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ARTICLE

Intramolecular Cyclization Assisted Oxidative Addition: Synthesis of Octahedral Cycloplatinated Methyl Complexes

Cite this: DOI: 10.1039/x0xx00000x

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Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Cycloplatinated of $\text{XMeC}_6\text{H}_4\text{C}\equiv\text{CC}-(\text{R}_f)$ ($\text{R}_f = \text{N-4-OCH}_3\text{C}_6\text{H}_4$) [$\text{X} = \text{S, Se}$ and $\text{R}_f =$ perfluoroalkyl groups] with PtCl_2 gave a monomeric platinum (IV) complex having an octahedral structure with one annulated heterocycles coordinated in a plane and other out of plane. The formation of platinum (IV) complex **2a**, confirmed by X-ray crystal structure, presumes simultaneous cyclization and oxidative addition of methyl chloride generated during the cyclization. The emission and reactivity study of platinum (IV) complexes is discussed.

Introduction

The oxidative addition reaction is one of the most fundamental processes in the catalytic reactions initiated by transition metals.¹ Though the oxidative addition of Pd^0 to Pd^{II} is well established process² compared to $\text{Pd}^{\text{II}}/\text{Pd}^{\text{IV}}$, numerous reports on the potential involvement of Pd^{IV} intermediates have been proposed in the catalysis and organic synthesis without definite evidences.^{3,4} In contrast to palladium chemistry, two electron oxidation and reduction reactions between Pt^0 , Pt^{II} and Pt^{IV} are an integral part of platinum chemistry and platinum, in lower oxidation state, dominates the oxidative reaction to its higher oxidation states.⁵ In this context, σ -alkyl complexes of platinum (II) have been thoroughly studied and demonstrated that coordinatively unsaturated 16-electron organoplatinum (II) complexes are highly amenable for the oxidative addition process to afford stable and inert coordinatively saturated 18-electron organoplatinum (IV) products.⁶ Further, the investigations suggest that diimines based nitrogen-donor ligands are far better than phosphine and arsine ligands in stabilizing the organoplatinum (IV) products due to favourable electronic and steric properties of nitrogen-donors.⁷

It has been also well studied that platinum (II) diimine complexes (2,2'-bipyridine or 1,10-phenanthroline) are extremely reactive towards the oxidative addition of alkyl halides⁸ and the oxidative addition of aryl halides can only takes place if the diimine ligand contains a pendant aryl-halogen bond (intramolecular oxidative addition).⁹ In contrast

to these reports, the examples on the intramolecular oxidative addition of alkyl/aryl halides are very rare.¹⁰

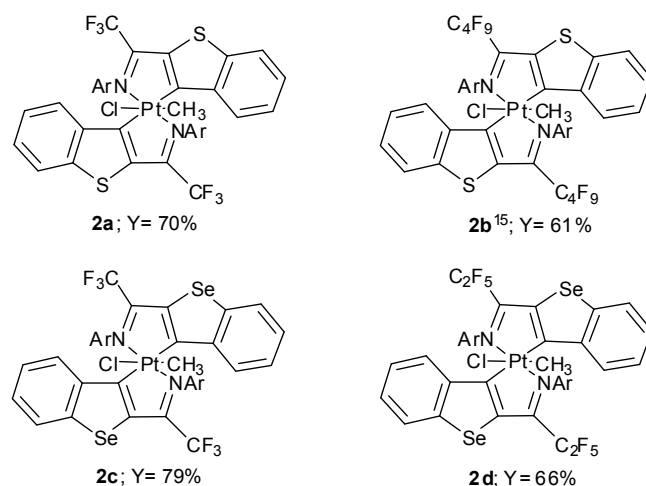
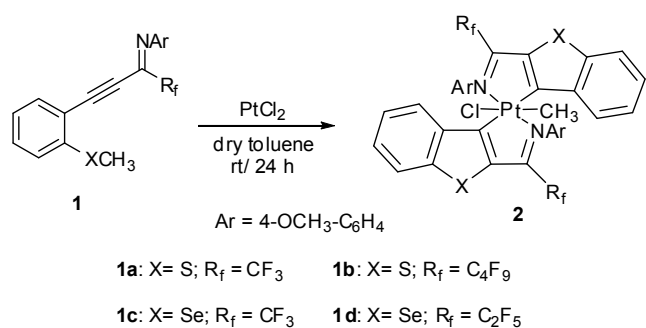
In our previous findings, we studied the intramolecular cyclizations of $o\text{-XMeC}_6\text{H}_4\text{C}\equiv\text{CC}-(\text{CF}_3)(\text{N-4-OCH}_3\text{C}_6\text{H}_4)$ where $\text{X} = \text{S}$ and Se , with $\text{PdCl}_2(\text{PhCN})_2$ to dimeric cyclopalladated benzothiophene and benzoselenophene.¹¹ Further, by changing the imine moiety with pyridine, we could successfully isolate the SCN pincer-type palladacycles.¹² The promising biological activities of palladacycles and their reactivity towards electrophiles encouraged us to investigate the further reactivity of propargyl imines with platinum metal. In continuation to our research interest in the synthesis of different metallocycles, we report here a cyclizations and platinacyclization of $o\text{-XMeC}_6\text{H}_4\text{C}\equiv\text{CC}-(\text{R}_f)(\text{N-4-OCH}_3\text{C}_6\text{H}_4)$ where $\text{X} = \text{S, Se}$ and $\text{R}_f =$ perfluoroalkyl groups with PtCl_2 to yield highly stable octahedral bis-ligated platinacycles. Interestingly, in the formation of octahedral platinacycles, Pt (II) get oxidise to Pt (IV) by oxidative addition of methyl group which was generated during the intramolecular cyclization.

Results and discussion

ortho thioanisole and *ortho* selenoanisole substituted perfluoroalkyl propargyl imines were prepared according to previously published results.¹³ The alkynes **1a**, **1b**, **1c**, and **1d** were obtained by palladium promoted Sonogashira coupling of corresponding perfluoroalkyl imidoyl iodides and the

corresponding alkynes.¹⁴ All the imines were fully characterised by ¹H NMR, ¹³C NMR and mass spectroscopy. Various platinum (II) salts were used to react with *ortho* thioanisole substituted perfluoromethyl propargyl imine **1a** to synthesise platinacycle (**2a**). However, the best yield of **2a** was achieved with platinum (II) dichloride. (Scheme 1) Thus, the reaction of *ortho* thioanisole substituted perfluoromethyl propargyl imine with excess PtCl₂ in dry toluene at room temperature for 24 h under N₂ atmosphere afforded air and water stable crude platinacycle as dark red solid which on subjected to column chromatography yielded 70% pure platinacycle (**2a**).

Though the preparation of all the platinacycles (**2a**, **2b**, **2c** and **2d**) were attempted at room temperature under rigorous nitrogen atmosphere, the aerobic atmosphere of the reaction afforded desired platinacycles along with inseparable unidentified compounds. In case of **2b**, the reaction of bulky perfluorobutyl propargyl imine (**1b**) with Pt(II)Cl₂ proceeded at high temperature (110 °C) with longer reaction time and afforded lesser yield compared to other platinacycles. The requirement of high temperature and longer reaction time might be due to the presence of bulky perfluorobutyl group.



Scheme 1 Preparation of platinacycle **2**.

All the platinacycles were characterised by ¹H NMR, ¹³C NMR, IR and CHN analysis. The ¹H NMR spectra of

platinacycles **2** containing S and Se shows two singlet peaks in the range of 3.6-3.9 and ¹³C NMR spectra shows peaks at 55.2 and 55.7 ppm correspond to methoxy group attached to phenyl ring. The ¹H NMR for methyl protons directly bonded to platinum atom shows a singlet with satellite peaks at around 1.97 to 2.20 ppm and ¹³C NMR shows around -6 to -7 ppm. Whereas all the propargyl imine ligands **1** show singlet peak at the range of 3.8-3.9 and 2.5 ppm corresponding to methoxy group attached to phenyl ring and methyl protons attached to sulphur or selenium. The ¹H NMR spectra of **2** clearly shows the absence of CH₃ signal of *o*-SCH₃C₆H₅ group after cyclization. Further, the change in chemical shift of ¹³C NMR of imine carbon atom (C=N) from 134 ppm to 159 ppm suggests the interaction of nitrogen to the platinum atom.¹⁶ The protons from the methyl group bonded to platinum center appeared at slightly down field (approx. 2.00 ppm) when compared to the proton from other methyl-platinum complexes (1.4-1.7ppm). In infrared study, the characteristic skeletal vibrations for alkyne ligands **1** were observed in the range of 2190-2000 cm⁻¹ which were absent after the formation of platinacycle **2**.

The dark reddish-yellow single crystal suitable for the X-ray single crystal study was obtained by slow evaporation of platinacycle **2a** solution (CH₃OH/EtOAc in 50:50) in air after three weeks at room temperature. Platinacycle **2a** crystallizes in a monoclinic space group *P*2₁/*n* and clearly reveals the formation of a bis-ligated platinum(IV) with chloride ion and methyl group in an octahedral fashion. The C24 and N2 of the imine substituted benzothiophene is approximately planar with Pt1, whereas C8 and N1 of the other imine substituted benzothiophene adopts axial (planar with Pt1) and equatorial position with significant decrease in bond angle of C8-Pt1-N1 to 79.63(16). The angles between adjacent atoms in the coordination sphere of platinum lie in the range 79.63-177.32. (Fig. 1)

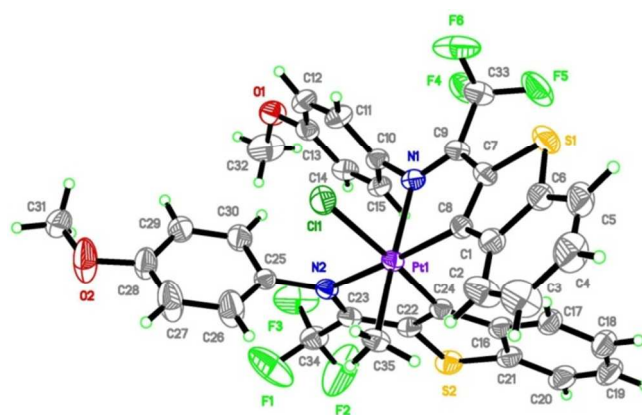
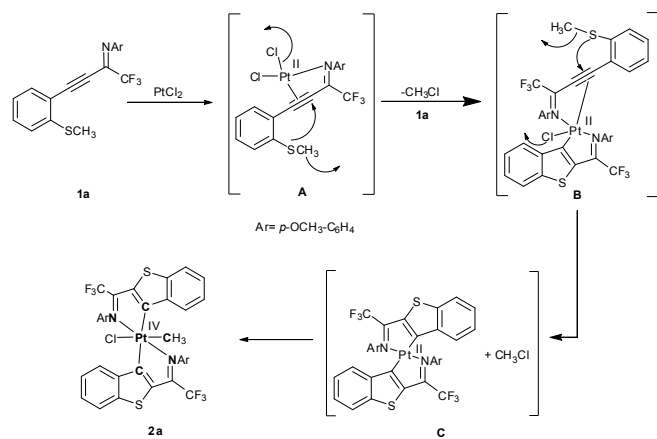


Fig. 1 The molecular structure of **2a**, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. Selected bond lengths[Å] and bond angles[°]: N1-Pt1 2.194(3), N2-Pt1 2.152(3), C8-Pt1 2.017(4),

C24-Pt1 2.008(4), C35-Pt1 2.090(4), C11-Pt1 2.3884(11); C8-Pt1-N1 79.63(16), C24-Pt1-N2 79.82(15), C35-Pt1-N1 177.32(15), C35-Pt1-C11 93.39(14).

The concerted intramolecular oxidative addition has been rarely known for the organoplatinum(II) complexes in the literature.^{17,10} The dissociation of one of the amine group prior to oxidative addition through *ortho*-metalation is the key step in the synthesis of Pt(IV) complexes. In the formation of platinacycle **2a**, we speculate that the first unit of **1a** initially reacts with Pt(II)Cl₂ through coordination of imine and alkyne bond with elimination of one equivalent methyl chloride.^{11b} In the later stage, second unit of **1a** reacts with intermediate **B** in a similar fashion to form intermediate **C**. The coordinatively unsaturated Pt(II) intermediate **C** tends to undergo oxidative addition by methyl chloride present in the reaction mixture to form a stable octahedral platinacycle coordinated by two diimines nitrogen, two benzothiophenes (at C3-position) and each chloride ion and methyl group. (Scheme 2)



Scheme 2. Plausible reaction mechanism for the formation of platinacycle.

In situ ESI mass spectrometry experiments were performed on the reaction mixture of propargyl imine **1a** and platinum dichloride (reaction was terminated at 12 h) to investigate the species generated during the reaction. It is easy to identify the Pt incorporate species in the mass spectrum by the specific isotopic pattern of Pt. The positive ion ESI mass spectrum (Figure 1, supporting information) showed platinum incorporated species above m/z 550, which indicates that only propargyl imine reacted (decomposition/dimerization) under given experimental conditions. The spectrum included three Pt containing ions; one major ion at m/z 878.09 (mass value of highest isotope) and two other abundant ions at m/z 602.07 and 638.04. The ion at m/z 878.09 identified as the species corresponding to platinum with bis-ligand and one methyl group (similar to the species **2a** in Scheme 2 without chlorine).

This is confirmed based on accurate mass values and isotopic pattern distribution (Table 1, supporting information). The identification of m/z 878.0894 species suggests that Pt(III) must be generated through the square planer Pt(II), **C** intermediate. The ion at m/z 602.07 matched to a platinum complex with one ligand, CH₃CN and CH₃OH (see supporting information). We assume that this ion is formed by replacement of two labile chlorides of PtCl₂ with cyclized propargyl imine, CH₃OH and CH₃CN (solvents used in ESI analysis). We could not propose a structure for the ion appeared at m/z 638.04.

The formation of platinacycle **2a** was investigated by absorption study. Initially, the absorption spectra for the reaction of ligand **1a** with Pt(II) Cl₂ was studied at time $t=0$; the uv-visible spectral changes occurred during the formation of **2a** are shown in Fig. 2. From Fig. 2, it was noticed that there was an increase in absorption peak near 260 nm and a decrease in absorption peak near 230 nm in the complex **2a** when compared to ligand **1a** which indicates increase in conjugation of ligand (hetero-annulation of ligand **1a**) in the UV region. This absorption band indicates that bis-ligated platinum complex with two discrete ligands bound to one metal centre favours high conjugation to yield the peak position at lower energy and this band can traditionally be assigned as MLCT (Metal-Ligand Charge Transfer).¹⁸

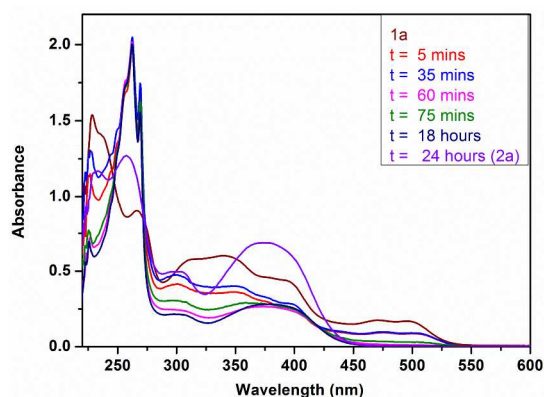


Fig. 2 In-situ UV-vis spectral changes during the formation of Pt(IV) complex **2a** at reaction time = 5 min, 35 min, 60 min, 75 min, 18h, 24 h. in CH₂Cl₂ solution (1.6×10^{-5} M).

We have observed an isosbestic point at 350 nm. All the ligands **1a**, **1b**, **1c** and **1d** do not absorb the light in the visible region (see SI), while the complexes **2a**, **2b**, **2c** and **2d** exhibit well-defined low energy absorption peak at 360-400 nm (near visible region) (Fig. 3).

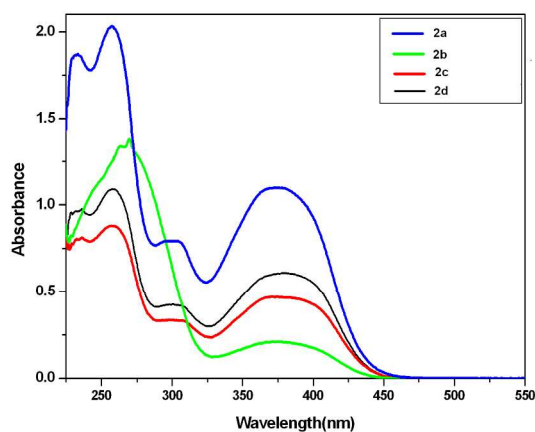


Fig. 3 UV-vis spectra of Pt(IV) complexes **2a**, **2b**, **2c** and **2d** in CH_2Cl_2 solution (2.4×10^{-4} M).

The redox properties of ligands and their platinum complexes were studied by cyclic and differential pulse voltammetry in CH_3CN containing 0.1 M TBAPF₆ at room temperature. Fig. 4 depicts representative differential pulse voltammogram of ligand **1a** and complex **2a**. The ligand **1a** showed one reversible oxidation wave at 1.72 V and two either reversible or quasireversible reduction potentials at -1.04 V and -1.47 V, while complex **2a** has also shown oxidation wave at 1.75 V and two reduction potentials at -1.03 V and -1.47 V. From the CV and DPV study, it can be concluded that both the ligands and complexes undergo either reversible or quasireversible oxidation and reduction reactions. We have observed similar electrochemistry in other ligands and complexes (See supporting information).

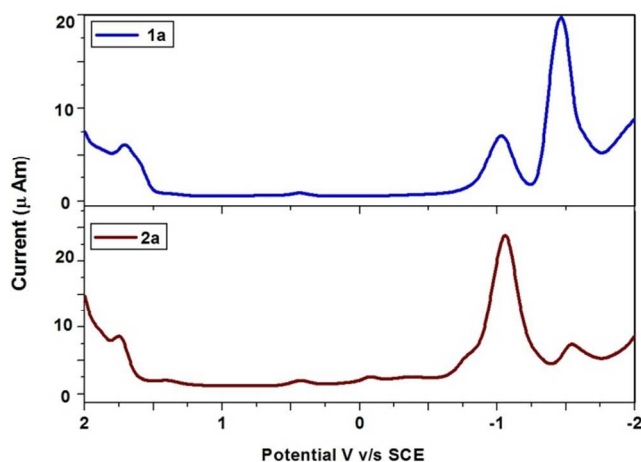


Fig. 4 Differential pulse voltammogram of ligand **1a** and platinumacycle **2a**.

The redox potentials of the ligand and its complex is indistinguishable and difficult to assign. Therefore, we have adopted a spectroelectrochemical technique to distinguish.

Using spectroelectrochemical technique, we could study both electrochemically reversible reduction and oxidation of organo platinum complexes.

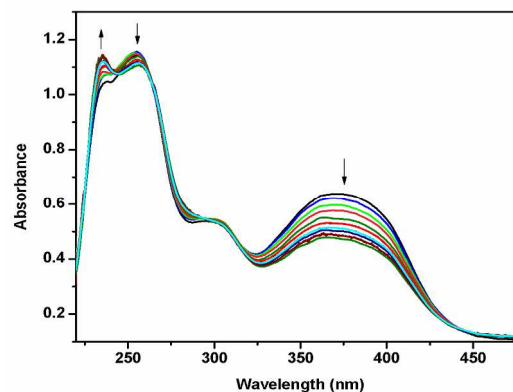


Fig. 5 In-situ UV-Visible absorption changes of Pt-complex **2a** at an applied potential of -1.30 V.

Fig. 5 shows the spectral changes of Pt(IV)-complex **2a** at controlled potential electrolysis. During the controlled potential reduction at -1.3 V, the intensity of absorption maxima at 235 nm increases while there was decrease in the absorption of the shoulder at 266 nm. The peak almost disappeared at 300 nm. The long wavelength MLCT band started decreasing its intensity at 350 nm. During this process, the isosbestic points were observed at 220, 250, 305 and 445 nm. The reduction was probably due to the conversion of Pt(IV) to Pt(III). When applied potential changes to -1.60 V, no changes were observed. Therefore the two reductions appeared at -1.03 and -1.47 V belong to both ligand and metal centered in complex **2a**.

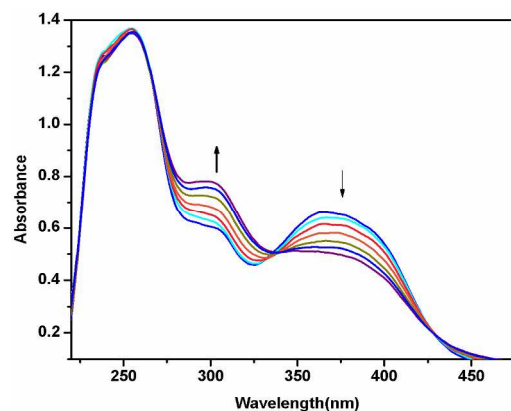


Fig. 6 In-situ UV-Visible absorption changes of Pt-complex **2a** at an applied potential of 1.80 V.

When applied potential was at 1.80 V, the longer wavelength MLCT band at 350 nm started decreasing in intensity as shown in Fig. 6. In contrast, the intraligand $\pi-\pi^*$ transitions at 300 nm

started increasing. The other intraligand absorption at 266 remained unchanged. During this process, clear isosbestic points were observed at 250 and 345 nm. As the oxidation of Pt(IV) to Pt(V) is not possible, the oxidations are probable and belong to ligand centered. Similar spectral changes were observed in other complexes during applied potential (See supporting information).

Emission study of platinacycles 2

We have carried out steady-state emission study of both ligands and Pt(IV) complexes in dichloromethane solvent at room temperature. We have collected the emission spectra of ligands by choosing the excitation wavelength at 270 nm as shown in Fig. 7. In all the four ligands, we have observed three emission peaks at 310, 353 and 372 nm with a stoke shift of 40 nm (Table 1). Fig. 8 demonstrates irradiation low-energy band (MLCT) of all Pt(IV) complexes at ambient temperature in dichloromethane solution. All the four complexes have shown emission maxima at around 425 nm with stoke shifts of 55-65 nm.

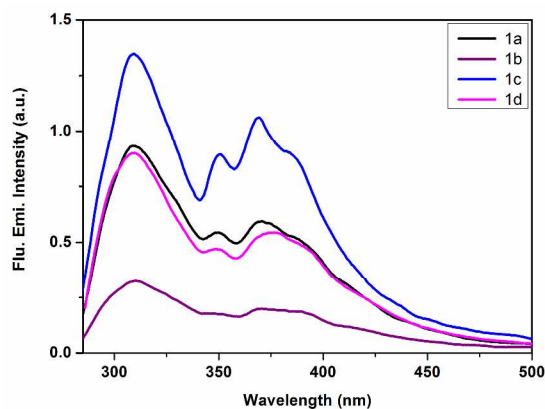


Fig. 7 Normalised emission spectra of ligands **1a**, **1b**, **1c** and **1d** in degassed CH_2Cl_2 solution (2.4×10^{-4} M) at 298K.

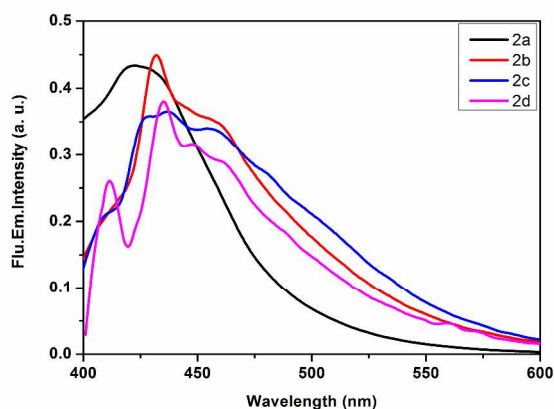


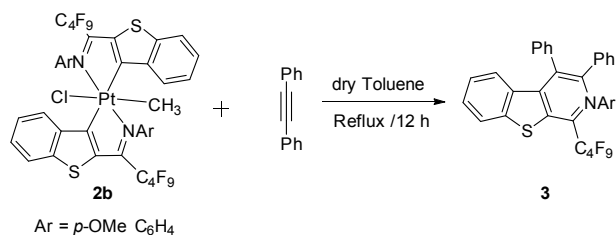
Fig. 8 Normalised emission spectra of platinacycles **2a**, **2b**, **2c** and **2d** in degassed CH_2Cl_2 solution (2.4×10^{-4} M) at 298K.

Table 1 The emission data of ligands **1** and platinacycles **2**.

Compounds	Absorption (nm)	Emission (nm)	Red shift (nm)
1a	270, 351	310, 353, 372	40
1b	227, 269	310, 354, 374	39
1c	269, 355	310, 353, 372	39
1d	228, 270, 345	310, 353, 373	40
2a	258, 371	425	54
2b	259, 380	435	55
2c	270, 373	438	65
2d	260, 380	436	56

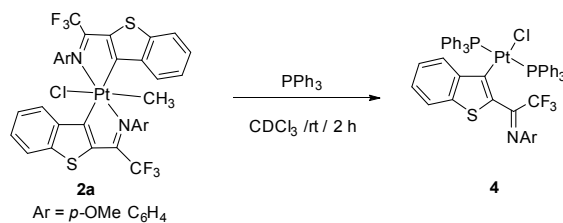
Reactivity of platinacycles 2

The insertion reactions of alkynes and carbon mono oxide have been extensively studied with dimeric palladacycles and platinacycles with the formation of expanded ring system.¹⁹ Here we investigated the reactivity of Pt(IV)-complex **2b** in the insertion of diphenyl acetylene. (Scheme 3) The mixture of complex **2b** and excess of diphenyl acetylene in dry toluene was refluxed for 12 h under nitrogen atmosphere to afford benzo[4,5]thieno[2,3c]pyridine skeletal in quantitative yield.



Scheme 3 Reactivity of platinacycle **2b** with diphenyl acetylene.

The reactivity of Pt(IV)-complex **2a** was further screened in the reaction with triphenyl phosphine. (Scheme 4) Interestingly, platinacycle (IV) complex **2a** was reduced to Pt(II) under the treatment of excess triphenyl phosphine in dry CHCl_3 at room temperature and formed monoligated Pt(II) complex quantitatively.²⁰



Scheme 4 Reactivity of platinacycle **2a** with triphenyl phosphine.

Experimental

All reactions were carried out in oven dried glassware and under an atmosphere of nitrogen using schlenk line. The chemicals were purchased from Aldrich and used as it is unless mentioned otherwise. All the solvents used for the reaction were dried before use. The purification of product was accomplished by column chromatography using silica gel 60-120 mesh. The technical grade solvents were used for chromatography and distilled prior to use. NMR spectra were recorded in Fourier transform mode. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker-Avance (300 MHz); Inova (400 MHz) and Avance (500 MHz) spectrophotometer using CDCl_3 and TMS as the internal standard. Multiplicities in the ^1H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, bs = broad singlet; coupling constants are reported in Hz. Infrared spectra were recorded on Thermo Nicolet Nexus 670 spectrometer and reported in cm^{-1} . The elemental (CHN) analysis was performed in vario MICRO cube. The perfluoroalkyl imidoyl iodides and alkynes were prepared according to literature procedure. The electrochemical measurements were performed on a PC-controlled CH instruments model CHI 620C electrochemical analyzer. The experiments were performed on 1 mM solution of either ligand or complex in CH_2Cl_2 solvent at scan rate of 100 mV/s using 0.1 M tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. The working electrode is glassy carbon, standard calomel electrode (SCE) is the reference electrode and platinum wire is an auxiliary electrode. After a cyclic voltammogram (CV) had been recorded, ferrocene was added, and a second voltammogram was measured. The optical thin layer electrochemical studies were carried on Maya 2000 Ocean Optics software using DT-MINI-2-GS, UV-VIS-NIR LIGHTSOURCE. Steady-state fluorescence spectra was recorded using a Fluorolog-3 spectrofluorometer (Spex model, Jobin Yvon) for solutions with optical density at the wavelength of excitation (λ_{ex}) ≈ 0.05 . In situ ESI-MS analysis was performed using Exactive Orbitrap mass spectrometer in positive ion mode and its mass resolution was 50,000 (FWHM). The sample was diluted with three volumes of acetonitrile and the resulting solution (10 μl) was injected into the source of mass spectrometer using flow-injection mode (mobile phase, methanol at a flow rate of 0.4 ml/min).

1. General procedure for the preparation of *N*-aryl perfluoroalkyl bis(methylthio)phenyl propargyl imines (1a, 1b, 1c, 1d)

To a stirred mixture of $\text{PdCl}_2(\text{PPh}_3)_2$ (2 mol%) and CuI (4 mol%) in Et_3N (4 mL), 2-(methylthio/methylseleno)phenylacetylene (1 mmol) and *N*-aryl trifluoromethylimidoyl iodide (1 mmol) were added successively under N_2 atmosphere. The mixture was stirred at room temperature until the starting materials were consumed. The reaction mixture was then filtered and from the filtrate the solvent was evaporated under reduced pressure. The crude

product obtained was purified by column chromatography using hexane/EtOAc(90:10) mixture.

2. General procedure for the preparation of platinumacycles (2a, 2b, 2c, 2d)

To a solution of PtCl_2 (67 mg, 0.25 mol) in dry toluene (5 mL) at 0 $^\circ\text{C}$, ligand 1 (0.25 mol) was added under N_2 atmosphere. The mixture was stirred for overnight at room temperature. On the completion of reaction (monitored by TLC), the mixture was concentrated to half volume. The addition of *n*-hexane to mixture affords dark reddish colour precipitation. The mixture was filtered and solid residue was washed with diethyl ether (10 mL). The crude product was subjected to column chromatography and purified using hexane/EtOAc (80:20) mixture.

Platinacycle 2a

The product was obtained as a reddish solid, ^1H NMR (500 MHz, CDCl_3) δ 8.49 (d, $J = 8.3$ Hz, 1H), 8.0 (d, $J = 8.1$ Hz, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.57 (t, $J = 7.3$ Hz, 1H), 7.42 (t, $J = 7.4$ Hz, 1H), 7.36 (t, $J = 7.3$ Hz, 1H), 7.08 (m, 2H), 6.97 (dd, $J = 2.6$ and 8.7 Hz, 1H), 6.83-6.91 (m, 3H), 6.64 (m, 1H), 6.20 (d, $J = 8.2$ Hz, 1H), 6.06 (d, $J = 8.5$ Hz, 1H), 5.50 (m, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 2.03 (s with satellites, J (Pt- CH_3) = 33.7 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.1, 158.9, 153.1, 147.2, 138.2, 136.1, 128.6, 127.9, 127.3, 125.4, 125.4, 125.3, 124.5, 123.9, 123.0, 122.6, 121.8, 114.3, 113.6, 112.7, 55.7, 55.3, 31.5, 30.9, 29.7, 29.0, 22.6, 14.1, -7.0; IR (Neat) $\nu(\text{cm}^{-1})$: 3064, 2997, 2923, 2834, 1603, 1578, 1501, 1445, 1413, 1327, 1294, 1243, 1182, 1028, 992, 840, 760, 729, 625, 584, 524, 499, 405; Elemental analysis Calculated for $\text{C}_{35}\text{H}_{25}\text{ClF}_6\text{N}_2\text{O}_2\text{PtS}_2$: C, 45.98; H, 2.76; N, 3.06; S, 7.01. Found C, 46.00; H, 2.73; N 2.97; S, 6.94.

Platinacycle 2b

The product was obtained as a reddish solid, ^1H NMR (500 MHz, CDCl_3) δ 9.60 (d, $J = 8.5$ Hz, 1H), 7.97 (d, $J = 8.2$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.76 (m, 1H), 7.64 (t, $J = 7.1$ Hz, 1H), 7.48 (m, 1H), 7.36 (m, 2H), 6.99 (dd, $J = 2.7$ and 8.7 Hz, 1H), 6.93 (m, 1H), 6.88 (m, 1H), 6.80 (dd, $J = 2.7$ and 8.7 Hz, 1H), 6.61 (dd, $J = 2.7$ and 8.8 Hz, 1H), 6.08 (m, 2H), 5.31 (d, $J = 9.3$ Hz, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 2.18 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 207.0, 158.8, 128.7, 128.2, 127.4, 127.3, 125.2, 125.1, 124.4, 123.6, 122.8, 122.3, 121.2, 114.1, 112.9, 112.7, 112.2, 112.1, 55.7, 55.2, 30.9, 29.6, -6.1; IR (Neat) $\nu(\text{cm}^{-1})$: 3447, 3050, 2958, 2839, 1605, 1564, 1525, 1438, 1408, 1348, 1298, 1240, 1201, 1165, 1134, 1030, 989, 851, 815, 739, 633, 554, 527, 495; Elemental analysis Calculated for $\text{C}_{41}\text{H}_{25}\text{ClF}_{18}\text{N}_2\text{O}_2\text{PtS}_2$: C, 40.52; H, 2.08; N, 2.31; S, 5.27. Found C, 40.52; H 2.06; N 2.30; S, 5.16.

Platinacycle 2c

The product was obtained as a reddish solid, ^1H NMR (500 MHz, CDCl_3) δ 8.51 (d, $J = 8.4$ Hz, 1H), 7.96 (d, $J = 8.2$ Hz, 1H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.52 (t, $J = 7.5$ and 7.6 Hz, 1H), 7.39 (t, $J = 7.3$ and 8.1 Hz, 1H), 7.31 (m, 2H), 7.13 (m, 1H), 7.05 (d, $J = 8.1$ Hz, 1H), 6.91 (t, $J = 7.3$ and 8.1 Hz, 2H), 6.83 (t, $J = 7.5$ and 7.6 Hz, 1H), 6.59 (m, 1H), 6.14 (d, $J = 8.4$ Hz, 1H), 5.93 (m, 1H), 4.79 (m, 1H), 3.83 (s, 3H), 3.61 (s, 3H), 2.20 (s with satellites, J (Pt- CH_3) = 34.7 Hz, 3H); ^{13}C NMR

(125 MHz, CDCl₃) δ 158.5, 128.7, 128.2, 127.3, 125.3, 125.1, 124.4, 123.6, 122.8, 122.4, 121.2, 114.1, 112.9, 112.3, 112.1, 55.7, 55.2, 29.7, -6.1; IR (Neat) ν (cm⁻¹): 3449, 2961, 2835, 1600, 1580, 1549, 1499, 1444, 1416, 1337, 1298, 1250, 1169, 1106, 982, 840, 781, 761, 718, 651, 576, 525; Elemental analysis Calculated for C₃₅H₂₅ClF₆N₂O₂PtSe₂: C, 41.70; H, 2.50; N, 2.78. Found C, 41.66; H, 2.48; N, 2.77.

Platinacycle 2d

The product was obtained as a reddish solid, ¹H NMR (500 MHz, CDCl₃) δ 8.39 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.49 (t, J = 8.1 Hz, 1H), 7.31 (m, 2H), 6.97 (m, 3H), 6.84 (t, J = 7.3 Hz, 1H), 6.77 (m, 2H), 6.55 (dd, J = 2.9 and 8.8 Hz, 1H), 6.01 (d, J = 8.4 Hz, 1H), 5.85 (d, J = 8.7 Hz, 1H), 5.22 (d, J = 8.7 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 1.97 (s with satellites, J (Pt-CH₃) = 33.7 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 207.0, 158.8, 158.5, 147.6, 144.9, 139.0, 138.1, 136.3, 128.7, 128.1, 127.3, 125.2, 125.1, 124.4, 123.6, 122.3, 121.3, 121.2, 114.0, 112.9, 112.7, 112.2, 112.0, 55.7, 55.2, 30.9, 29.7, 22.6, -6.2; IR (Neat) ν (cm⁻¹) 3423, 2957, 2836, 1603, 1547, 1502, 1448, 1333, 1304, 1253, 1180, 1143, 1032, 993, 839, 779, 755, 721, 657, 588, 534, 404; Elemental analysis calculated for C₃₇H₂₅ClF₁₀N₂O₂PtSe₂: C, 40.77; H, 2.27; N, 2.52. Found C, 40.77; H, 2.25; N, 2.52.

Compound 3

The product was obtained as a greenish solid, ¹H NMR (500 MHz, CDCl₃) δ 7.93 (m, 1H), 7.41 (m, 1H), 7.23 (m, 6H), 7.05 (d, J = 8.9 Hz, 3H), 6.93 (m, 5H), 6.74 (d, J = 8.9, 2H), 6.63 (m, 1H), 3.72 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 160.8, 154.6, 149.8, 145.4, 139.0, 137.8, 135.8, 133.5, 132.9, 131.5, 131.2, 131.5, 131.5, 130.8, 130.2, 129.2, 129.1, 129.0, 128.5, 127.5, 126.2, 122.6, 113.4, 55.5; ESI-MS: m/z = 662[M]⁺

Compound 4

The product was obtained as a Yellowish solid, ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, J = 7.9 Hz, 1H), 7.71 (dd, J = 5.6 and 12.4 Hz, 1H), 7.45 (m, 12H), 7.39 (m, 2H), 7.29 (t, J = 7.3 Hz, 6H), 7.15 (m, 12H), 7.07 (m, 1H), 6.88 (m, 2H), 6.80 (m, 1H), 6.58 (m, 2H), 3.90 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 179.6, 156.1, 143.7, 142.8, 140.9, 135.0, 134.2, 133.7, 133.6, 131.0, 130.8, 130.6, 130.4, 129.8, 129.7, 129.5, 129.3, 128.6, 128.5, 128.4, 128.0, 127.7, 125.6, 122.8, 121.0, 120.0, 117.6, 113.6, 96.0, 60.0, 55.6, 45.7, 8.6; ESI-MS: m/z = 852 [M - 237]⁺

X-ray Crystallography

Crystal data for **2a**: C₃₅H₂₅ClF₆N₂O₂PtS₂, M = 914.23, reddish-yellow block, 0.15 x 0.13 x 0.05 mm³, monoclinic, space group $P2_1/n$ (No. 14), a = 13.4868(14), b = 15.2064(16), c = 17.7733(19) Å, β = 107.750(2)°, V = 3471.5(6) Å³, Z = 4, D_c = 1.749 g/cm³, F_{000} = 1784, Bruker SMART APEX CCD area-detector, MoK α radiation, λ = 0.71073 Å, T = 294(2)K, $2\theta_{max}$ = 50.0°, 32599 reflections collected, 6105 unique (R_{int} = 0.0397). Final $GooF$ = 1.018, RI = 0.0293, $wR2$ = 0.0735, R indices based on 5390 reflections with $I > 2\sigma(I)$ (refinement on F^2), 445 parameters, 0 restraints, μ = 4.306 mm⁻¹. **CCDC 1019738** contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at

www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

Conclusions

In conclusion, we have prepared a series of new octahedral cycloplatinated methyl complexes from the reaction of *ortho* thioanisole and *ortho* selenoanisole substituted perfluoroalkyl propargyl imines and Pt(II)Cl₂ via intramolecular heterocyclization. The oxidation of Pt(II) to octahedral Pt(IV) methyl complexes is attributed to the in situ generated methyl chloride during the intramolecular cyclization. Both the ligands and complexes have observed similar redox potentials. The reduction potentials of complex are probable due to reduction Pt(IV) to Pt(II). All the Pt(IV) complexes are emissive and the stoke shifts are found to be in the range of 55-65 nm. The reactivity of these complexes suggests that they can be easily undergo insertion and reduction reaction. Further studies on the bioactivity and catalytic applications of Pt(IV) complexes are in progress.

Acknowledgements

DS and KJ are thankful to UGC and CSIR, New delhi for their fellowships.

Notes and references

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† Electronic Supplementary Information (ESI) available: [General remarks, preparation of ligands, platinacycles, in situ ESI-MS study, absorption spectra, electrochemical spectra and spectroelectrochemical spectra, spectroscopic characterizations (¹H NMR and ¹³C NMR) of the ligands and platinacycles See DOI: 10.1039/b000000x/]

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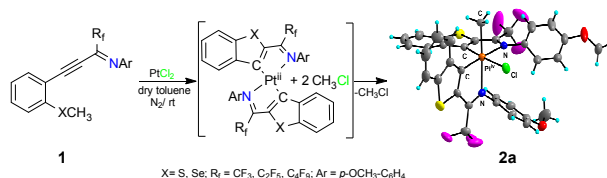
Intramolecular Heterocyclization Assisted Oxidative Addition: Synthesis of Octahedral Cycloplatinated Methyl Complexes

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Cycloplatination of XMeC₆H₄C≡CC-(R_f) (=N-4-OCH₃C₆H₄) [X= S, Se and R_f = perfluoroalkyl groups] with PtCl₂ gave a monomeric platinum (IV) complex having an octahedral structure with one annulated heterocycles coordinated in a plane and other out of plane. The formation of platinum (IV) complex **2a**, confirmed by X-ray crystal structure, presumes simultaneous heterocyclization and oxidative addition of methyl chloride generated during the heterocyclization. The emission and reactivity study of platinum (IV) complexes is discussed.