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# Kinetics and mechanism of oxidative addition of MeI to binuclear cycloplatinated complexes containing biphosphine bridges: Effects of ligands

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#### ABSTRACT

The binuclear complex  $[Pt_2Me_2(bhg)_2(\mu-dppf)]$ . **1a.** in which  $bhgH = benzo{h}guinoline and$ dppf = 1,1'-bis(diphenylphosphino)ferrocene, was synthesized by the reaction of [PtMe(SMe<sub>2</sub>)(bhq)] with 0.5 equiv of dppf at room temperature. The reaction of Pt(II)–Pt(II) complex 1a with excess MeI gave the Pt(IV)–Pt(IV) complex  $[Pt_2I_2Me_4(bhq)_2(\mu-dppf)]$ , **2a**. The complexes were fully characterized using multinuclear (<sup>1</sup>H, <sup>31</sup>P and <sup>195</sup>Pt) NMR spectroscopy and elemental analysis. The kinetic and mechanism of the reaction of complex 1a with MeI was investigated in CHCl<sub>3</sub> and based on the data, obtained from UV-vis and low temperature <sup>31</sup>P NMR spectroscopies, a mechanism involving stepwise oxidative addition of MeI to the two Pt(II) centers is suggested. Reaction rates concerning the complex **1a**, having bhq ligand, are almost 1.4 times slower than those involving the ppy complex  $[Pt_2Me_2(p-1)]$  $py_{2}(\mu-dppf)$ ], ppyH = 2-phenylpyridine, reported previously (Inorg. Chem. 2008, 47, 5441). This is attributed to the stronger donor ability of the ppy ligand as compared to that of the bhg ligand as is further confirmed using density functional theory (DFT) calculations through finding approximate structures for the described complexes. A comparative kinetic study of reaction of the dimeric platinum(II) complex [Pt<sub>2</sub>Me<sub>2</sub>(bhq)<sub>2</sub>( $\mu$ -dppm)], **1b**, where dppm = bis(diphenylphosphino)methane, with MeI was also performed to investigate the effect of bridging biphosphine ligand on the kinetic and mechanism of the dimeric complexes with MeI. A double MeI oxidative addition was observed for which the classical  $S_N2$  mechanism for both steps, as well as the possible intermediates, is suggested. © 2012 Elsevier B.V. All rights reserved.

#### 1. Introduction

Oxidative addition is a fundamental reaction which is the base for many applications of organometallic compounds in many homogeneous catalytic processes and organic synthesis [1–3]. Oxidative addition of carbon-halide or other bonds to monomeric organoplatinum(II) complexes, especially those containing diimine ligands, has been extensively studied [4–10]. The most common mechanism of oxidative addition of alkyl halides is the classical S<sub>N</sub>2 mechanism involving a second-order rate law (rate =  $k_2$ [complex] [halide]), although in some relatively rare cases, the reactions proceed by concerted addition *via* a three–center transition state (mostly for aryl halides) [5,11,12] or by radical mechanisms, e.g. as observed for isopropyl iodide [13]. In all of these, the addition product has the halide and organic group bound to the same metal atom, increasing the oxidation state of the metal by 2. Despite these, examples of the related oxidative addition to binuclear complexes are much rarer [14–18]. The oxidative addition to the binuclear complexes is interesting because cooperative electronic or steric effects between the two adjacent metal centers can give rise to reaction pathways or products not possible in the mononuclear analogous [19–23]. In some cases, increased steric hindrance in binuclear complexes are thought to decrease the reactivity of systems [16], but in other cases, cooperative effects between the two metal centers lead to an increase in reactivity [24,25].

On the other hand, transition metal cyclometalated complexes, in particular those involving platinum, are of interest because of their potential applications in many areas, such as chemosensors [26,27], photocatalysts [28,29], and optoelectronic devices [30,31]. Square planar cyclometalated platinum complex species have also

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been used as "building blocks" for complex systems such as dendrimers [32].

Although oxidative addition reactions on mononuclear square planar platinum(II) complexes, as a key step in many catalytic reactions, have been extensively studied, to the best of our knowledge, such reactions have rarely been studied on binuclear platinum complexes, especially complexes having two cycloplatinated centers [18]. Cyclometalated platinum(II) complexes can be highly reactive *via* oxidative addition to give the corresponding platinum(IV) products.

A series of cycloplatinated complexes containing bridging biphosphine ligands of the types  $[Pt_2R_2(C-N)_2(\mu-dppf)]$ ,  $[Pt_2R_2(C-N)_2(\mu-dppm)]$  and  $[Pt_2R_2(C-N)_2(\mu-dppe)]$ , in which, dppf = 1,1'- bis(diphenylphosphino)ferrocene (R = Me or aryl), dppm = bis(diphenylphosphino)methane (R = aryl),dppe = bis(diphenylphosphino)ethane (R = Me or aryl) and $C-N = ppy (ppyH = 2-phenylpyrine) or bhq (bhqH = benzo{h}$ quinoline) ligands have recently been prepared [18,33-36]. In continuation of our interest in oxidative addition reactions of cyclometalated Pt(II) complexes, in this study, we attempted to investigate influence of the nature of biphosphine bridges on the kinetic and mechanism of oxidative addition of MeI to binuclear cyclometalated methylplatinum(II) complexes [Pt<sub>2</sub>Me<sub>2</sub>(bhq)<sub>2</sub>(µdppf)], **1a**, and [Pt<sub>2</sub>Me<sub>2</sub>(bhq)<sub>2</sub>(µ-dppm)], **1b**. By comparing the data to those reported previously for the corresponding reaction involving the ppy analogous [Pt<sub>2</sub>Me<sub>2</sub>(ppy)<sub>2</sub>(µ-dppf)] [18], it was possible to describe the effect of cycloplatinated rings on rate of the related reactions.

#### 2. Experimental

The NMR spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer. The operating frequencies and references, respectively, are shown in parentheses as follows: <sup>1</sup>H (500 MHz, TMS), <sup>31</sup>P (202 MHz, 85% H<sub>3</sub>PO<sub>4</sub>) and <sup>195</sup>Pt (107 MHz, aqueous Na<sub>2</sub>PtCl<sub>4</sub>). All 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. Benzo{h}quinoline and 1,1'-bis(diphenylphosphino)ferrocene were purchased from commercial sources. [PtMe(bhq)(SMe<sub>2</sub>)] [34] and [Pt<sub>2</sub>Me<sub>2</sub>(bhq)<sub>2</sub>(µ-dppm)] [36] were prepared as reported.

#### 2.1. [Pt<sub>2</sub>Me<sub>2</sub>(bhq)<sub>2</sub>(μ-dppf)], 1a

1,1'-Bis(diphenylphosphino)ferrocene (275 mg, 0.5 mmol) was added to a solution of [Pt(Me)(bhq)(SMe<sub>2</sub>)], (450 mg, 1.0 mmol) in acetone (20 ml). The mixture was stirred at room temperature for 2 h. After removal of the solvent by evaporation, a yellow residue was obtained which was further purified by repeated washing with ether and cold acetone. Yield 66%, mp = 258 °C (decomp). Anal. Calcd for C<sub>62</sub>H<sub>50</sub>FeN<sub>2</sub>P<sub>2</sub>Pt<sub>2</sub>: C, 56.0; H, 3.8; N, 2.1; Found: C, 55.6; H, 4.0; N, 2.4. NMR data in CDCl<sub>3</sub>:  $\delta$ (<sup>1</sup>H) 1.17 (d, 6H, <sup>2</sup>J<sub>PtH</sub> = 85.9 Hz,  ${}^{3}J_{PH} = 8.1$  Hz, 2 Me), 4.38 (br s, 4H,  $\beta$ ,  $\beta'$  Cp protons), 4.44 (br s, 4H,  $\alpha$ ,  $\alpha'$  Cp protons), (aromatic protons): 6.81 (m, 2H,  ${}^{3}J_{PtH} = 7.7$  Hz,  ${}^{3}J_{HH} = 2.5$  Hz, CH groups adjacent to coordinated C atoms), 7.3–8.1 (m, 32H, overlapping multiplets), 8.18 (m, 2H,  ${}^{3}J_{PtH} = 49.2$ , 2 CH groups adjacent to coordinated N atoms);  $\delta(^{13}C) - 14.5$  (d,  ${}^{1}J_{PtC} = 735 \text{ Hz}, {}^{2}J_{PC} = 7 \text{ Hz}, \text{ Me ligands}), 73.8 (d, {}^{3}J_{PC} = 10 \text{ Hz}, \beta, \beta' \text{ Cp}$ carbons), 75.8 (d,  ${}^{2}J_{PC} = 12.5$  Hz,  $\alpha$ ,  $\alpha'$  Cp carbons), 76.6 (d,  ${}^{1}J_{PC} = 46$  Hz,  ${}^{2}J_{PtC} = 31$  Hz, *ipso* Cp carbons),  $\delta({}^{31}P)$  24.1 ( ${}^{1}J_{PtP} = 2226$  Hz, 2P of dppf);  $\delta({}^{195}Pt) - 2588$  (d,  ${}^{1}J_{PtP} = 2225$  Hz, 2Pt).

#### 2.2. [Pt<sub>2</sub>I<sub>2</sub>Me<sub>4</sub>(bhq)<sub>2</sub>(μ-dppf)], 2a

An excess of MeI (50 µL) was added to a solution of complex **1a** (100 mg in 20 mL of chloroform) at room temperature. The mixture was stirred at this condition for 1 h, then the solvent was removed under reduced pressure and the residue was triturated with ether (2 × 3 mL). The product was dried under vacuum. Yield: 84 mg, 70%. Anal. Calcd for C<sub>64</sub>H<sub>56</sub>I<sub>2</sub>FeN<sub>2</sub>P<sub>2</sub>Pt<sub>2</sub>: C, 47.6; H, 3.5; N, 1.7; Found: C, 47.2; H, 3.7; N, 1.6. NMR data in CDCI<sub>3</sub>:  $\delta$ (<sup>1</sup>H) 1.03 (d, 6H, <sup>2</sup>J<sub>PtH</sub> = 60.5 Hz, <sup>3</sup>J<sub>PH</sub> = 7.6 Hz, 2 Me ligands *trans* to P), 1.55 (d, 3H, <sup>2</sup>J<sub>PtH</sub> = 71.2 Hz, <sup>3</sup>J<sub>PH</sub> = 2.9 Hz, 1 Me ligand *trans* to N), 2.51, 2.63, 2.96 (each a br s,1H, 1H, 2H, respectively,  $\beta$ ,  $\beta'$  Cp protons), 3.44 (br s, 4H,  $\alpha$ ,  $\alpha'$  Cp protons), aromatic protons: 6.6–8.2 (overlapping multiplets), 9.55 (d, 1H, J<sub>HH</sub> = 5.1 Hz, <sup>3</sup>J<sub>PtH</sub> = 9 Hz, CH group adjacent to coordinated N atom), 9.56 (d, 1H, J<sub>HH</sub> = 5.2 Hz, <sup>3</sup>J<sub>PtH</sub> = 9 Hz, CH group adjacent to coordinated N atom);  $\delta$ (<sup>31</sup>P) –13.1(s, <sup>1</sup>J<sub>PtP</sub> = 1012 Hz, 1P), -13.0 (s, <sup>1</sup>J<sub>PtP</sub> = 992 Hz, 1P).

#### 2.3. Kinetic study

In a typical experiment, a solution of complex **1a** or **1b** in CHCl<sub>3</sub> (3 ml,  $3 \times 10^{-4}$  M) in a cuvette was thermostated at 25 °C and a known excess of MeI was added using a micro syringe. After rapid stirring, the absorbance at corresponding wavelength was monitored with time.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization of the new binuclear complexes

As is depicted in Scheme 1, the reaction of a solution of  $[PtMe(SMe_2)(bhq)]$  in acetone, with 0.5 equiv of dppf at room temperature gave in good yield the new binuclear cyclometalated Pt(II)-Pt(II) complex  $[Pt_2Me_2(bhq)_2(\mu-dppf)]$ , **1a**, in which bhq = deprotonated benzo{h}quinoline or dppf = 1,1'-bis(diphe-nylphosphino)ferrocene, by replacement of SMe<sub>2</sub> ligands with the P ligating atoms of dppf. Complex **1a** is an air-stable yellow solid which is stable in acetone or chloroform solution for several hours. Reaction of the complex **1a** with excess methyl iodide at room temperature led to formation of the binuclear Pt(IV)-Pt(IV) complex  $[Pt_2I_2Me_4(bhq)_2(\mu-dppf)]$ , **2a**.

In the <sup>1</sup>H NMR spectrum of complex **1a** (see Fig. 1), the two equivalent methyl ligands, being *trans* to imine N atoms, are resonated as a doublet signal at  $\delta$  1.17 with  ${}^{3}J_{PH} = 8.1$  Hz which is coupled to the platinum center to give satellites with  ${}^{2}J_{PtH} = 85.9$  Hz. The 4 equivalent  $\alpha$  and 4 equivalent  $\beta$  protons of the cyclopentadienyl rings are appeared as two broad singlets at  $\delta$  4.44 and 4.38, respectively. In the  ${}^{31}P$  NMR spectrum of complex **1a**, the two equivalent P atoms are appeared as a singlet signal at  $\delta$  24.1 which are coupled to Pt atoms to give satellites with  ${}^{1}J_{PtP} = 2226$  Hz. Consistent with this, in the  ${}^{195}Pt$  NMR spectrum of **1a**, a doublet is observed at  $\delta$  –2588 with  ${}^{1}J_{PtP} = 2225$  Hz. The equivalency of the P atoms suggests that dppf is acting as a spacer ligand between the two PtMe(bhq) moieties and thus each P atom is coordinated to a Pt atom in a *trans* disposition to coordinating C atom of the phenyl ring of bhq ligand and each Me ligand is ought to be located *trans* to one of the coordinated N atom of bhq ligand.

In the <sup>1</sup>H NMR spectrum of complex **2a** (see Fig. 1), the relative intensity of Me ligands protons to cp protons of the dppf ligand is 12:8, confirming that the complex is a dimer. The two Me ligands locating *trans* to P are observed as overlapping doublets at  $\delta$  1.03 with  ${}^{3}J_{PH} = 7.6$  Hz and  ${}^{2}J_{PtH} = 61.5$  Hz. However, the two Me ligands locating *trans* to N ligating atoms are appeared as two different doublets at  $\delta$  1.55 ( ${}^{3}J_{PH} = 2.9$  Hz) and 1.59 ( ${}^{3}J_{PH} = 2.9$  Hz), each with



Scheme 1. Synthesis of complexes 1a and 2a.

a considerably higher  ${}^{2}J_{PtH}$  value of close to 72 Hz, complying with the *trans* influence of N atom being lower than that of P atom. The 4  $\alpha$  protons (as a broad singlet at  $\delta$  3.44) and 4  $\beta$  protons (as 3 broad singlets at  $\delta$  2.51, 2.63, and 2.96, with relative intensity 1:1:2) of the cyclopentadienyl rings are appeared at significantly higher field as compared with those involving in the starting complex **1a** (described above), with the effect being more pronounced for the  $\beta$  protons than for the  $\alpha$  protons. We believe that the conversion from square planar to octahedral geometry moves the Cp groups into the shielding region of the aromatic bhq ligand. In the  ${}^{31}$ P NMR spectrum of complex **2a**, the two P ligating atoms are appeared as two different signals at  $\delta$  -13.0 and -13.1, each with  ${}^{1}J_{\text{PtP}} \approx 1000 \text{ Hz}$ , a value much smaller than the corresponding value of around 2226 Hz observed in the spectrum of the Pt(II) complex **1a**. Similar to what has previously been reported for the analogous Pt(IV)—Pt(IV) complex [Pt<sub>2</sub>I<sub>2</sub>Me<sub>4</sub>(ppy)<sub>2</sub>( $\mu$ -dppf)] [18], in which the C–N ligand is ppy = deprotonated 2-phenylpyridyl (rather than bhq in complex **2a**). Although the data would well establish the relative disposition of the different ligands on each Pt center as indicated in Scheme 1 (with chirality at each Pt center), it is impossible to use the present data to actually propose any "frozen" conformer(s) for complex **2a** resulting from rotation around one or two of the Pt–P bonds. Yet again, as twice the "expected" number of signals is observed in the NMR spectra of complex **2a**, the formation



Fig. 1. <sup>1</sup>H NMR spectra of complexes 1a (top) and 2a (bottom) in the cp rings of dppf ligand (left) and Me ligands (right) regions.

of a statistical 1:1:2 mixture of three stereoisomers (the first two being enantiomers that are not distinguishable by NMR spectroscopy) may be a reasonable explanation.

### 3.2. Kinetic and mechanistic study of reaction of $[Pt_2Me_2(bhq)_2(\mu-dppf)]$ , **1a**, with Mel

The binuclear complex **1a** contains an MLCT band in the visible region that could be used to monitor its reaction with MeI and study the kinetics of the reaction by using UV–vis spectroscopy. Thus, an excess of MeI was used at 25 °C and the disappearance of the MLCT band at  $\lambda = 345$  nm in a CHCl<sub>3</sub> solution was used to monitor the reaction. The change in the spectrum during a typical run is shown in Fig. 2. Thus, the pseudo-first-order rate constants  $k_{obs}$  were evaluated by nonlinear least-squares fitting of the absorbance–time profiles to the following monophasic first-order equation:

$$Abs_{t} = Abs_{\infty} + (Abs_{0} - Abs_{\infty})\exp(-k_{obs}t)$$
(1)

Plots of the first-order rate constants,  $k_{obs}$ , versus [MeI] was linear with no intercepts (Fig. 3), showing a first-order dependence of the rate on the concentration of MeI. The slope in each case gave the second-order rate constant, and the results are collected in Table 1. Therefore, the reaction obeys a simple second-order rate law, first order in both the corresponding dimer and MeI. The reproducibility of the data was remarkable (4%). The same method was used at other temperatures, and activation parameters were obtained from the Eyring equation. The data are collected in Table 1.

The large negative value of  $\Delta S^{\ddagger}$  obtained for the reaction of complex **1a** with MeI is typical of oxidative addition by a common S<sub>N</sub>2 mechanism which involves nucleophilic attack of the metallic center at the methyl group of MeI and strongly confirms the associative nature of the reaction.

The reaction of complex **1a** with MeI was also monitored by <sup>31</sup>P NMR spectroscopy (see next section and Fig. 4) and on the basis of the gathered data and the data obtained from the above kinetic investigations, a mechanism depicted in Scheme 2 is suggested. Thus, after the addition of MeI, complex **B**, which is supposed to be the result of  $S_N2$  addition of MeI to one of the Pt(II) centers of the starting complex **1a** (i.e. complex **A**) followed by a rapid *trans–cis* isomerization of the resulting Pt(IV) center, was mainly appeared. Then, the second MeI was added to Pt(II) center of complex **B** to

2.5

2 θOUPGUOSE 1.5 0 1.5 0 1.5 0 340 360 380 400 420 440 460 λ/nm

**Fig. 2.** Changes in the UV–vis spectrum during the reaction of complex **1a**,  $(1.5 \times 10^{-4} \text{ M})$  with MeI (0.53 M) in CHCl<sub>3</sub> at T = 25 °C; successive spectra were recorded at intervals of 35 s.



Fig. 3. Plots of first-order rate constants for the reaction of complex 1a, with Mel at different temperatures versus the concentration of Mel in CHCl<sub>3</sub>.

form Pt(IV)–Pt(IV) complex **C**. Occurrence of the second *trans–cis* isomerization converted complex **C** to the final Pt(IV)–Pt(IV) complex, **2a**. All the related intermediates have been characterized by monitoring of the reaction at low temperatures by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy (see next section and Fig. 4).

## 3.3. Monitoring the reaction by variable temperature <sup>31</sup>P NMR spectroscopy

In order to investigate the details of mechanism, the reaction of complex **1a** with excess MeI was monitored by <sup>31</sup>P NMR spectroscopy at low temperatures, as shown in Fig. 4. Based on the results, the complexes and intermediates suggested for the reaction sequence, described in Scheme 2, were assigned. Note that complexes 1a and 2a are characterized as described in the main text and so their characteristic <sup>31</sup>P NMR data were used to indicate the complexes. Thus, immediately after the addition of MeI at -20 °C, apart from complex 1a, a Pt(II)-Pt(IV) species assigned as intermediate **A**, was detected. Two singlet signals, one at  $\delta$  23.3 (with  ${}^{1}J_{PtP} = 2166$  Hz), which is located in the Pt(II) region and its  ${}^{1}J_{PtP}$  value is close to that of the Pt(II)–Pt(II) starting complex **1a**, and another one at  $\delta$  –10.3, located in the Pt(IV) region with  ${}^{1}J_{\text{PtP}} = 1275$  Hz, were observed. The latter value is typical for Pt(IV)-P coupling, but is significantly higher than the corresponding value found for Pt(IV)-Pt(IV) complex 2a; this is probably due to higher trans influence of Me as compared to that of the bhq-*C* ligand. Although the data provide a reasonable support for the relative disposition of the different ligands on both Pt(II) and Pt(IV) centers as indicated in Scheme 2 for A, by the limited available data it is not possible to suggest any specific conformation for the intermediate **A**. As the time was passing on and the temperature was raised up, the signals due to the starting material 1a was disappearing while those due to the intermediate A were growing and then later started to fade away and meanwhile comparatively weak signals due to complex **B** were also observed in the first stages. For intermediate **B**, two singlet signals, one at  $\delta$  23.0 (with  ${}^{1}J_{\text{PtP}} = 2085$  Hz, located in the Pt(II) region) and another one at  $\delta$  –10.4, located in the Pt(IV) region with  ${}^{1}J_{PtP} = 1255$  Hz, were observed. In the meantime the suggested intermediate C was

|   | $\frac{[Pt_2Me_2(ppy)_2}{(\mu-dppf)]^a}$ 10 <sup>2</sup> k <sub>2</sub> /Lmol <sup>-1</sup> s <sup>-1</sup> | Complex 1a<br>$10^2 k_2 / \text{Lmol}^{-1} \text{s}^{-1}$ | Complex 1b <sup>b</sup>  |   |  |
|---|---|---|--|---|--|
|   |   |   | first step $10^2 k_2/L \text{ mol}^{-1}\text{s}^{-1}$<br>$(10^2 k_{-2} / \text{s}^{-1})$ | second step $10^2 k_{2'}/\text{Lmol}^{-1}\text{s}^{-1}$<br>$(10^2 k_{-2'} / \text{s}^{-1})$ | $K_{\rm eq}$ [or $K_{\rm eq}'$ ] <sup>c</sup> / Lmol <sup>-1</sup> |
| <i>T</i> = 10 °C  | 1.11 ± 0.02   | 0.79 ± 0.01   | $0.89 \pm 0.05 ~(0.064 \pm 0.003)$   | $0.15\pm 0.01~(0.02\pm 0.01)$   | $13.90 \pm 1.02 \ [7.50 \pm 3.78]$                                 |
| <i>T</i> = 15 °C  | $1.57\pm0.02$   | $\textbf{4.84} \pm \textbf{0.04}^{d}$                     |  |   |  |
| <i>T</i> = 20 °C  | $\textbf{2.17} \pm \textbf{0.03}$   | $1.56\pm0.02$   | $1.58 \pm 0.09 ~(0.24 \pm 0.05)$   | $0.29 \pm 0.06 \; (0.06 \pm 0.01)$  | $6.58 \pm 1.42 \ [4.83 \pm 1.28]$                                  |
| $T = 25 \ ^{\circ}\text{C}$                                 | $3.00\pm0.05$   | $2.15\pm0.01$   | $2.09 \pm 0.02 \; (0.39 \pm 0.08)$   | $0.38 \pm 0.07 \; (0.08 \pm 0.02)$  | $5.36 \pm 1.10 \ [4.75 \pm 1.47]$                                  |
| $T = 30 ^{\circ}\text{C}$                                   | $\textbf{3.79} \pm \textbf{0.06}$   | $\textbf{3.39} \pm \textbf{0.05}$                         | $2.71 \pm 0.03 \; (0.63 \pm 0.10)$   | $0.54 \pm 0.05 \; (0.18 \pm 0.05)$  | $4.30\pm0.68\;[3.00\pm0.88]$                                       |
| $\Delta H^{\ddagger e}/kJ \text{ mol}^{-1}$                 | $41.8 \pm 1.2$  | $49.9 \pm 2.4$  | $37.4 \pm 0.2 \; (79.5 \pm 3.7)$   | $43.6 \pm 1.3 \ (72.5 \pm 7.8)$   |  |
| $\Delta S^{\ddagger e}$ /JK <sup>-1</sup> mol <sup>-1</sup> | $-134\pm4$  | $-109\pm8$  | $-152 \pm 1 \ (-23 \pm 12)$  | $-144 \pm 4 \ (-59 \pm 37)$   |  |
| $\Delta H^{\circ}$ /kJ mol <sup>-1</sup>                    |   |   | $-42.2\pm3.7$  | $-29.8\pm6.5$   |  |
| $\Delta S^{\circ} / IK^{-1} mol^{-1}$                       |   |   | $-127 \pm 13$  | $-88 \pm 22$  |  |

| Table 1   |
|---|
| Rate constants and activation parameters for the reaction of the diplatinum(II) complexes with MeI in CHCl <sub>2</sub> |

<sup>a</sup> Data from ref. [18].

<sup>b</sup> Values in parenthesis are parameters for reverse reactions (see Scheme 3;  $D \rightarrow 1b$  and  $F \rightarrow E$ ).

<sup>c</sup>  $K_{eq}$  and  $K_{eq'}$  are equilibrium constants for first and second steps, respectively.

<sup>d</sup> At 35 °C.

<sup>e</sup> Standard errors of  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  correlate as  $\sigma(\Delta S^{\ddagger}) = (1/T_{av}) \sigma(\Delta H^{\ddagger})$  [37].

started to show up. For the intermediate **C** we observed two signals in the Pt(IV) regions with expected  ${}^{1}J_{PtP}$  values (one signal at  $\delta$  –11.0, with  ${}^{1}J_{PtP}$  = 1234 Hz, another signal at  $\delta$  –12.5, with  ${}^{1}J_{PtP}$  = 1032 Hz). As the reaction was progressed, the Pt(IV)–Pt(IV) intermediates **C** was quickly being disappeared and the final Pt(IV)–Pt(IV) complex **2a** started to appear. After 70 min (room temperature) all the signals were completely disappeared and the final Pt(IV)–Pt(IV) product **2a** was purely obtained.

#### 3.4. Effect of ligands

By comparing the above kinetic results with those of the previously reported reaction of MeI with the ppy analogous complex  $[Pt_2Me_2(ppy)_2(\mu-dppf)]$  [18] (see Table 1), we now find that the nature of C–N ligand has significant impact on rate and mechanism of the reaction of MeI with the studied complexes containing dppf as spacer ligand. In the suggested mechanism for the reaction of binuclear complex  $[Pt_2Me_2(ppy)_2(\mu-dppf)]$  with excess MeI [18], a side reaction has been detected during which the cyclometalated C–N ligand is opened up from the N site at the expense of dppf ligand becoming chelated forming the complex

[PtMe(dppf)(ppy- $\kappa^{1}$ C)]. However, no such scenario was observed for the corresponding reaction involving the bhg analog complex studied in the present work, i.e.  $[Pt_2Me_2(bhq)_2(\mu-dppf)]$ , **1a**. Thus, as is depicted in Scheme 2, the latter reaction proceeded more straightforward than the former one. We believe that as a result of the bhq ligand being more rigid than the ppy ligand, formation the related side product [PtMe(dppf)(bhq- $\kappa^{1}$ C)] has not been favorable during the latter reaction. Consistently, attempts to prepare the complex [PtMe(dppf)(bhq- $\kappa^{1}$ C)] with the reaction of [PtMe(bhq)(SMe<sub>2</sub>)] with 1 equiv of dppf was unsuccessful. These observations indicate that the rigid ligand bhq, as compared to the more flexible ppy ligand, is less prone to bind as the  $\kappa^1$  form [34]. Besides, as is clear from Table 1, the reaction rates of complex  $[Pt_2Me_2(bhq)_2(\mu-dppf)]$ , **1a**, with MeI in CHCl<sub>3</sub> at different temperatures, are at least 1.3 times slower than the corresponding reaction involving ppy. For example, MeI at 25 °C reacted nearly 1.5 times faster with  $[Pt_2Me_2(ppy)_2(\mu-dppf)]$   $(k_2 = 3.00 \times 10^{-2} \text{ Lmol}^{-1}\text{s}^{-1})$  than with **1a**  $(k_2 = 2.15 \times 10^{-2} \text{ Lmol}^{-1}\text{s}^{-1})$ . This confirms the stronger donor ability of the ppy ligand as compared to that of the bhg ligand and shows that the platinum center in the ppy complex  $[Pt_2Me_2(ppy)_2(\mu-dppf)]$  is more electron rich than the



Fig. 4. Reaction of complex 1a with excess methyl iodide as monitored by <sup>31</sup>P NMR spectroscopy at low temperatures. Left view: Pt(II) region. Right view: Pt(IV) region. (a) Pure 1a (253 K), (b) immediately after addition of excess MeI (253 K), (c) 20 min after addition (265 K), (d) 34 min after addition (275 K), (e) 46 min after addition (285 K), (f) 55 min after addition (285 K) and (g) 70 min after the temperature was raised up to room temperature. Peak assignments are shown; platinum satellites are observed and shown for all involved species including intermediates **A**, **B** and **C**.



Scheme 2. Suggested mechanism for reaction of complex 1a with Mel.

platinum center in complex **1a** toward nucleophilic attacks. This is consistent with the trends found for  ${}^{1}J_{PtP}$  values in the  ${}^{31}P$  NMR spectra of the analogous complexes [Pt<sub>2</sub>Me<sub>2</sub>(ppy)<sub>2</sub>( $\mu$ -dppf)] (2090 Hz) and [Pt<sub>2</sub>Me<sub>2</sub>(bhq)<sub>2</sub>( $\mu$ -dppf)] (2226 Hz). These results also suggest that the *trans* influence of metalated C atom of ppy ligand should be greater than that of bhq ligand [35]. This was further confirmed using density functional theory (DFT) calculations through finding approximate structures for the described complexes and charge on the involved platinum center. The DFT-optimized structures for complexes [Pt<sub>2</sub>Me<sub>2</sub>(bhq)<sub>2</sub>( $\mu$ -dppf)] and [Pt<sub>2</sub>Me<sub>2</sub>(ppy)<sub>2</sub>( $\mu$ -dppf)] at B3LYP level along with the calculated bond distances are shown in Fig. 5.

As is clear from Fig. 5, the charge on the platinum atom in  $[Pt_2Me_2(ppy)_2(\mu-dppf)]$  complex (-0.034) is lower than that on the platinum atom in the analog bhq complex (-0.026). This lower charge (meaning higher electron density) at the platinum center, complies with the higher reaction rates of the ppy complex as compared with that of the analogs bhq complex toward their nucleophilic attack on MeI operating by an S<sub>N</sub>2 mechanism. Also Pt–P bond length for the complex having ppy ligand (Pt-P = 2.413 Å) is longer than that involving the bhq ligand (Pt-P = 2.408 Å) complying with the smaller <sup>1</sup>*J*<sub>PtP</sub> value in the ppy complex as compared to that of the bhq analog, and the stronger donor ability of the ppy ligand as compared with that of the bhq ligand.

### 3.5. Kinetic and mechanistic study of reaction of $[Pt_2Me_2(bhq)_2(\mu-dppm)]$ , with Mel

As has been reported previously [36], on the basis of <sup>31</sup>P NMR studies, reaction of the binuclear Pt(II)-Pt(II) complex  $[Pt_2Me_2(bhq)_2(\mu-dppm)]$ , **1b**, in which dppm, bis(diphenylphosphino)methane, acts as a bridging ligand, with excess MeI first gives a Pt(II)-Pt(IV) intermediate which is finally converted to a mixture of two Pt(IV)-Pt(IV) binuclear complexes. In this work in an attempt to shed some light on mechanism of the reaction, we investigated kinetics of the reaction using UV–vis spectroscopy.

The binuclear complex **1b** contains an MLCT band in the visible region that could be used to monitor its reaction with MeI and study the kinetics of the reaction by using UV–vis spectroscopy. Thus, an excess of MeI was used at 25 °C and the disappearance of the MLCT band at  $\lambda = 425$  nm in a CHCl<sub>3</sub> solution was used to monitor the reaction. The change in the spectrum during a typical run is shown in Fig. 6.

The time-dependence curves of the spectra of the reaction in CHCl<sub>3</sub> at this condition are shown in Fig. 7. As is clear from this figure, low concentration of MeI did not allow the reaction to shift to completion and equilibrium has been established, but under a large excess of MeI, the reaction was completed. The data failed to fit properly in the monophasic first-order equation (Eq. (1)). However, the data were successfully fitted in Eq. (2) with two exponentials, showing a clear biphasic kinetic behavior. Thus, the



Fig. 5. DFT calculated structures of (a) [Pt<sub>2</sub>Me<sub>2</sub>(bhq)<sub>2</sub>( $\mu$ -dppf)] and (b) [Pt<sub>2</sub>Me<sub>2</sub>(ppy)<sub>2</sub>( $\mu$ -dppf)]. Selected bond distances (Å) and Pt charges are shown. The H atoms are omitted for more clarity.

pseudo-first-order rate constants  $k_{obs}$  and  $k_{obs}'$  for the two steps of the reaction were evaluated by nonlinear least-square fitting of the absorbance—time profiles to the biphasic first-order equation (Eq. (2)).

$$A_{\rm t} = A_{\infty} + \alpha [\exp(-k_{\rm obs}t)] + \beta [\exp(-k_{\rm obs}t)]$$
<sup>(2)</sup>

Plots of the first-order rate constants,  $k_{obs}$  and  $k_{obs}'$ , versus [MeI] was linear with a two-term rate law for both steps of the reaction (see Fig. 8 and Scheme 3):

$$-d[\mathbf{1b}]/dt = k_{obs}[1]$$
, where  $k_{obs} = k_{-2} + k_2[Mel]$ 

$$-d[E]/dt = k'_{obs}[E]$$
, where  $k'_{obs} = k'_{-2} + k'_{2}[MeI]$ 

The slope and intercept of the  $k_{obs}$ –[MeI] and  $k_{obs}$ –[MeI] plots in each case gave the second-order rate constants ( $k_2$  and  $k_2'$ ) and reverse rate constants ( $k_{-2}$  and  $k_{-2}'$ ), respectively and the results are collected in Table 1. Therefore, the reaction obeys a simple second-order rate law, first order in both the corresponding dimer and MeI. The reproducibility of the data was remarkable (4%). The same method was used at other temperatures, and activation parameters were obtained from the Eyring equation (see Fig. 9) and reported in Table 1. Equilibrium constants ( $K_{eq} = k_2/k_{-2}$  and  $K_{eq}' = k_2'/k_{-2}'$ ) at different temperatures have also been calculated and reported in Table 1.

The  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  values for the first and second equilibrium steps of the reaction of complex **1b** with MeI were evaluated from



**Fig. 6.** Changes in the UV–vis spectrum during the reaction of complex **1b**,  $(3 \times 10^{-4} \text{ M})$  with Mel (0.66 M) in CHCl<sub>3</sub> at  $T = 25 \degree$ C; successive spectra were recorded at intervals of 30 s.

the corresponding temperature data by applying a linear ln  $K_{eq}$  least-squares analysis according to the van't Hoff equation (see Table 1).

On the basis of the NMR and kinetic data, we suggest that, as is indicated in Scheme 3, Mel first performs an electrophilic attack on one of the electron-rich platinum(II) centers of diplatinum(II) complex **1b** with an S<sub>N</sub>2-type mechanism with the rate constant  $k_2$  and the mixed-valence Pt(II)—Pt(IV) binuclear intermediate **D** is formed. The reaction followed by a rapid *trans*—*cis* isomerization of the resulting Pt(IV) center to form complex **E**. Intermediate **E** is then reacted with MeI in step 2, again by an S<sub>N</sub>2-type mechanism, with the rate constant  $k_2'$  that is nearly 5–6 times smaller than the corresponding value for  $k_2$  (see Table 1) to give the Pt(IV)—Pt(IV) intermediate **F**. A rapid *trans*—*cis* isomerization of the second Pt(IV) center in **F** is then occurs to give an almost 1:1 mixture of two isomeric Pt(IV)—Pt(IV) complexes, suggested to have structures **2b** and **2b**'.

As shown above, the step 2 of MeI addition (i.e.  $\mathbf{E} \rightarrow \mathbf{F}$ ) is slower than the step 1 ( $\mathbf{1b} \rightarrow \mathbf{D}$ ). It is suggested that in a two-step oxidative addition reaction of this type in which none of the components of the reaction contains any metal—metal bond and yet the metallic centers are not too far from each other, the first addition occurs faster than the second [23,38]. In the present work, we believe that this has actually been the case. In the first step, MeI



**Fig. 7.** The plots show the time course of absorbance for the reaction of complex **1b** with Mel (0.26-0.80 M) in CHCl<sub>3</sub> at 20 °C. The three top curves show the approach to equilibrium; the other one, the reaction drawn to completion. The biexponential fit for the reaction of **1b** with Mel (0.37 M) is shown.





**Fig. 9.** Eyring plots for the reaction of complex **1b** with Mel (0.26–0.80 M) in CHCl<sub>3</sub>: (a) first step, forward reaction; (b) second step, forward reaction; (c) first step, reverse reaction; (d) second step, reverse reaction.

**Fig. 8.** Plots of first-order rate constants [(a) first step,  $k_{obs}/s^{-1}$ , and (b) second step,  $k_{obs}'/s^{-1}$ ] for the reaction of complex **1b** with MeI at 20 °C versus the concentration of MeI in CHCl<sub>3</sub>.

attacks the platinum(II) center of a Pt(II)-Pt(II) complex, **1b**, while in the second step, MeI reacts with the platinum(II) center of a Pt(II)-Pt(IV) species (complex **E**). As such, the reaction should be slower in the second step because, in contrast to complex **1b**, in species **E** the adjacent Pt(IV) moiety not only creates a more severe steric hindrance for the attacked Pt(II) center but also reduces its nucleophilicity through the bridging biphosphine ligand. This assignment has also been confirmed by Espenson's approach [39] as the value of extinction coefficient of complex **E** at 425 nm is found to be almost  $1.95 \times 10^3 \, \text{M}^{-1} \, \text{cm}^{-1}$ . This value lies close to the value of extinction coefficient of complex **1b** ( $2.20 \times 10^3 \, \text{M}^{-1} \, \text{cm}^{-1}$ ), in which both of the related complexes have MLCT bands, and far from  $\epsilon_p$  ( $0.90 \times 10^3 \, \text{M}^{-1} \, \text{cm}^{-1}$ ), as one would expect for the final products **2b** and **2b'** with no MLCT band in the visible region.



Scheme 3. Suggested mechanism for reaction of complex 1b with Mel.

#### 4. Conclusion

On the basis of UV-vis and <sup>31</sup>P NMR spectroscopy studies, reaction of the Pt(II)-Pt(II) binuclear complex [Pt<sub>2</sub>Me<sub>2</sub>(bhq)<sub>2</sub>(µdppf)], **1a**, in which  $bhqH = benzo{h}quinoline and dppf = 1,1'$ bis(diphenylphosphino)ferrocene, with excess MeI, to give the Pt(IV)-Pt(IV) complex  $[Pt_2I_2Me_4(bhq)_2(\mu-dppf)]$ , **2a**, in CHCl<sub>3</sub>, is suggested to occur through stepwise oxidative addition of MeI to the two Pt(II) centers by the classical S<sub>N</sub>2 mechanism. The reaction rates at different temperatures are almost 1.4 times slower than those involving the ppy analogous complex  $[Pt_2Me_2(ppy)_2(\mu$ dppf)], ppyH = 2-phenylpyridine, reported previously to proceed by similar mechanism [18]. This is attributed to the stronger donor ability of the ppy ligand as compared to that of the bhg ligand as was further confirmed using density functional theory (DFT) calculations through finding approximate structures for the described complexes. The higher rate of the latter reaction is discussed to be enthalpy driven.

In the above two-step reaction, after each *trans* MeI addition, a *trans* to *cis* isomerization is observed. We believe that this is most probably due to higher *trans* influence of the ligating C atom of either ppy or bhq ligand, as compared to that of Me ligand, that prefers to stay *trans* to I ligand, which has a lower *trans* influence than P ligand (see Scheme 2 and 3).

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