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Exchange of pyridine and bipyridine ligands in trimethylplatinum(IV) iodide complexes: Substituent and solvent effects

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Abstract

A series of mononuclear trimethylplatinum(IV) complexes of bipyridine ligands, [$PtMe_3$(L-L)I] (L-L = bipy, 4-Mebipy, 4-MeObipy and 4-Me_2Nbipy) has been synthesized by the reaction of trimethylplatinum(IV) iodide with bipyridine ligands L-L in equimolar ratio. Also, treatment of mononuclear trimethylplatinum(IV) iodide complexes of pyridine ligands, [$PtMe_3L_2$I] (L = py, 4-Mepy, 4-MeOpy and 4-Me_2Npy) with the corresponding bipyridine ligands leads to the exchange of the pyridines by the bipyridine ligands, thereby resulting in the formation of the more stable chelate bipyridine complexes. The ligand-exchange reactions have been studied by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of 1:1 mixture of mononuclear pyridine complexes [$PtMe_3L_2$I] and corresponding bipyridine ligands L-L reveal the formation of two chelate bipyridine complexes, [$PtMe_3$(L-L)I] and [$PtMe_3$(L-L)L]I, in solution. Speciation of the pyridine and bipyridine complexes in solution was found to be dependent on the substituent as well as on the nature of solvent. Furthermore, crystal structures of three bipyridine complexes [$PtMe_3$(L-L)I] (L-L = 4-Mebipy, 4-MeObipy and 4-Me_2Nbipy) have also been investigated here.

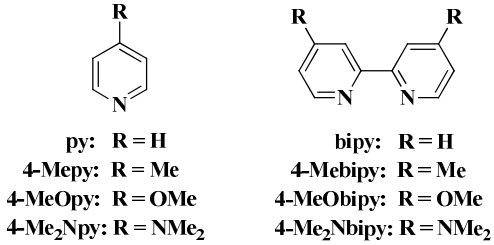
Introduction

The well-known nitrogen based heterocyclic ligands play an important role in coordination and supramolecular chemistry as well as material science.[1-6] In particular, 2,2′-bipyridine and its derivatives have received much attention because of their remarkable coordination chemistry. Extremely strong chelation properties, due to the arrangement of two pyridinic nitrogen atoms in addition to strong affinity towards the most transition metals ions, make bipyridines a highly useful ligand in research. It has been found that 2,2′-bipyridine and its complexes with

ruthenium(II), osmium(II) or platinum(II) exhibit interesting electrochemical and photochemical properties.[7-9] In addition, the transition metal complexes of 2,2′-bipyridine and its derivatives are also used as building blocks in supra-molecular assemblies,[10, 11] as electrochemical probes for DNA detection,[9, 12] as electron transfer mediators for glucose oxidase,[13] or as sensitizers in solar energy conversion.[14]

The chemistry of Pt^{IV} emerged as one of the leading research interest in organometallic chemistry, because of the involvement as a key intermediate in Shilov type-chemistry for C-H/C-X (X=C, N, O) bond breaking or bond formation processes.[15-17] In order to study the mechanism for these Pt^{II}/Pt^{IV} mediated catalytic processes, several trimethylplatinum(IV) complexes of nitrogen-based ligands have been synthesized.[18-21] It was also found that trimethylplatinum(IV) complexes of bipyridine ligands exhibit curious dynamic behavior in solution.[22] In this regard, it is somewhat surprising that there exists very few structural reports of trimethylplatinum(IV) complexes of simple 2,2′-bipyridine ligand[22-26] and to the best of our knowledge, no structural characterization of simple 4,4′-disubstituted 2,2′-bipyridine ligands of trimethylplatinum(IV) iodide complexes has yet been reported. Herein, in the present paper, we report the synthesis and spectroscopic characterization of a series of mononuclear trimethylplatinum(IV) complexes of 2,2′-bipyridine ligands, $[PtMe_3(L\text{-}L)I]$ where L-L = 2,2′-bipyridine (bipy), 4,4′-dimethyl-2,2′-bipyridine (4-Mebipy), 4,4′-dimethoxy-2,2′-bipyridine (4-MeObipy), 4,4′-bis(dimethylamino)-2,2′-bipyridine (4-Me_2Nbipy). The crystal structures of three 4,4′-disubstituted 2,2′-bipyridine complexes, $[PtMe_3(L\text{-}L)I]$ (L-L = 4-Mebipy, 4-MeObipy and 4-Me_2Nbipy) have also been described. The presence of low-spin d^6 electron configuration of central metal ion makes ligand substitution reactions in Pt^{IV} complexes very slow and thus ligand-exchange study was performed in Pt^{IV} complexes having trimethylplatinum unit where the leaving ligand is activated by the presence of methyl groups having high *trans* effect.[27-29] It was also observed that reaction of mononuclear pyridine complex, $[PtMe_3(py)_2I]$ (py = pyridine) with 2,2′-bipyridine (bipy) leads to the substitution of pyridine by the bipy ligand, resulting in the formation of the chelate bipyridine complex. In order to explore the influence of the substituent on the above ligand-exchange reaction, we have hereby carried out the exchange of different pyridine ligands (py, 4-methylpyridine (4-Mepy), 4-methoxypyridine (4-MeOpy), 4-dimethylaminopyridine (4-Me_2Npy)) with the corresponding bipyridine ligands (bipy, 4-Mebipy, 4-MeObipy and 4-

Me_2Nbipy) in mononuclear trimethylplatinum(IV) iodide complexes. The substitution reactions were carried in two different solvents ($CDCl_3$, an apolar solvent and nitrobenzene-d_5, a polar solvent) to investigate the solvent effect on the chelation reaction.



Scheme 1 Different pyridines and corresponding 2,2′-bipyridines used to study the ligand-exchange study in trimethylplatinum(IV) iodide system.

Experimental Section

General methods and materials: Trimethylplatinum(IV) iodide was purchased from Strem Chemicals. The ligand 4,4′-bis(dimethylamino)-2,2′-bipyridine (4-Me_2Nbipy) was prepared following the modified literature procedure.[30, 31] Other bipyridine ligands, pyridine ligands and solvents were of analytical reagent grade, purchased commercially and used as received. The mononuclear pyridine complexes [$PtMe_3L_2I$] (L = py, 4-Mepy, 4-MeOpy and 4-Me_2Npy) and bipyridine complex [$PtMe_3(bipy)I$] were synthesized following literature methods.[32-34] ^1H NMR spectra recorded on a Bruker Avance II 400 MHz spectrometer at room temperature. Spin-spin coupling constants are considered accurate to ± 0.5 Hz and δ values to ± 0.01 ppm. Elemental analyses were performed on a Thermo Electron Flash EA 1112 series. Mass spectra were recorded on a Finnigan MAT 95 mass spectrometer.

Synthesis of the ligand 4-Me_2Nbipy: A 30 mL solution of 30% hydrogen peroxide was added to 2,2′-bipyridine (10.0 g, 64 mmol) in 50 mL of glacial acetic acid at a rate that maintained the temperature between 70-80 °C. The mixture was stirred at 75 °C for an additional 8 h. The solution was then cooled to room temperature, and a large amount (750 mL) of acetone was added to precipitate the product 2,2′-bipyridine N,N′-dioxide as a white solid, which was collected by filtration and air-dried. Yield: 11.3 g (60 mmol, 94% yield). ^1H NMR (400 MHz, D_2O, 27 °C) δ/ppm: δ 8.47 (m, 2H), 7.85 (m, 2H), 7.76 (m, 4H). Then a solution of 2,2′-

bipyridine N,N′-dioxide (9.0 g, 47.8 mmol) in 26 mL of oleum-sulfuric acid was cooled to 0 °C. Fuming nitric acid (20 mL) was carefully added, and the mixture was stirred at 100 °C for 8 h. The solution was then cooled to 0 °C and very cautiously poured onto ice water (200 g). The resultant yellow product, 4,4′-dinitro-2,2′-bipyridine N,N′-dioxide (O_2N-bipy N-Oxide), was filtered off and washed with water until neutral. Yield: 9.6 g (34.5 mmol, 72%). ^{1}H NMR (400 MHz, DMSO-d_6, 27 °C) δ/ppm: 8.70 (d, 2H), 8.60 (d, 2H), 8.38 (dd, 2H). After that, a suspension of 1 g of O_2N-bipy N-Oxide (3.59 mmol) in 50 mL of acetyl chloride was refluxed under argon for 3 h. The resultant solid product, 4,4′-dichloro-2,2′-bipyridine N,N′-dioxide (Cl-bipy N-Oxide), was filtered off, washed with 50 mL of diethyl ether, and dried under vacuum. Yield: 700 mg of pale yellow powder (2.72 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ/ppm: 8.25 (d, 2H), 7.72 (d, 2H), 7.35 (dd, 2H). A suspension of 1 g of Cl-bipy N-Oxide (3.89 mmol) in 150 mL DMF was refluxed under argon for 48 h. The solvent was evaporated nearly completely, and the crude product was dissolved in 100 mL of chloroform. Phosphorous trichloride (8.5 mL, 97.4 mmol) was added drop wise to the cooled solution at 0 °C. The reaction mixture was then refluxed for 3 h and then poured onto 250 mL of ice water. The chloroform layer was washed with 3 × 50 mL of water and the combined aqueous extracts were concentrated under vacuum to 75 mL and made alkaline with saturated aqueous sodium hydroxide. The resulting precipitate was recrystallized twice from water/methanol (1.5 v/v) to give 150 mg of the beige product 4,4′-bis(dimethylamino)-2,2′-bipyridine (**4-Me$_2$Nbipy**) (0.62 mmol, 16%). ^{1}H NMR (400 MHz, nitrobenzene-d_5, 27 °C) δ/ppm: 8.37 (d, 2H), 8.01 (d, 2H), 6.50 (dd, 2H), 2.94 [s, 12H, $N(CH_3)_2$].

Synthesis of [PtMe$_3$(4-Mebipy)I]: Trimethylplatinum(IV) iodide (200 mg, 0.54 mmol) was dissolved in benzene (15 mL) and 4-Mebipy (100 mg, 0.54 mmol) added to it. The solution was stirred for 1.5 h and the resulting pale yellow solid [$PtMe_3$(4-Mebipy)I] was filtered off, washed several times with *n*-hexane and dried under vacuum. Yield: 258 mg (0.47 mmol, 86%). Also, diffraction quality single crystals were obtained after a few days, when a 1:1 mixture of trimethylplatinum iodide and 4-Mebipy were mixed in benzene solution and left undisturbed. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ/ppm: 8.82 (d, 2H, $^3J_{H\text{-}H}$: 5.8 Hz, $^3J_{Pt\text{-}H}$: 19.4 Hz), 8.01 (s, br, 2H), 7.42 (d, 2H), 2.57 (s, 6H, CH_3), 1.51 [s, 6H, Pt-CH_3 (*trans* to N), $^2J_{Pt\text{-}H}$: 70.3 Hz], 0.63 [s, 3H, Pt-CH_3 (*trans* to I), $^2J_{Pt\text{-}H}$: 73.5 Hz]. ^{1}H NMR (400 MHz, nitrobenzene-d_5, 27 °C) δ/ppm:

8.87 (d, 2H, $^{3}J_{H\text{-}H}$: 5.6 Hz, $^{3}J_{Pt\text{-}H}$: 19.6 Hz), 8.05 (s, br, 2H), 7.42 (d, 2H), 2.52 (s, 6H, CH_3), 1.78 [s, 6H, Pt-CH_3 (*trans* to N), $^{2}J_{Pt\text{-}H}$: 70.3 Hz], 0.81 [s, 3H, Pt-CH_3 (*trans* to I), $^{2}J_{Pt\text{-}H}$: 72.9 Hz]. MS (ESI-TOF) $[PtMe_3(4\text{-Mebipy})]^+$ *m/z* 424.1342 (calcd 424.1347). Anal. calcd. for $C_{15}H_{21}IN_2Pt$ (551.33 g.mol^{-1}): C: 32.68, H: 3.84, N: 5.08. Found: C: 32.46, H: 3.97, N: 4.98%.

Synthesis of [$PtMe_3$(4-MeObipy)I]: To a benzene solution (10 mL) of trimethylplatinum iodide (200 mg, 0.54 mmol), the ligand 4-MeObipy (120 mg, 0.56 mmol) was added and the solution was stirred at room temperature for 2 h. The pale yellow solid formed was then filtered off, washed several times with *n*-hexane and dried under vacuum. Yield: 267 mg (0.46 mmol, 84%). X-ray quality single crystals were obtained by slow diffusion of *n*-hexane into its chloroform solution at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ/ppm: 8.77 (d, 2H, $^{3}J_{H\text{-}H}$: 6.4 Hz, $^{3}J_{Pt\text{-}H}$: 19.8 Hz), 7.58 (d, 2H), 7.08 (dd, 2H), 4.02 (s, 6H, OCH_3), 1.48 [s, 6H, Pt-CH_3 (*trans* to N), $^{2}J_{Pt\text{-}H}$: 70.2 Hz], 0.65 [s, 3H, Pt-CH_3 (*trans* to I), $^{2}J_{Pt\text{-}H}$: 73.7 Hz]. ^{1}H NMR (400 MHz, nitrobenzene-d_5, 27 °C) δ/ppm: 8.83 (d, 2H, $^{3}J_{H\text{-}H}$: 6.4 Hz, $^{3}J_{Pt\text{-}H}$: 19.9 Hz), 7.61 (d, 2H), 7.09 (d, 2H), 3.96 (s, 6H, OCH_3), 1.77 [s, 6H, $PtCH_3$ (*trans* to N), $^{2}J_{Pt\text{-}H}$: 70.5 Hz], 0.86 [s, 3H, $PtCH_3$ (*trans* to I), $^{2}J_{Pt\text{-}H}$: 73.0 Hz]. MS (ESI-TOF) $[PtMe_3(4\text{-MeObipy})]^+$ *m/z* 456.1238 (calcd 456.1245). Anal. calcd. for $C_{15}H_{21}IN_2O_2Pt$ (583.33 g.mol^{-1}): C: 30.89, H: 3.63, N: 4.80. Found: C: 30.78, H: 3.76, N: 4.72%.

Synthesis of [$PtMe_3$(4-Me_2Nbipy)I]: 132 mg of 4-Me_2Nbipy (0.55 mmol) was added to a stirred solution of trimethylplatinum iodide (200 mg, 0.54 mmol) in benzene (15 mL) and the reactants were stirred at room temperature for 1 h, after which the resultant pale yellow solid of [$PtMe_3$(4-Me_2Nbipy)I] was isolated, washed several times with *n*-hexane and dried in vacuum. Yield: 286 mg (0.47 mmol, 87%). Also, 1:1 mixture of trimethylplatinum iodide and 4-Me_2Nbipy in benzene on standing for few days afforded yellow colored single crystals of the complexes. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ/ppm: 8.46 (d, 2H, $^{3}J_{H\text{-}H}$: 6.6 Hz, $^{3}J_{Pt\text{-}H}$: 20.0 Hz), 7.14 (d, 2H), 6.68 (dd, 2H), 3.16 [s, 12H, $N(CH_3)_2$], 1.40 [s, 6H, $PtCH_3$ (*trans* to N), $^{2}J_{Pt\text{-}H}$: 69.6 Hz], 0.68 [s, 3H, $PtCH_3$ (*trans* to I), $^{2}J_{Pt\text{-}H}$: 74.9 Hz]. ^{1}H NMR (400 MHz, nitrobenzene-d_5, 27 °C) δ/ppm: 8.50 (d, 2H, $^{3}J_{H\text{-}H}$: 6.6 Hz, $^{3}J_{Pt\text{-}H}$: 20.0 Hz), 7.16 (d, 2H), 6.58 (dd, 2H), 3.04 [s, 12H, $N(CH_3)_2$], 1.76 [s, 6H, $PtCH_3$ (*trans* to N), $^{2}J_{Pt\text{-}H}$: 69.5 Hz], 0.97 [s, 3H, $PtCH_3$ (*trans* to I), $^{2}J_{Pt\text{-}H}$: 74.2 Hz]. MS (ESI-TOF) $[PtMe_3(4\text{-}Me_2Nbipy)]^+$ *m/z* 482.1871 (calcd 482.1878). Anal.

calcd. for$C_{17}H_{27}IN_4Pt$ (609.42 g.mol^{-1}): C: 33.51, H: 4.47, N: 9.19. Found: C: 33.66, H: 4.29, N: 8.96%.

^{1}H NMR spectroscopic data of [PtMe$_3$(bipy)I]: ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ/ppm: 9.02 (d, 2H, $^3J_{H-H}$: 6.1 Hz, $^3J_{Pt-H}$: 17.8 Hz), 8.23 (d, 2H), 8.07 (m, 2H), 7.64 (m, 2H), 1.56 [s, 6H, $PtCH_3$ (*trans* to N), $^2J_{Pt-H}$: 70.5 Hz], 0.64 [s, 3H, $PtCH_3$ (*trans* to I), $^2J_{Pt-H}$: 73.1 Hz]. ^{1}H NMR (400 MHz, nitrobenzene-d_5, 27 °C) δ/ppm: 9.08 (d, 2H, $^3J_{H-H}$: 6.4 Hz, $^3J_{Pt-H}$: 18.5 Hz), 8.33 (d, 2H), 8.08 (m, 2H), 7.67 (m, 2H), 1.81 [s, 6H, $PtCH_3$ (*trans* to N), $^2J_{Pt-H}$: 70.5 Hz], 0.78 [s, 3H, $PtCH_3$ (*trans* to I), $^2J_{Pt-H}$: 72.6 Hz].

^{1}H NMR spectroscopic data of [PtMe$_3$(py)$_2$I]: ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ/ppm: 8.80 (d, 4H, $^3J_{H-H}$: 4.9 Hz, $^3J_{Pt-H}$: 17.3 Hz), 7.85 (t, 4H),7.35 (t, 2H), 1.50 [s, 6H, $PtCH_3$ (*trans* to N), $^2J_{Pt-H}$: 70.3 Hz], 1.20 [s, 3H, $PtCH_3$ (*trans* to I), $^2J_{Pt-H}$: 69.6 Hz]. ^{1}H NMR (400 MHz, nitrobenzene-d_5, 27 °C) δ/ppm: 8.93 (d, 4H, $^3J_{H-H}$: 5.5 Hz, $^3J_{Pt-H}$: 18.0 Hz), 7.88 (t, 4H), 7.37 (t, 2H), 1.70 [s, 6H, $PtCH_3$ (*trans* to N), $^2J_{Pt-H}$: 70.4 Hz], 1.29 [s, 3H, $PtCH_3$ (*trans* to I), $^2J_{Pt-H}$: 68.9 Hz].

^{1}H NMR spectroscopic data of [PtMe$_3$(4-Mepy)$_2$I]: ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ/ppm: 8.61 (d, 4H, $^3J_{H-H}$: 6.4 Hz, $^3J_{Pt-H}$: 19.0 Hz), 7.12 (d, 4H, $^3J_{H-H}$: 6.0 Hz), 2.38 (s, 6H, CH_3), 1.45 [s, 6H, $PtCH_3$ (*trans* to N), $^2J_{Pt-H}$: 70.0 Hz], 1.17 [s, 3H, $PtCH_3$ (*trans* to I), $^2J_{Pt-H}$: 70.0 Hz]. ^{1}H NMR (400 MHz, nitrobenzene-d_5, 27 °C) δ/ppm: 8.73 (d, 4H, $^3J_{H-H}$: 6.4 Hz, $^3J_{H-Pt}$: 19.1 Hz), 7.12 (d, 4H, $^3J_{H-H}$: 5.9 Hz), 2.28 (s, 6H, CH_3), 1.69 [s, 6H, $PtCH_3$ (*trans* to N), $^2J_{Pt-H}$: 70.1 Hz], 1.28 [s, 3H, $PtCH_3$ (*trans* to I), $^2J_{Pt-H}$: 69.2 Hz].

^{1}H NMR spectroscopic data of [PtMe$_3$(4-MeOpy)$_2$I]: ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ/ppm: 8.58 (d, 4H, $^3J_{H-H}$: 7.0 Hz, $^3J_{Pt-H}$: 19.0 Hz), 6.80 (d, 4H), 3.89 (s, 6H, OCH_3), 1.42 [s, 6H, $PtCH_3$ (*trans* to N), $^2J_{Pt-H}$: 70.0 Hz], 1.15 [s, 3H, $PtCH_3$ (*trans* to I), $^2J_{Pt-H}$: 70.2 Hz]. ^{1}H NMR (400 MHz, nitrobenzene-d_5, 27 °C) δ/ppm: 8.70 (d, 4H, $^3J_{H-H}$: 6.8 Hz, $^3J_{H-Pt}$: 19.1 Hz), 6.79 (d, 4H), 3.81 (s, 6H, OCH_3), 1.69 [s, 6H, $PtCH_3$ (*trans* to N), $^2J_{Pt-H}$: 70.2 Hz], 1.29 [s, 3H, $PtCH_3$ (*trans* to I), $^2J_{Pt-H}$: 69.4 Hz].

^{1}H NMR spectroscopic data of [PtMe$_3$(4-Me$_2$Npy)$_2$I]: ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ/ppm: 8.29 (d, 4H, $^3J_{H-H}$: 7.2 Hz, $^3J_{Pt-H}$: 19.6 Hz), 6.40 (d, 4H), 3.02 [s, 12H, $N(CH_3)_2$], 1.35 [s, 6H, $PtCH_3$ (*trans* to N), $^2J_{Pt-H}$: 69.3 Hz], 1.14 [s, 3H, $PtCH_3$ (*trans* to I), $^2J_{Pt-H}$: 71.5 Hz]. ^{1}H NMR (400 MHz, nitrobenzene-d_5, 27 °C) δ/ppm: 8.38 (d, 4H, $^3J_{H-H}$: 6.9 Hz, $^3J_{H-Pt}$: 19.4 Hz), 6.28 (d, 4H), 2.89 [s, 12H, $N(CH_3)_2$], 1.70 [s, 6H, $PtCH_3$ (*trans* to N), $^2J_{Pt-H}$: 69.3 Hz], 1.33 [s, 3H, $PtCH_3$ (*trans* to I), $^2J_{Pt-H}$: 70.6 Hz].

Crystal structure determinations: Diffraction data for the complexes [PtMe$_3$(L-L)I] (L-L = 4-Mebipy, 4-MeObipy and 4-Me$_2$Nbipy) were collected on a STOE IPDS diffractometer (Karlsruher Glastechnisches Werk). MoK_α radiation (λ = 0.71073 Å) was used. Frames were integrated with *STOE* software package.[35] Multi-scan absorption correction was applied.[36] The structures were solved with the program *Superflip*[37] and refined by full-matrix least squares on F^2 using the *WinGX*[38] software equipped with *SHELXL-2014*.[39] All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were calculated to their optimal positions and treated as riding atoms using isotropic displacement parameters 1.2 larger than the respective host atoms. The asymmetric unit of [PtMe$_3$(4-Me$_2$Nbipy)I] contains disordered solvent molecule, which could not be modeled as discrete atomic sites. So the structure was subjected to the *SQUEEZE* procedure from the *PLATON* suite to calculate the diffraction contribution of the solvent molecules and thereby produce a set of solvent-free diffraction intensities. A void volume of 138 Å^3 contains approximately 41 electrons. Prior to *SQUEEZE*, all non-hydrogen atoms were made anisotropic and all hydrogen atoms were inserted at their calculated positions. Details of the *SQUEEZE* procedure are given in the CIF file. X-ray crystallographic data and structural refinement parameters for the complexes are listed in Table 1. The *ORTEP* figures were drawn using the program *Mercuryv3.3*.[40] CCDC numbers are 1418664-1418666.

^{1}H NMR spectroscopic studies on the reaction of mononuclear pyridine complexes[PtMe$_3$L$_2$I] (L = py, 4-Mepy, 4-MeOpy and 4-Me$_2$Npy) with corresponding 2,2´-bipyridine ligands L-L (L-L = bipy, 4-Mebipy, 4-MeObipy and 4-Me$_2$Nbipy): An equimolar mixture of mononuclear pyridine complexes [PtMe$_3$L$_2$I] and corresponding 2,2´-bipyridine ligands were dissolved in $CDCl_3$ and in nitrobenzene-d_5 in vials and the progress of the reactions

were monitored by sequential ^{1}H NMR measurements at room temperature at different time interval.

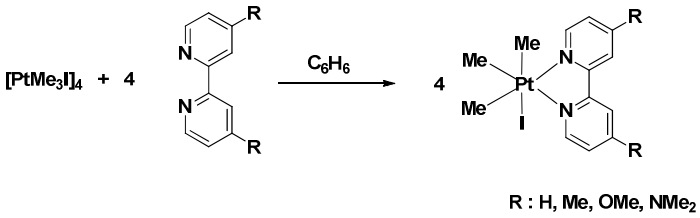
Table 1 Crystallographic data and structure refinement for [PtMe$_3$(L-L)I] (L-L = 4-Mebipy, 4-MeObipy and 4-Me$_2$Nbipy) complexes

Complex	**[PtMe$_3$(4-Mebipy)I]·0.5(C$_6$H$_6$)**	**[PtMe$_3$(4-MeObipy)I]**	**[PtMe$_3$(4-Me$_2$Nbipy)I]**
CCDC No.	1418664	1418665	1418666
Empirical formula	$C_{18}H_{24}IN_2Pt$	$C_{15}H_{21}IN_2O_2Pt$	$C_{17}H_{27}IN_4Pt$
Formula weight	590.38	583.33	609.42
T /K	193(2)	193(2)	193(2)
λ /Å	0.71073	0.71073	0.71073
Crystal color, shape	yellow, block	yellow, block	yellow, block
Crystal size/mm^3	0.330x0.300x0.290	0.270x0.250x0.220	0.580x0.240x0.160
Crystal system	Monoclinic	Monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$Pcan$
a /Å	11.8248(12)	11.1515(11)	13.7054(11)
b /Å	8.3843(7)	11.6097(15)	17.6237(14)
c /Å	19.403(2)	13.6162(14)	18.1731(16)
α /°	90	90	90
β /°	96.794(12)	103.077(12)	90
γ /°	90	90	90
V /Å^3	1910.2(3)	1717.1(3)	4389.5(6)
Z	4	4	8
$D_{calc.}$ (g cm^{-3})	2.053	2.256	1.844
μ /mm^{-1}	8.961	9.975	7.804
$F(000)$	1108	1088	2303
θ /°	3.22 to 25.25	2.68 to 25.25	2.19 to 25.50
Completeness to θ_{full}	97.8%	97.5%	99.0 %
Reflections collected	12605	11671	20808
Independent reflections	3381 [R_{int} = 0.0320]	3041 [R_{int}= 0.0423]	4046 [R_{int}= 0.0821]
Data/restraints/parameters	3381/0/206	3041/12/196	4046/0/216
Goodness-of-fit on F^2	1.040	0.998	0.860
Final R indices [I>2σ(I)]	R_1 = 0.0236, wR_2 = 0.0561	R_1 = 0.0321, wR_2 = 0.0703	R_1 = 0.0521, wR_2 = 0.1096
R indices (all data)	R_1 = 0.0269, wR_2 = 0.0561	R_1 = 0.0381, wR_2 = 0.0723	R_1 = 0.1110, wR_2 = 0.1244
Largest diff. peak and hole/eÅ^{-3}	1.254, -0.664	1.848, -2.262	1.499, -1.060

Result and Discussion

The mononuclear pyridine complexes [PtMe$_3$L$_2$I] (L = py, 4-Mepy, 4-MeOpy, 4-Me$_2$Npy) were synthesized by the reaction of trimethylplatinum(IV) iodide with pyridine ligands, following literature methods.[32-34] On the other hand, the pale-yellow to yellow crystalline mononuclear trimethylplatinum(IV) bipyridine complexes, [PtMe$_3$(L-L)I] (L-L = bipy, 4-Mebipy, 4-MeObipy, 4-Me$_2$Nbipy) were obtained in 84-87% yield through treatment of trimethylplatinum iodide with

2,2′-bipyridine ligands in equimolar ratio (Scheme 2). Among these complexes, $[PtMe_3(bipy)I]$ was synthesized according to a literature method.[34] The synthesized pyridine and bipyridine complexes are soluble in nitrobenzene, chloroform. They have been characterized by ^{1}H NMR spectroscopy, elemental analyses, mass spectroscopy and single-crystal X-ray diffraction analysis. Full synthetic and analytical data of the newly synthesized bipyridine complexes are given in the experimental section. ^{1}H NMR spectroscopic data of the mononuclear pyridine complexes and $[PtMe_3(bipy)I]$ are also given in the experimental section.



Scheme 2 Syntheses of mononuclear trimethylplatinum(IV) iodide complexes of bipyridines.

The room temperature ^{1}H NMR spectra of all the synthesized bipyridine complexes exhibit sharp, well resolved signals. The ^{1}H NMR spectra of the bipyridine complexes in $CDCl_3$ and in nitrobenzene-d_5 at room temperature are given in the supporting information. The platinum-methyl region in all the complexes exhibit two signals, each with two satellites due to ^{195}Pt-H scalar coupling, in an intensity ratio 2:1, reveals the presence of two non-equivalent methyl groups in the complexes: equatorial methyl (*trans* to bipyridines) and axial methyl (*trans* to iodide ligand) environments. The $^2J_{Pt\text{-}H}$ scalar coupling constants observed for the methyl groups *trans* to iodide ligands were higher than for the methyl groups *trans* to bipyridines, which indicates that the bipyridines exert stronger *trans* influence than iodide. For the bipy complex, the aromatic region comprised of four signals while it is three for the 4,4′-disubstituted 2,2′-bipyridine complexes. The highest frequency signal in each of the complexes displayed measurable ^{195}Pt coupling by virtue of its proximity to the metal-coordinated nitrogen. Similar to the bipyridine complexes, the platinum-methyl region in the mononuclear pyridine complexes also exhibit well-resolved, sharp signals (with satellites) for the two different types of methyl groups (*trans* to pyridine ligands and *trans* to iodide ligands) in an intensity ratio 2:1.[32] ESI-MS analysis of synthesized bipyridine complexes showed that the most abundant *m/z* value corresponds to the loss of iodide, giving $[PtMe_3(L\text{-}L)]^+$ (L-L = bipyridines). In addition, the

isotope patterns observed for each of the complexes were consistent with those calculated for the formulated species.

X-ray crystallographic characterization of the complexes, [$PtMe_3$(L-L)I] (L-L = 4-Mebipy, 4-MeObipy and 4-Me_2Nbipy)

Single crystals of [$PtMe_3$(4-MeObipy)I] were obtained by slow diffusion of *n*-hexane into its chloroform solution, while single crystals of [$PtMe_3$(4-Mebipy)I] and [$PtMe_3$(4-Me_2Nbipy)I] were separated from the solution when 1:1 mixture of trimethylplatinum(IV) iodide and corresponding bipyridine ligands in benzene were left undisturbed for few days. Complexes [$PtMe_3$(4-Mebipy)I] and [$PtMe_3$(4-MeObipy)I] were crystallize in monoclinic crystal system, whereas [$PtMe_3$(4-Me_2Nbipy)I] crystallizes in orthorhombic crystal system. Selected bond distances and angles of the complexes are given in Table S1 in the supporting information. The crystal structure of [$PtMe_3$(4-Mebipy)I] contains molecule of the crystallization solvent (benzene) in the crystal lattice. The crystal structure of all the complexes consists of a discrete monomeric unit in which the platinum atom is hexa-coordinated by the three methyl groups in a *facial* arrangement, a 2,2′-bipyridine ligand in a *bidentate* fashion and an iodine atom (see Fig. 1). The platinum(IV) metal center in all the complexes exhibits distorted octahedral geometry with intra-ligand bite angle (N1-Pt1-N2) in the range 75.9(4)-76.42(13)°. The structure of [$PtMe_3$(4-MeObipy)I] was found to be closely related to the previously reported structure [$PtMe_3$(bipy)(OAc)].(H_2O) in which the primary coordination sphere of the platinum atom was also built up by three methyl ligands in *facial* binding fashion, a bipyridine ligand and a monodentate acetate ligand.[25] The N1-Pt1-N2 bite angle in the complexes is close to the value found in [$PtMe_3$(bipy)(OAc)].(H_2O) (76.7°),[25] [$PtMe_3$(bipy)I] (76.5°),[23] [$PtMe_3$(bipy)Br] (76.6°),[24] [$PtMe_3$(bipy)(pydz)][BF_4] (75.3°),[22] [$PtMe_3$(terpy)I] (76.1°).[41]

The Pt-N bond distances in all the structures do not differ significantly (2.12-2.16 Å). Similar feature of almost equal Pt-N bond distances also observed in previously reported bipyridine complexes[23-26] and is in contrast to the situation found for the mononuclear trimethylplatinum(IV)-terpyridine complexes where the metal-nitrogen bond distance to the central pyridine ring is longer than the corresponding distance to the outer ring.[41, 42] This shows

that the Pt-N bond distances in the bipyridine complexes are not influenced significantly by the electronic effect of the bipyridine substituent as observed in the case of pyridine substituent.[32, 33] However, the Pt-N bond distances in the bipyridine complexes are marginally shorter than the Pt-N bond distances in the corresponding pyridine complexes,[32, 33] reflecting the better π acceptor character of the bipyridines compared to the pyridines. The Pt-I bond distance in all the structures is almost the same. All other key bond distances and angles (see Table S1 in the supporting information) are very much comparable to the value for the previously reported mononuclear trimethylplatinum(IV)-bipyridine complexes.[22, 25]

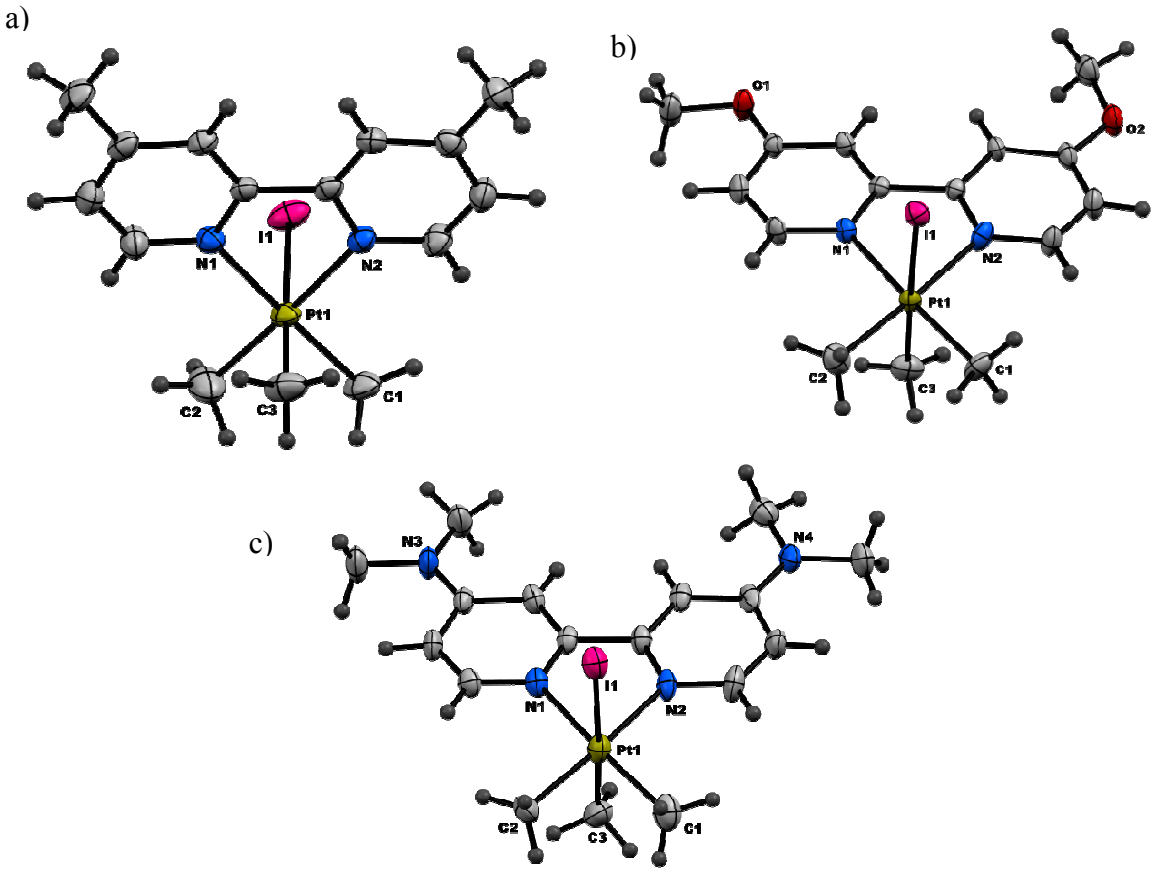
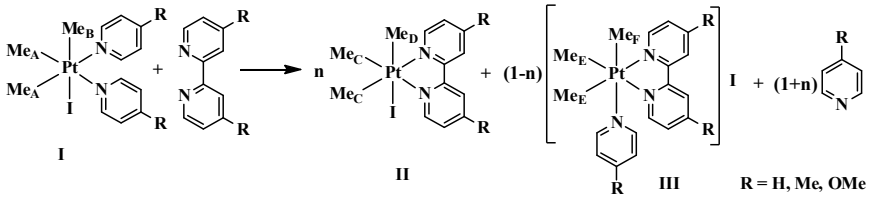


Fig. 1 ORTEP plots of crystal structures of [$PtMe_3$(4-Mebipy)I] (a), [$PtMe_3$(4-OMebipy)I] (b) and [$PtMe_3$(Me_2N-bipy)I] (c) showing the atom labelling scheme. In case of [$PtMe_3$(4-Mebipy)I], solvated benzene molecule omitted for clarity.

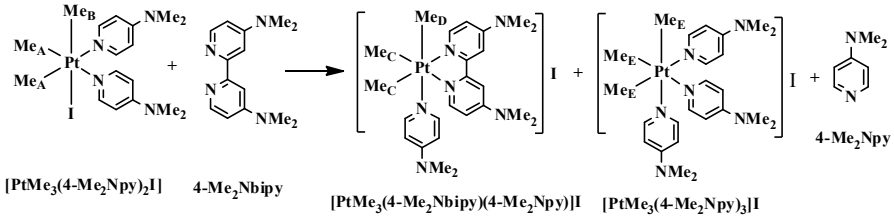
Reaction of mononuclear pyridine complexes [$PtMe_3L_2I$] (L = py, 4-Mepy, 4-MeOpy, 4-Me_2Npy) with corresponding 2,2′-bipyridine ligands L-L (L-L = bipy, 4-Mebipy, 4-OMebipy and 4-Me_2Nbipy): Ligand-Exchange study

Reaction of mononuclear pyridine complexes [$PtMe_3L_2I$] (L = py, 4-Mepy, 4-MeOpy, 4-Me_2Npy) with the corresponding 2,2′-bipyridines L-L (L-L = bipy, 4-Mebipy, 4-MeObipy and 4-Me_2Nbipy) in both the solvents ($CDCl_3$ and nitrobenzene-d_5) leads to the substitution of pyridines by the corresponding bipyridine ligands, thereby resulting in the formation of more stable chelate bipyridine complexes. The progress of each of the four ligand substitution reactions was monitored by sequential NMR spectroscopic measurements until the population of the pyridine and bipyridine complexes changes extremely slowly; however, true thermodynamic equilibrium is most likely not achieved within a reasonable time period in these reaction mixtures due to the inertness of the platinum(IV) complexes. The ^{1}H NMR spectra of an equimolar mixture of pyridine complexes and the corresponding 2,2′-bipyridine ligands, measured at room temperature, exhibit well resolved signals for the three trimethylplatinum(IV) complexes (pyridine complex [$PtMe_3L_2I$] (**I**), two chelate bipyridine complexes [$PtMe_3$(L-L)I] (**II**) and [$PtMe_3$(L-L)L]I (**III**)), free pyridine ligand L, and unreacted 2,2′-bipyridine ligand L-L (see Scheme 3). The ^{1}H NMR measurements of 1:1 reaction mixtures for the ligand-exchange reactions show that two chelate bipyridine complexes **II** and **III** are formed in solution (see Fig. 2); however, reaction of complex [$PtMe_3$(4-Me_2Npy)$_2$I] with the bipyridine ligand 4-Me_2Nbipy results in the formation of exclusively one chelate complex, [$PtMe_3$(4-Me_2Nbipy)(4-Me_2Npy)]I (**III**) (see Scheme 4). A very small traces of [$PtMe_3$(4-Me_2Npy)$_3$]I is also formed in solution. As expected, ^{1}H NMR spectra for each of the three trimethylplatinum(IV) complexes exhibit two platinum-methyl resonances with satellites, due to ^{195}Pt-H scalar coupling, with an intensity ratio of 2:1 (see Fig. 2 and supporting information). The individual components in the solution were identified by comparison with reference data for the pyridine and bipyridine complexes and free ligands.[32-34] The ^{1}H NMR spectrum of a 1:1 mixture of [$PtMe_3$(4-MeOpy)$_2$I] and 4-MeObipy at room temperature in nitrobenzene-d_5, measured after 7 days, is shown in Fig. 2, while ^{1}H NMR spectra of 1:1 mixture of [$PtMe_3$(4-Mepy)$_2$I] and 4-Mebipy at different time interval in nitrobenzene-d_5 are plotted in Fig. 3. The ^{1}H NMR spectra of other pyridine complexes and corresponding bipyridine ligands, measured at different time interval at room temperature, in

$CDCl_3$ and in nitrobenzene-d_5 are illustrated in supporting information. The ^1H NMR spectroscopic data for the ligand-exchange reactions in $CDCl_3$ and in nitrobenzene-d_5 are also reported in Table S2 in supporting information.



Scheme 3 The substitution of pyridine ligands by the corresponding 2,2′-bipyridines in trimethylplatinum(IV) iodide complexes.



Scheme 4 The substitution of 4-Me_2Npy by 4-Me_2Nbipy in trimethylplatinum(IV) iodide complex.

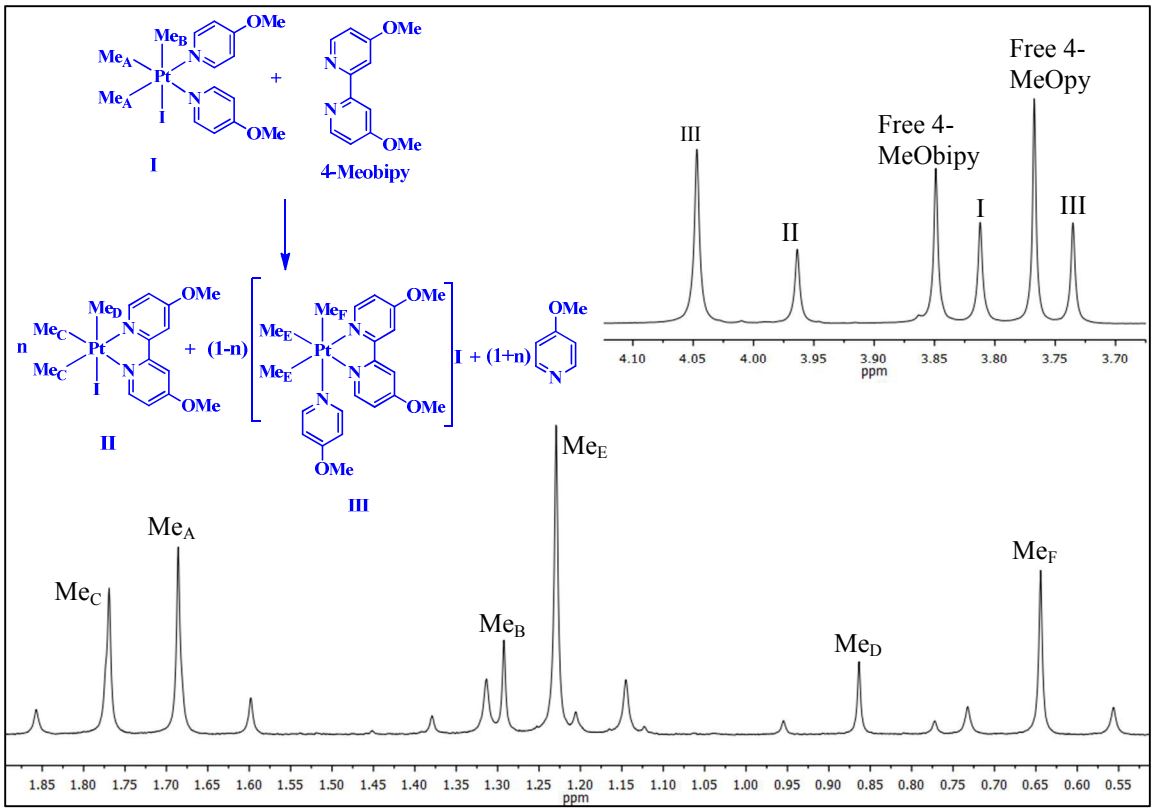


Fig. 2 The platinum-methyl region in the ^1H NMR spectrum (measured after 7 days) of 1:1 mixture of $[PtMe_3(4\text{-MeOpy})_2I]$ and 4-MeObipy in nitrobenzene-d_5 at room temperature, showing presence of three

platinum(IV) complexes [$PtMe_3$(4-MeOpy)$_2$I] (**I**), [$PtMe_3$(4-MeObipy)I] (**II**) and [$PtMe_3$(4-MeObipy)(4-MeOpy)]I (**III**) in solution. Inset showing the methoxy region for the spectrum. The signal at the left correspond to the methoxy group of 4-MeObipy in complex **III**, while the signal at the utmost right correspond to the methoxy group of 4-MeOpy in **III**.

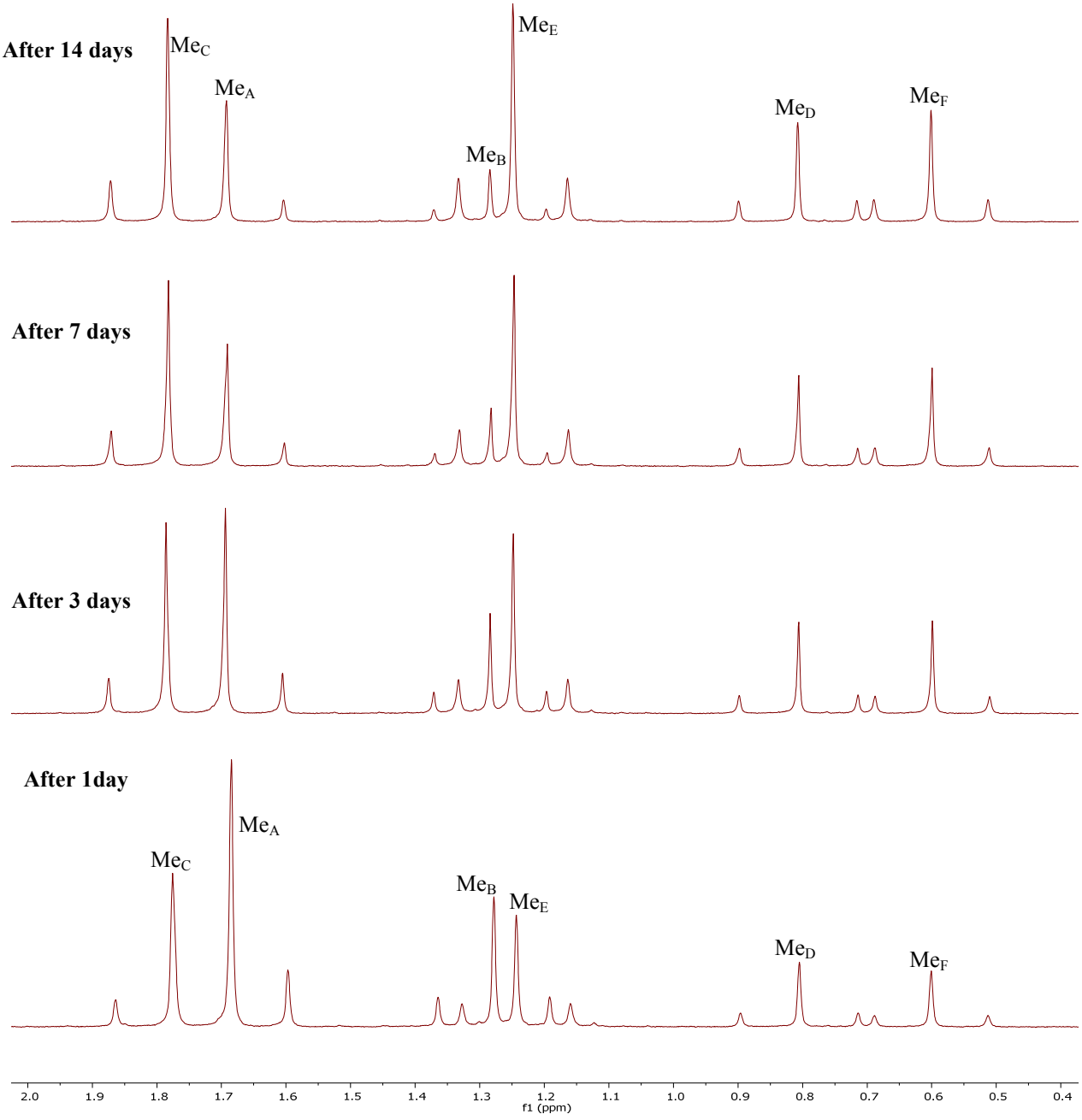


Fig. 3 The platinum-methyl region in the ^{1}H NMR spectrum of 1:1 mixture of [$PtMe_3$(4-Mepy)$_2$I] and 4-Mebipy in nitrobenzene-d_5 at 300 K at different time interval, showing presence of three platinum(IV) complexes **I**, **II** and **III** in solution. For labelling of methyl groups, see Scheme 2.

An analysis of Table S2 in the supporting information shows that on changing the solvent from $CDCl_3$ to nitrobenzene-d_5, the platinum-methyl resonance shifted to higher frequency in the ^1H NMR spectrum. The difference in chemical shifts for the two platinum-methyl resonances is larger in the bipyridine complexes than in the pyridine complexes. Moreover, chemical shift difference for the two platinum-methyl resonances is greater in the bipyridine complexes **II** ([$PtMe_3$(L-L)I] (L-L = 2,2′-bipyridines)) than in bipyridine-pyridine complexes **III** ([$PtMe_3$(L-L)L]I where L-L = 2,2′-bipyridines, L = corresponding pyridines) complexes. The $^2J_{Pt\text{-}H}$ scalar coupling constants *trans* to bipyridines are lower than to the corresponding pyridines in **III**, which indicates that the *trans* influence of the 2,2′-bipyridines is stronger than the corresponding pyridines (*trans* influence: bipy>py, 4-Mebipy>4-Mepy, 4-MeObipy>4-MeOpy, 4-Me_2Nbipy>4-Me_2Npy).

Table 2 Population of different Pt(IV) complexes in 1:1 mixture of [$PtMe_3L_2I$] (L= pyridines) and corresponding 2,2′-bipyridines (L-L) at different time interval at 300 K in $CDCl_3$ and in nitrobenzene-d_5

Substitution of pyridine ligands by 2,2′-bipyridines	Reaction time	In $CDCl_3$		In nitrobenzene-d_5	
		Bipyridine complexes (**II** + **III**) /pyridine complex (**I**)	Bipyridine Complex **III** /bipyridine Complex **II**	Bipyridine complexes (**II** + **III**) /pyridine complex (**I**)	Bipyridine Complex **III** /bipyridine Complex **II**
py by bipy	after 1d	1.65	0.08	1.17	0.50
	after 3d	4.05	0.11	3.06	0.56
	after 7d	10.63	0.17	8.26	0.56
	after 14d	15.67	0.19	13.28	0.55
4-Mepy by 4-Mebipy	after 1d	1.12	0.30	0.96	0.85
	after 3d	2.66	0.43	1.90	0.98
	after 7d	9.20	0.60	3.37	1.11
	after 14d	12.16	0.65	4.00	1.10
4-MeOpy by 4-MeObipy	after 1d	0.88	1.00	0.62	1.82
	after 3d	2.40	1.40	1.32	1.87
	after 7d	7.55	1.68	2.60	2.19
	after 14d	8.52	1.98	3.29	2.24
4-Me_2Npy by 4-Me_2Nbipy	after 1d	1.86	only **III** present[a]	3.85	only **III** present[a]
	after 3d	7.06	only **III** present[a]	9.31	only **III** present[a]
	after 7d	10.36	only **III** present[a]	12.51	only **III** present[a]
	after 14d	19.00	only **III** present[a]	15.67	only **III** present[a]

[a]In the case of the substitution of 4-Me_2Npy by 4-Me_2Nbipy, only the bipyridine complex [$PtMe_3$(Me_2N-bipy)(4-Me_2Npy)]I is present in solution.

The population ratios of the bipyridine complexes to the pyridine complexes and the relative population of different bipyridine complexes for the reaction of 1:1 mixture of mononuclear pyridine complexes and corresponding 2,2′-bipyridine ligands in two different solvents ($CDCl_3$ and nitrobenzene-d_5) at different time intervals are tabulated in Table 2. The compositions of the platinum(IV) complexes at different time intervals for all the four ligand-exchange reactions are also given in Tables S3-S10 in the supporting information. Inspection of the data in Table 2 immediately shows that the solution speciation in both the solvents strongly favours the formation of chelate bipyridine complexes over the non-chelate pyridine complexes for all the four ligand-exchange reactions, which reveals that the bipyridine complexes are thermodynamically more stable than the corresponding pyridine complexes. Although bipyridine complexes are more stable compared to the corresponding pyridine complexes as indicated from the population ratio of the bipyridine complexes to the corresponding pyridine complexes, a close analysis of Table 2 reveals that the speciation of the different platinum(IV) complexes in solution was found to be dependent on the nature of the substituent as well as on the type of solvent used for carrying out the reaction. As the electron donating property of the substituent increases from H to NMe_2, the population ratio of bipyridine-pyridine complex **III** to bipyridine complex **II** also increases in both the solvents. This can be rationalized in terms of the stability of complex **III** in solution. As the electron donating ability of the substituent increases, the electron density in both the pyridine and bipyridine ring nitrogen also increases which in turn causes an increase in the extent of Pt-N interaction in solution. This leads to an increase in the stability of complex **III** in solution and in the case of $–NMe_2$ substituent, the stability of complex **III** is so high (due to extremely strong Pt-N interaction) that exclusively $[PtMe_3(4\text{-}Me_2Nbipy)(4\text{-}Me_2Npy)]I$ is formed in solution. Furthermore, we have also found that for a particular substituent, the population ratio of **III** to **II** is higher in nitrobenzene-d_5 than in $CDCl_3$. This is supported by the fact that the complex **III** being ionic in nature is more stable in polar solvent (nitrobenzene-d_5) than in apolar solvent ($CDCl_3$). The strength of the chelate effect (determined from the population ratio of the chelate bipyridine complexes (**II** + **III**) to the non-chelate corresponding pyridine complexes **I** after keeping the reaction mixtures for 2 weeks at room temperature) for the different substituents in both the solvents is in the order: NMe_2 > H > Me > OMe. To explain the above order of chelation among the substituents (H, Me, and OMe), the stability of the reactant complexes in solution can also be taken into consideration. As the

electron donating ability of the substituent increases from H to OMe, the stability of the reactant non-chelate pyridine complexes also increases due to the increasing Pt-N interaction in the reactant complexes, thereby leading to a decrease in the strength of the chelate effect. Also, the strength of chelation for a particular substituent is greater in $CDCl_3$ than in nitrobenzene-d_5. This is most likely due to the lower solvent stabilization of the reactant pyridine complexes in $CDCl_3$ than in nitrobenzene-d_5. Investigation of the kinetics of the reactions (see Tables S3-S10 in the supporting information) also indicates that all the four ligand-exchange reactions are not proceeding to the same extent and advancement of the reactions depends on the substituent as well as on the nature of solvent. Compositions of the platinum(IV) complexes at different time intervals (see Tables S3-S10 in supporting information) show that for a strongly electron donating substituent such as $–NMe_2$, the progress of the ligand-exchange reaction is much faster compared to substituents like H, Me and OMe groups. Among H, Me and OMe groups, the ligand-exchange reactions follows the order: H > Me > OMe. The observed differences in the advancement of the reactions can again be explained on the basis of the stability of the reactant and product platinum(IV) complexes associated with Pt-N interactions. The advancement of the reaction for a particular substituent is found to be faster in $CDCl_3$ than in nitrobenzene-d_5. The sequential ^{1}H NMR measurements of the reaction mixtures also gives an idea regarding the mechanism of the above ligand substitution reactions. The composition of the platinum complexes reveals that both the bipyridine complexes **II** and **III** are forming at the same time, i.e., substitution of both the pyridines by the bipyridine ligand leading to the formation of bipyridine complex **II** as well as substitution of one iodide and one pyridine by the bipyridine ligands (for formation of bipyridine-pyridine complex **III**) found to take place at the same time; however, formation of bipyridine complexes **II** and **III** depends very much on the nature of the substituent as well as on the solvent. Increasing electron donating nature of the substituent leads to an increase in the affinity for the formation of bipyridine-pyridine complexes **III** in solution which is further enhanced in polar solvent due to better solvent stabilization.

Conclusion

Reaction of trimethylplatinum(IV) iodide with 2,2′-bipyridine ligands (bipy, 4-Mebipy, 4-Meobipy and 4-Me_2Nbipy) results in the formation of trimethylplatinum(IV)-bipyridine complexes. The complexes were characterized by ^{1}H NMR, elemental analysis, mass

spectroscopy and X-ray single crystal diffraction analysis. Also, the mononuclear trimethylplatinum(IV) iodide complexes of pyridines, $[PtMe_3L_2I]$ (L = py, 4-Mepy, 4-MeOpy, 4-Me_2Npy) undergo reaction with the corresponding 2,2′-bipyridines (bipy, 4-Mebipy, 4-MeObipy, 4-Me_2Nbipy) to form the chelate bipyridine complexes, $[PtMe_3(L\text{-}L)I]$ and $[PtMe_3(L\text{-}L)L]I$ (L-L = 2,2′-bipyridines, L = corresponding pyridines). Each of the four substitution reactions strongly favours the formation of chelate complexes. The formation of chelate bipyridine complexes in solution also found to be dependent on the electronic effect of the substituents. Increasing electron donating ability of the substituent leads to an increase in the stability of the $[PtMe_3(L\text{-}L)L]I$ in solution. The tendency for the chelation is very high for strong electron donating substituents such as NMe_2; however, for H and moderately electron donating substituents such as methyl and methoxy, increasing electron donating ability decreases the strength of the chelate effect. The nature of solvent also played a significant role in the solution speciation in the substitution reaction. As the polarity of the solvent increases, the stability of the bipyridine-pyridine complex $[PtMe_3(L\text{-}L)L]I$ also increases; however, the strength of chelation is greater in $CDCl_3$ than in nitrobenzene-d_5. Analysis of the kinetics of the ligand-exchange reactions shows that both the nature of the substituent and solvent played an important role in the advancement of the reactions. Investigation of the kinetics of the reactions also reveals that both the bipyridine complex $[PtMe_3(L\text{-}L)I]$ (formed through substitution of both the pyridine ligands by bipyridine ligand) and bipyridine-pyridine complex$[PtMe_3(L\text{-}L)I]$ (results via exchange of iodide and one pyridine ligand by bipyridine ligand) are formed at the same time.

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Graphical Abstract

A series of trimethylplatinum(IV) iodide complexes of 2,2′-bipyridine ligands have been synthesized and characterized. Also, exchange of pyridine ligands with 2,2′-bipyridines in trimethylplatinum(IV) iodide complexes have been studied. Substituent as well as solvent effects on the ligand-exchange studies have also been investigated.