(phpz)(PPh₃)], **2a**, and [PtMe₂I(phpz)(PPh₃)], **3a**.

	2a	3a
Formula	C ₂₈ H ₂₅ N ₂ PPt	C ₂₉ H ₂₈ IN ₂ PPt
Formula weight	615.56	757.49
Temperature/K	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
<i>a</i> /Å	9.6620(19)	18.476(4)
<i>b</i> /Å	10.994(2)	9.2608(19)
<i>c</i> /Å	22.766(5)	17.192(3)
α (°)	90	90
β (°)	100.14(3)	113.12(3)
γ (°)	90	90
vol/Å ³	2380.6(8)	2705.3(11)
<i>Z</i>	4	4
<i>D</i> (calc)/Mg m ⁻³	1.717	1.860
μ /mm ⁻¹	5.979	6.407
<i>F</i> (000)	1200	1448
No. of independent reflns	12321	12928
<i>R</i> _{int}	0.0231	0.0642
GooF (<i>F</i> ²)	0.936	0.840
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> >2σ(<i>I</i>)]	0.0199, 0.0396	0.0308, 0.0654
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0327, 0.0410	0.0498, 0.0687

2.4. Computational details

Gaussian 03[21] was used to fully optimize all the structures at the B3LYP level of density functional theory. The solvation energies were calculated by CPCM model in CHCl_3 . The effective core potential of Hay and Wadt with a double- ξ valence basis set (LANL2DZ) was chosen to describe Pt and I [22, 23]. The 6-31G(d) basis set was used for other atoms. Frequency calculations were carried out at the same level of theory to identify whether the calculated stationary point is a minimum (zero imaginary frequency) or a transition structure (one imaginary frequency).

3. Results and discussion

3.1. Synthesis and characterization of the platinum complexes

Preparative routes to the cyclometalated complexes are described in Scheme 1. The Pt(II) complex $[\text{PtMe}(\text{phpz})(\text{DMSO})]$, **1**, was prepared by reaction of 1-phenylpyrazole (= phpzH) with $[\text{PtMe}_2(\text{DMSO})_2]$ and was readily characterized from its ^1H NMR spectrum. The complex **1** gave a single methyl platinum resonance at $\delta = 0.69$, with coupling constant $^2J_{\text{PtH}} = 82.5$ Hz. A singlet signal at $\delta = 3.20$ with platinum satellites with $^3J_{\text{PtH}} = 17.5$ Hz was attributed to protons of terminal DMSO ligand, while the phenylpyrazole protons appeared in the range of $\delta = 6.49$ -8.29 ppm. Substitution reactions of the complex **1** with either of the phosphine ligands $\text{L} = \text{PPh}_3$, PPh_2Me or P(OPh)_3 , in a 1:1 molar ratio, gave the corresponding cyclometalated organoplatinum(II) complexes $[\text{PtMe}(\text{phpz})(\text{L})]$, **2**, which were isolated as stable solids and characterized by their ^1H and ^{31}P NMR spectra; the complex **2a** was further characterized by X-ray crystallography.

Scheme 1. Routes to preparation of the Pt complexes

Typically, the ^1H NMR spectrum of $[\text{PtMe}(\text{phpz})(\text{PPh}_3)]$, **2a**, (Figure 1) contains a Pt-Me resonance at $\delta = 0.79$ as a doublet due to coupling to phosphorus (with $^3J_{\text{PH}} = 7.5$ Hz) which is further coupled to ^{195}Pt (with $^2J_{\text{PtH}} = 85.0$ Hz); magnitudes of the coupling constant $^2J_{\text{PtH}}$ complies with the complex having a square-planar Pt(II) center with the methyl group being located *trans* to nitrogen [24]. Proton of C-H group of the coordinated phpz ligand is observed at $\delta = 6.13$ as a doublet signal (with $^3J_{\text{HH}} = 12.5$ Hz). In the ^{31}P NMR spectrum of **2a**, as expected, a singlet at $\delta = 27.8$ having ^{195}Pt satellites with $^1J_{\text{PtP}} = 2334$ Hz was observed. Notice that $^1J_{\text{PtP}}$ values for the other types of 5-membered C^N chelate rings analogous, e.g. the phenylpyridinate (ppy) complex $[\text{PtMe}(\text{ppy})(\text{PPh}_3)]$ [3] and the 2,2'-bipyridine rollover cycloplatinated complex $[\text{PtMe}(\text{bpy-H})(\text{PPh}_3)]$ [6] ($\text{bpy-H} = \kappa^2\text{N},\text{C-2,2'-bipyridine}$), being reported elsewhere, are 2105 Hz and 2229 Hz, respectively; the values are significantly lower

than that mentioned above for the phpz complex **2a** (2334 Hz), presenting a series of “*trans* influence of the metalated C atom” for these analogous complexes as ppy > bpy-H > phpz.

Figure 1. ^1H (Me region, A and B) and ^{31}P (C and D) NMR spectra of complexes **2a** (A and C) and **3a** (B and D). Peaks labeled ■ in the ^1H NMR spectra are due to water of CDCl_3 solvent.

Crystal structure of the complex $[\text{PtMe}(\text{phpz})(\text{PPh}_3)]$, **2a**, has been determined by X-ray diffraction (see Figure 2). Selected bond lengths and angles are also given. The complex **2a**, has square planar stereochemistry at platinum center. The two C atoms are *cis* in the square-planar structure, as expected, [24, 25] and the largest deviation from ideal geometry is the angle $\text{C}(2)\text{-Pt}(1)\text{-N}(1) = 78.83(10)^\circ$, which is associated with the $\text{Pt}(\text{phpz})$ chelate ring. The structure of **2a** is slightly distorted due to the presence of the bulky PPh_3 in the coordination plane and this is reflected by the angle N1-Pt-CH_3 , $170.96(11)^\circ$.

Figure 2. ORTEP view of structure of the complex [PtMe(phpz)(PPh₃)], **2a**. Selected bond lengths (Å) and angles (°): Pt(1)-C(2) 2.049(3); Pt(1)-C(1) 2.055(3); Pt(1)-N(1) 2.107(2); Pt(1)-P(1) 2.2860(8); C(2)-Pt(1)-C(1) 92.33(12); C(2)-Pt(1)-N(1) 78.83(10); C(1)-Pt(1)-N(1) 170.96(11); C(2)-Pt(1)-P(1) 174.51(8); C(1)-Pt(1)-P(1) 92.60(10); N(1)-Pt(1)-P(1) 96.16(6).

Bond distances (in Å) for the complex [PtMe(phpz)(PPh₃)], **2a** (Figure 2), with a five-membered pyrazole ring [Pt-C(2) = 2.049(3), Pt-C(1) = 2.055(3), Pt-N(1) = 2.107(2), Pt-P(1) = 2.2860(8)] are generally in fair agreement with those reported for the similar complex [PtMe(bpy-H)(PPh₃)][26] with a six-membered pyridine ring [Pt-C2 = 2.043(3), Pt-C1 = 2.077(4), Pt-N1 = 2.130(2), Pt-P(1) = 2.2904(7)]; Pt-CH₃ distance in the complex **2a**, Pt-C(1) = 2.055(3), is considerably smaller than that in [PtMe(bpy-H)(PPh₃)], Pt-C(1) = 2.077(4). The latter is consistent with the corresponding *trans* N atom of five-membered pyrazole ring in complex **2a** having a stronger sigma donor ability (higher *trans* influence), with Pt-N1 = 2.107(2) Å, than that of the *trans* N atom of six-membered pyridine of bpy-H ring in [PtMe(bpy-H)(PPh₃)], with a longer Pt-N1 distance of 2.130(2) Å. This has been reflected consistently in ²J_{PtH} values in the ¹H NMR spectra of the complexes, **2a** being 85.0 Hz which is higher than that for [PtMe(bpy-H)(PPh₃)] being 83.0 Hz.

Oxidative addition reactions at room temperature of the electron-rich cyclometalated Pt(II) complexes **2a-2c** with MeI gave high yields of the corresponding Pt(IV) complexes [PtMe₂I(phpz)(L)], L = PPh₃, **3a**; L = PPh₂Me, **3b**; L = P(OPh)₃, **3c** (see Scheme 1), which were characterized using elemental analysis and NMR spectroscopy; the complex **3a** was further characterized by X-ray structural determination.

The ³¹P NMR spectrum of **3a** shows Pt-P coupling constant value (¹J_{PtP} = 951 Hz) in agreement with a Pt(IV) species [27, 28], which as expected is much lower than the corresponding value of 2334 Hz found for the starting cyclometalated Pt(II) complex [PtMe(phpz)(PPh₃)], **2a** (see Figure 1). The ¹H NMR spectrum of complex **3a** shows two different platinum-bonded methyl groups as doublets with satellites due to coupling to ¹⁹⁵Pt and ³¹P nuclei (δ = 1.20 ppm, ³J_{PH} = 7.5 Hz, ²J_{PtH} = 60.0 Hz for the methyl group *trans* to P; 1.57 ppm, ³J_{PH} = 7.5 Hz, ²J_{PtH} = 72.5 Hz for the methyl group *trans* to N).

Structure of the complex **3a** was also determined by single crystal X-ray diffraction analysis as shown in Figure 3. The complex has octahedral coordination geometry. The coordination geometry around platinum centre contains two Me groups, the nitrogen atom and the *ortho* C of the phpz ligand, one iodide and P atom of PPh₃. The bond distances between platinum and carbon atoms are 2.024(4), 2.102(5) and 2.083(4) Å for Pt(1)-C(4) (*trans* to I), Pt(1)-C(10) (*trans* to P), and Pt(1)-C(11) (*trans* to N), respectively. These values are consistent with *trans* influence of I, P and N. These three C coordinated atoms are located in the facial conformation, being in agreement with the other experimental observations for Pt(IV) and Pd(IV) complexes [29]. The iodide atom is located *trans* to the C atom of the phpz ligand with the bond distance of Pt(1)-I(1) = 2.7373(10) Å. The N atom of phpz ligand is coordinated to platinum centre to form cyclometalated complex and is positioned *trans* to Me group.

Figure 3. ORTEP view of structure of the complex $[\text{PtMe}_2\text{I}(\text{phpz})(\text{PPh}_3)]$, **3a**. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Pt(1)-C(4) 2.024(4); Pt(1)-C(11) 2.083(4); Pt(1)-C(10) 2.102(5); Pt(1)-N(1) 2.121(4); Pt(1)-P(1) 2.4532(12); Pt(1)-I(1) 2.7373(10); C(4)-Pt(1)-C(11) 92.92(19); C(4)-Pt(1)-C(10) 85.63(19); C(11)-Pt(1)-C(10) 86.0(2); C(4)-Pt(1)-N(1) 79.44(17); C(11)-Pt(1)-N(1) 170.88(19); C(10)-Pt(1)-N(1) 88.4(2); C(4)-Pt(1)-P(1) 94.29(13); C(11)-Pt(1)-P(1) 90.30(16); C(10)-Pt(1)-P(1) 176.28(17); N(1)-Pt(1)-P(1) 95.20(12); C(4)-Pt(1)-I(1) 171.34(14); C(11)-Pt(1)-I(1) 93.59(14); C(10)-Pt(1)-I(1) 89.14(14); N(1)-Pt(1)-I(1) 93.54(10); P(1)-Pt(1)-I(1) 91.37(3); C(12)-P(1)-C(24) 103.79(19).

As expected, bond lengths of the Pt(II) complex **2a** are shorter than those of the Pt(IV) product **3a**. For example the Pt-P bond in **2a** is shorter (2.2860(8) $\text{\AA}$) than that in **3a** (2.4532 $\text{\AA}$), complying with a larger $^1J_{\text{PtP}}$ value for the complex **2a** ($^1J_{\text{PtP}} = 2334 \text{ Hz}$) as compared with that for the complex **3a** ($^1J_{\text{PtP}} = 951 \text{ Hz}$).

3.2. Kinetic studies

Kinetic measurements for reaction of the Pt(II) complexes **2a** and **2b** with methyl iodide in CHCl_3 were carried out using UV-visible spectroscopy by monitoring the changes in their

MLCT bands at suitable wavelengths. It should be noted that reaction of the complex [PtMe(phpz)(P(OPh)₃)], **2c**, with MeI was too slow for any meaningful kinetic investigation. The UV-visible spectroscopic observations made during oxidative addition reaction of the complex **2b** in presence of a large excess of MeI (such that its concentration can be considered constant in each experiment) in CHCl₃ solution, shown in Figure 4, typically illustrate absorbance–time curves monitored at the corresponding wavelength. The kinetic data were in accord with the occurrence of first–order reaction. The pseudo–first–order rate constants, k_{obs} , for the reaction were calculated by nonlinear least–square fitting of kinetic data to the first order equation (see inset of Figure 4). The MeI concentration dependence of the oxidative addition reactions is illustrated in Figure 5. Plots of k_{obs} for the reactions *versus* [MeI] were linear with no intercepts, indicating the reactions to be first order in MeI reagent and therefore second order overall. This linear dependence on concentration of alkyl halides is characteristic of oxidative addition to d⁸ transition-metal complexes [30–34]. Second order rate constants, k_2 , and activation parameters, which were obtained from the temperature dependence study using Eyring plots (see Figure 6) are summarized in Table 2. The large negative values obtained for activation entropy ($\Delta S^\ddagger \ll 0$) are consistent with an interpretation that the transition state for the oxidative addition reaction occurs *via* an S_N2 mechanism [4, 35]. On the basis of the kinetic data, we suggest that (see Scheme 2) Pt(II) center of each of the complexes **2**, first attacks as a nucleophile on the carbon atom of MeI to give an ionic five-coordinate intermediate [PtMe₂(phpz)(L)]⁺I[−] with a square pyramidal geometry having the incoming Me in the apical position and the iodide ion in the outer sphere of the Pt complex. At the end of reaction, the free iodide ion coordinates to Pt(IV) center of the [PtMe₂(phpz)(L)]⁺ cationic intermediate to form the rollover cyclometalated Pt(IV) product [PtMe₂I(phpz)(L)], **3**, with an octahedral geometry.

Figure 4. Changes in UV-vis spectrum during reaction of the complex [PtMe(phpz)(PPh₂Me)], **2b**, (3×10^{-4} M) with MeI (0.27 M) in CHCl₃ at 25 °C with optical path length of 1 cm; successive spectra were recorded at intervals of 45 s. The inset shows the fitting of Abs (at $\lambda = 335$ nm)–time data to the first-order equation $Abs_t = Abs_{\infty} + (Abs_{\infty} - Abs_0) \exp(-k_{\text{obs}}t)$.

Figure 5. Plots of first-order rate constants for reactions of the complexes **2a** (A) and **2b** (B) with MeI (0.4–1.37 M) at different temperatures (15, 25, 30, 35 and 40 °C) versus [MeI] in

CHCl_3 . Absorbance data are collected at $\lambda = 330$ and 335 nm for complexes **2a** and **2b**, respectively with optical path length of 1 cm.

Figure 6. Eyring plots for reaction of the complexes **2a** and **2b** with MeI in CHCl_3

Table 2. Second-order rate constants^a and activation parameters for reaction of the complexes $[\text{PtMe}(\text{phpz})(\text{L})]$, **2**, $[\text{PtMe}(\text{ppy})(\text{L})]$ ^b and $[\text{PtMe}(\text{bpy-H})(\text{L})]$ ^c (bpy-H = κ^2N,C -2,2'-bipyridine) (ppy= 2-phenylpyridinate, L = PPh_3 and PPh_2Me) with MeI in CHCl_3 .

complex	$10^2 k_2 / \text{Lmol}^{-1} \text{s}^{-1}$ at different temperatures ($^{\circ}\text{C}$)					$\Delta H^{\ddagger} / \text{kJmol}^{-1}$	$\Delta S^{\ddagger} / \text{J mol}^{-1} \text{K}^{-1}$
	15	25	30	35	40
(2a)	0.19	0.35	0.45	0.59	0.71	37.6	-166
	± 0.01	± 0.02	± 0.02	± 0.04	± 0.04	± 1.4	± 5
(2b)	0.77	1.31	1.69	2.13	2.80	35.7	-161
	± 0.04	± 0.05	± 0.08	± 0.11	± 0.13	± 0.5	± 2

0.40 ±0.01	0.85 ±0.04	1.10 ±0.05	---	---	47.9±0.4	-124±2
1.77 ±0.08	2.87 ±0.14	3.84 ±0.19	---	---	35.8±0.2	-154±1
0.07 ±0.01	0.15 ±0.02	0.20 ±0.01	---	0.46 ±0.02	55.1±3.2	-114±10
---	0.70 ±0.01	0.90 ±0.04	---	1.38 ±0.07	38.1±2.0	-158±6

^a Estimated errors in k_2 values are ±5%. ^b Data from ref. [3]. ^c Data from ref. [6].

As shown in Table 2, MeI (typically at 25 °C) reacts with the PPh₂Me complex **2b** (with $k_2 = 1.31 \times 10^{-2} \text{ Lmol}^{-1}\text{s}^{-1}$) nearly 4 times faster than with the PPh₃ complex **2a** (with $k_2 = 0.35 \times 10^{-2} \text{ Lmol}^{-1}\text{s}^{-1}$). This could be related to higher σ -donor ability, lower π -acceptance ability and less steric hindrance of PPh₂Me ligand as compared with those of the PPh₃ ligand which was also confirmed theoretically by the application of density functional theory (*vide infra*). Notice that rate of reaction of the complex [PtMe(phpz)(P(OPh)₃)], **2c**, with MeI was too slow for any useful kinetic investigation. Besides, rate constants in reactions involving the 1-phenylpyrazolate complexes [PtMe(phpz)(L)], **2**, are more than two times less than those involving the ppy (2-phenylpyridinate) complexes [PtMe(ppy)(L)] [3] (see Table 2). For example, rate constants for reactions of the PPh₃ complexes [PtMe(phpz)(PPh₃)], **2a**, and [PtMe(ppy)(PPh₃)] with MeI in chloroform at 25 °C are $0.35 \times 10^{-2} \text{ Lmol}^{-1}\text{s}^{-1}$ and 0.85×10^{-2}

$\text{Lmol}^{-1}\text{s}^{-1}$, respectively. The existence of extra electronegative nitrogen atom in phpz ligand as compared to that in ppy ligand possibly makes the former ligand slightly weaker donor than the latter ligand and thus decreasing the reaction rates for **2a** as compared to that for $[\text{PtMe}(\text{ppy})(\text{PPh}_3)]$. In line with this, the effect seems to be more manifested in reaction involving the corresponding rollover 2,2'-bipyridine complexes $[\text{PtMe}(\text{bpy-H})(\text{PPh}_3)]$ with its k_2 value being estimated as $0.15 \times 10^{-2} \text{ Lmol}^{-1}\text{s}^{-1}$ at the same conditions.[6] Note also that k_2 value for the related MeI reaction, in chloroform at 25 °C, of the rollover 2,2'-bipyridine complex $[\text{PtMe}(\text{bpy-H})(\text{PPh}_3)]$ ($0.15 \times 10^{-2} \text{ Lmol}^{-1}\text{s}^{-1}$) is more than 2 times slower than the corresponding reaction involving the phpz containing complex **2a** ($0.35 \times 10^{-2} \text{ Lmol}^{-1}\text{s}^{-1}$), with two nitrogen atoms in the structures of both phpz or bpy-H ligand; this is probably due to the stronger donor ability of five-membered pyrazole moiety of phpz ligand as compared with the six-membered moiety of bpy-H ligand, which are responsible for providing electron density on Pt(II) center and thus influencing the reaction rate with MeI.

As was mentioned before, oxidative addition of MeI to each of the complexes **2** yielded almost quantitatively the related *cis* addition isomer, **3**, as the stable thermodynamic product (see suggested mechanism in Scheme 2). This observation may be due to steric effect in which the more sterically demanding **L** ligand is preferred to be located in the axial position as compared with the *trans* addition isomer (kinetic product) with **L** ligand in the equatorial position [9, 26]. This is consistent with our DFT calculations which will be discussed in the next section.

Scheme 2. Suggested mechanism for oxidation of Pt(II) to Pt(IV) complexes

3.3. Computational studies

The cycloplatinated(II) complexes [PtMe(phpz)(L)], **2**, are very reactive towards oxidative addition reagents. In order to understand the observed differences in rate of their reactions with MeI when the solvent is chloroform, DFT calculations were carried out on reaction of the complexes **2a-b** with MeI and the potential transition states and intermediates were found. A likely mechanism of reaction of MeI with the complexes [PtMe(phpz)(PPh₃)], **2a**, and [PtMe(phpz)(PPh₂Me)], **2b**, expecting to occur by the polar, bimolecular S_N2 mechanism, [7, 36-38] is shown in Scheme 2. Calculations resulting in finding an energy profile for oxidative addition of MeI to the complex **2a** in CHCl₃ is typically shown in Figure 7, suggesting that the reaction is initiated, by nucleophilic attack of the 5d_{z²} HOMO of **2a** on the σ* LUMO of MeI, to give the transition state **TSa** (calculated energy +43.9 kJmol⁻¹); the result being in

excellent agreement with the observed value of $\Delta H^\ddagger = 37.6 \text{ kJmol}^{-1}$ (see Table 2); similarly, for the related reaction involving **2b** ($L = \text{PPh}_2\text{Me}$), the calculated energy barrier (+38.2 kJmol^{-1}) and experimental enthalpy of activation (35.8 kJmol^{-1}) are close. The cationic intermediate **IMa-t** is then formed *via* the transition state **TSa** (Scheme 2 and Figure 7), followed by reversible coordination of iodide to vacant site of the intermediate **IMa-t** to form the *trans* addition product **3a-t**, being considered as the experimentally non-observed kinetic product. The intermediate **IMa-t** isomerizes to the intermediate **IMa-c** (*via* pseudo-rotation) [3, 9, 26, 39, 40], and then is coordinated to iodide to give the corresponding thermodynamic observed product **3a**. We believe that the thermodynamic isomer **3a** is favored over the kinetic isomer **3a-t** as in the former more sterically demanding phosphine ligand L is situated in the “axial” position as compared with that in the latter in which L is located in the “equatorial” position. Thus, the five-coordinate ionic intermediate **IMa-t**, formed by iodide dissociation from **3a-t**, isomerizes to the ionic intermediate **IMa-c**.

Figure. 7. Energy profile for oxidative addition of MeI to the complex **2a** in CHCl_3 .

Calculated charge on platinum is significantly lower in the starting Pt(II) complex **2a** ($Q_{\text{Pt}} = -0.208$) than in the Pt(IV) product complex **3a** ($Q_{\text{Pt}} = 0.548$), supporting the view that **2a** acts as nucleophile in the reaction with MeI. The $\text{S}_{\text{N}}2$ reaction occurs with a single energy maximum, in which structure of the transition state **TSa** includes I- C_{Me} -Pt and Pt- C_{Me} -H arrangements with the bond angles being 176.1° and 88.8° , respectively, showing a linear $\text{I}\cdots\text{C}_{\text{Me}}\cdots\text{Pt}$ arrangement in this transition state. H atoms of the CH_3 group (from MeI) in **TSa** are located in the equatorial plane of the 5-coordinated carbon center. The most significant changes in bond lengths of **TSa** are observed for I-Me and Pt-Me bonds; the calculated C-I bond distance in MeI ($2.195 \text{ \AA}$) increases to $2.688 \text{ \AA}$ in the transition state **TSa**, while the Pt $\cdots$ Me distance decreases from far apart in the reactants to $2.517 \text{ \AA}$ in **TSa**.

4. Conclusion

The following concluding remarks, drawn on the basis of experimental results and confirmed by theoretical calculations, worth noting:

1- The new cycloplatinated(II) complexes [PtMe(phpz)(L)], in which phpz is deprotonated 1-phenylpyrazole and L is PPh₃ (**2a**), PPh₂Me (**2b**), or P(OPh₃) (**2c**), were reacted with MeI to give the related cycloplatinated(IV) complexes [PtMe₂I(C[^]N)(L)], **3**. The reactions, as monitored by Uv-vis spectroscopy, was suggested to occur through a classical S_N2 mechanism and the rate of reaction involving **2b** ($k_2 = 1.31 \times 10^{-2} \text{ Lmol}^{-1}\text{s}^{-1}$) is significantly faster than that involving **2a** (with $k_2 = 0.35 \times 10^{-2} \text{ Lmol}^{-1}\text{s}^{-1}$). This is believed to be related to higher σ -donor ability, lower π -acceptance ability and less steric hindrance of PPh₂Me ligand (with cone angle = 136°) as compared with those of the PPh₃ ligand (with cone angle = 145°). The related reaction involving **2c** was too slow for any meaningful measurement. Poorer σ -donor/better π -acid P(OPh₃) ligand (as compared to the other two P ligands) makes the metallic center less electron rich, to the extent of making the reaction rate too slow; notice that steric effect is not the determining factor here as the P(OPh₃) cone angle (= 128°) is even smaller than that of PPh₃.

2- Trend of the rate constants for reactions of MeI in CHCl₃ with the phpz cycloplatinated(II) complexes [PtMe(phpz)(L)], **2**, each containing a 5-membered C[^]N chelate ring, and the previously reported analogous complexes [PtMe(bpy-H)(L)][6] (bpy-H = κ^2N,C -2,2'-bipyridine) and [PtMe(ppy)(L)][3] (ppy= 2-phenylpyridinate), each containing a 6-membered C[^]N chelate ring, is as follows

In line with this, for example trend of the reaction rates in chloroform at 25 °C for the PPh₂Me analogous complexes is [PtMe(ppy)(PPh₂Me)] ($k_2 = 2.87 \times 10^{-2} \text{ Lmol}^{-1}\text{s}^{-1}$) [3] > [PtMe(phpz)(PPh₂Me)], **2b** ($k_2 = 1.31 \times 10^{-2} \text{ Lmol}^{-1}\text{s}^{-1}$) > [PtMe(bpy-H)(PPh₂Me)]

($k_2 = 0.70 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$)[6]. Existence of an extra electronegative nitrogen atom in each of the two phpz and bpy-H ligands, as compared to the ppy ligand, is probably responsible for making the former two ligands weaker donor than the latter one and thus the ppy complex should react faster than the other two phpz and bpy-H complexes. Besides, in this trend, the rate constant for the complex $[\text{PtMe}(\text{phpz})(\text{PPh}_2\text{Me})]$, **2b**, is greater than that for the complex $[\text{PtMe}(\text{bpy-H})(\text{PPh}_2\text{Me})]$, both being a C^N ligand with an extra N atom. The N donor atom of the phpz 5-membered C^N chelate ring is *non-aromatic* and so is a better electron donor to the metallic center in **2b** as compared with N donor atom of the 6-membered C^N *aromatic* chelate ring in the complex $[\text{PtMe}(\text{bpy-H})(\text{PPh}_2\text{Me})]$.

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