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Platinum complexes of diazo ligands. Studies of regioselective aromatic ring amination, oxidative halogen addition and reductive halogen elimination reactions†

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2-(Arylazo)pyridine ligands, L^{1a-1c} react with the salt $K_2[PtCl_4]$ to give the mononuclear complexes $[PtCl_2(L^1)]$ (**1**), which readily react with $ArNH_2$ to yield the monochloro complexes of type $[PtCl(L^2)]$ (HL^2 = 2-[(2-(arylamino)phenyl)azo]pyridine) (**2**) *via* regioselective *ortho*-amine fusion at the pendent aryl ring of coordinated L^1. Oxidative addition of the electrophiles Y_2 (Y = Cl, Br, I) to the square-planar platinum(II) complex, **2** has led to syntheses of the corresponding octahedral platinum(IV) complexes, $[PtY_3(L^2)]$ (**3**) in high yields. Ascorbate ion reductions of the platinum(IV) complexes, **3**, resulted in reductive halogen elimination to revert to the platinum(II) complexes **2** almost quantitatively. Isolation of products and X-ray structure determination of the representative complexes followed all these chemical reactions. In crystal packing, the compound $[PtCl_2(L^{1c})]$ (**1c**) forms dimeric units with a Pt···Pt distance of 3.699(1) Å. In contrast, the crystal packing of **2b** revealed that the molecules are arranged in an antiparallel fashion to form a noncovalent 1D chain to accommodate π(aryl)–π(pyridyl) and Pt–π(aryl) interactions. Notably, the oxidation of $[Pt^{II}Cl(L^{2a})]$ (**2a**) by I_2 produced a mixed halide complex $[Pt^{IV}ClI_2(L^{2a})]$ (**5**), which, in turn, is reduced by ascorbate ion to produce $[Pt^{II}I(L^{2a})]$ with the elimination of ClI. All the platinum(II) complexes are brown, the platinum(IV) complexes, on the other hand, are green. Low-energy visible range transitions in the complexes of the extended ligand $[L^2]^-$ are ascribed to ligand based π–π* transitions. Cyclic voltammetric behaviour of the complexes is reported.

Introduction

This work has originated from our interest in the coordination chemistry[1] of 2-(arylazo)pyridine (AAP, L^1) ligands involving transition metal complexes in general, and platinum group metal complexes, in particular. Rich redox as well as spectral properties of these systems have been studied over the past two decades. During the recent years much attention has focused on unusual metal mediated reactions[2–4] on the coordinated diazo ligand. The first example of such a reaction, *viz.* palladium promoted hydroxylation of the phenyl ring on coordinated L^1 was noted[2] in 1982. During the recent past we have been engaged in the systematic study of aromatic ring amination reactions on coordinated L^1. The scope of these reactions appears to be high particularly in the context of design and synthesis[5] of new ligands of multiple denticities whose coordination chemistry is interesting with many novel features. Furthermore, the recent discovery of cytotoxic activity[6] of the isomeric ruthenium complex, $[RuCl_2(L^1)_2]$, has yielded the possibility of similar activities in the corresponding or related platinum complexes. Our literature survey has revealed that platinum–azo complexes are scarce.[7]

In this paper we wish to report synthesis and reactivities of the dichloro platinum complexes $[PtCl_2(L^1)]$ (**1**). The pendent aryl ring of coordinated L^1 in **1** undergoes *ortho*-amination reaction regioselectively to result a monochloro platinum(II) complex $[PtCl(L^2)]$ (**2**) of a tridentate ligand (HL^2) formed due to amine fusion *via* C–X (X = H, Cl) activation of the coordinated L^1. Oxidative halogen addition to these monochloro complexes (**2**) produce platinum(IV) complexes, $[PtY_3(L^2)]$ (Y = Cl, Br, I) (**3**–**5**). The tetravalent complexes, in turn, are reduced to the bivalent complexes, **2** by L-ascorbic acid. The chemical isolation as well as X-ray structure characterization of the products follow all these reactions. In the present context we note that oxidative addition coupled with reductive elimination in platinum complexes forms the basis of catalytic cycles[8] that are used in catalyzed organic reactions. While the examples of oxidative I_2 addition to bivalent platinum complexes are not common,[9] the reductive elimination by potential bio-reductants[10] such as ascorbic acid has biological significance.

Results and discussion

A: $[PtCl_2(L^1)]$ 1

The three AAP ligands, *viz.* 2-(phenylazo)pyridine (L^{1a}), 2-(*m*-tolylazo)pyridine (L^{1b}) and 2-(*o*-chlorophenylazo)pyridine (L^{1c}) were used in this work (Scheme 1). The ligands,[11] L^{1a}–L^{1c} react with the salt $K_2[PtCl_4]$ in boiling aqueous acetonitrile (CH_3CN–H_2O, 9 : 1) to produce platinum complexes of general formula $[PtCl_2(L^1)]$ (**1**) in excellent yields (>80%). The complexes are freely soluble in dimethyl formamide and are only sparingly soluble in acetonitrile. The single-crystal X-ray structure of a

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† Electronic supplementary information (ESI) available: Table S1: Secondary interactions for the complexes **1c**, **2b**, **4** and **5**. Fig. S1: A supramolecular dimer of $[PtCl_2(L^{1c})]$ **1c** formed by π···π interaction. Fig. S2: 1D supramolecular chain of $[PtCl(L^{2b})]$ **2b** constructed by π···π, Pt···π interaction running along *b* axis. Fig. S3: ORTEP and atom numbering scheme for $[PtBr_3(L^{2a})]$ **4**. Fig. S4: A 2D sheet of $[PtBr_3(L^{2a})]$ **4** constructed from π-stacking and Br···Br contacts. Fig. S5: A dimeric unit of $[PtClI_2(L^{2a})]$ **5** constructed by π···π stacking interaction. Fig. S6: Segmented cyclic voltammograms of $[PtCl_2(L^{1a})]$ **1a**, $[PtCl(L^{2a})]$ **2a** and $[PtClI_2(L^{2a})]$ **5**. Fig. S7: UV-Vis spectra of **1a**, **2a** and **5**. See http://www.rsc.org/suppdata/dt/b4/b418470j/

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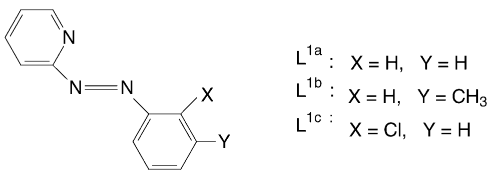


Scheme 1

representative, $[PtCl_2(L^{1c})]$, **1c** is solved. Fig. 1 shows the ORTEP and atom numbering scheme for **1c**. Selected bond parameters are collected in Table 1.

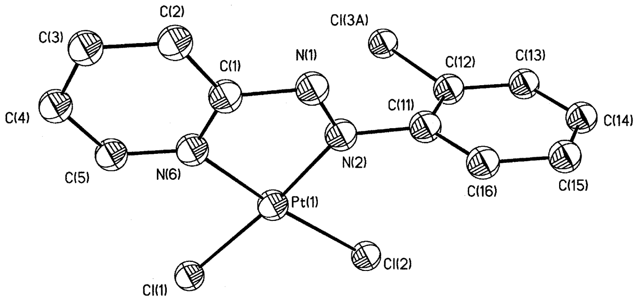


Fig. 1 ORTEP and atom numbering scheme for $[PtCl_2(L^{1c})]$, **1c**. Hydrogen atoms are omitted for clarity.

The complex **1c** is essentially planar with the platinum atom in a distorted square-planar geometry. The two *cis*-chlorides lie almost equidistant from the metal center. Notably, Pt–N(azo) length, *e.g.* Pt(1)–N(2) (1.959(3) Å) is shorter than that of Pt–N(py), 1.992(3) Å. This may be attributed to greater π-acceptor ability[1] of the azo-chromophore of L^1 over the pyridyl function. As a consequence, the N–N length[12] of the coordinated azo ligand is elongated (1.271(4) Å). In the crystal packing, the compound **1c** forms dimeric units; the two molecules of the dimer interact weakly with one another by a center of inversion[13] (Fig. S1, ESI†). The platinum complexes are diamagnetic. Their ^1H NMR spectra are broad (Fig. 2) due to some unidentified dynamic processes.[14]

B: Amination of coordinated L^1 in $[PtCl_2(L^1)]$ 1

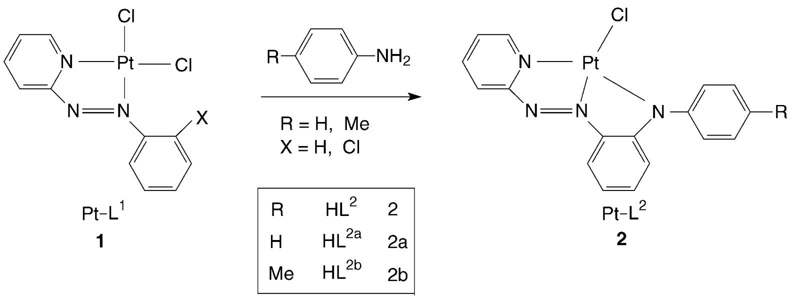
The bivalent platinum complexes **1** were found to react freely with primary aromatic amines in neat to yield platinum complexes of the anionic tridentate ligand, $[L^2]^-$ due to regioselective C–N bond fusion at *ortho* carbon of the pendent aryl ring of coordinated L^1. The reddish-brown mixture of **1** with neat $ArNH_2$, upon heating on a steam-bath, produced a brown paste in about an hour. The crude product, after initial work-up, was purified by repeated crystallization from dichloromethane–hexane solvent mixture. The structural analysis of a representative, $[PtCl(L^{2b})]$, **2b** (R = Me) confirms amine fusion at the pendent aryl ring specifically at a position *ortho* to the azo-group of L^1 (Scheme 2 and Fig. 3).

The extended N,N,N-donor (HL^2) binds as a bischelate with deprotonation of the amine nitrogen (N(14)). In the above transformation, one of the two coordinated chlorides dissociated from the starting dichloro complex **1**, which, is an essential prerequisite[4c] for such an *ortho*-amine fusion reaction.

The yield of the compound **2** is high (>75%). Formally this ligand transformation involves nucleophilic aromatic ring substitution of hydride (as in **1a**) or halide (as in **1c**). Such substitution reactions at coordinated ligands generally occur

Table 1 Selected bond lengths (Å) and angles (°) for the complexes **1c**, **2b**, **4** and **5**

1c					
Pt(1)–Cl(1)	2.2888(10)	Pt(1)–Cl(2)	2.2796(11)	Pt(1)–N(2)	1.959(3)
Pt(1)–N(6)	1.992(3)	N(2)–N(1)	1.271(4)	N(1)–C(1)	1.394(5)
C(1)–N(6)	1.350(5)	C(11)–N(2)	1.445(5)		
Cl(1)–Pt(1)–Cl(2)	90.74(4)	N(2)–Pt(1)–N(6)	78.11(14)		
2b					
Pt(1)–Cl(1)	2.3090(10)	Pt(1)–N(14)	2.031(3)	Pt(1)–N(13)	1.928(3)
Pt(1)–N(11)	2.018(3)	N(14)–C(21)	1.345(4)	C(21)–C(16)	1.438(5)
C(16)–N(13)	1.363(4)	N(13)–N(12)	1.303(4)	N(12)–C(15)	1.398(4)
C(15)–N(11)	1.370(4)	N(14)–C(22)	1.402(5)		
N(14)–Pt(1)–N(13)	82.06(13)	N(13)–Pt(1)–N(11)	79.19(13)		
N(11)–Pt(1)–Cl(1)	97.79(9)	Cl(1)–Pt(1)–N(14)	100.95(9)		
4					
Pt(1)–Br(1)	2.4602(7)	Pt(1)–Br(2)	2.4560(6)	Pt(1)–Br(3)	2.4501(7)
Pt(1)–N(1)	2.051(5)	Pt(1)–N(3)	1.972(4)	Pt(1)–N(4)	2.035(4)
N(1)–C(5)	1.381(8)	C(5)–N(2)	1.380(8)	N(2)–N(3)	1.297(7)
N(3)–C(6)	1.349(7)	C(6)–C(11)	1.431(8)	C(11)–N(4)	1.333(7)
N(4)–C(12)	1.427(8)				
N(1)–Pt(1)–N(3)	79.2(2)	N(3)–Pt(1)–N(4)	81.8(2)		
Br(1)–Pt(1)–Br(3)	177.53(2)				
5					
Pt(1)–I(1)	2.6567(4)	Pt(1)–I(2)	2.6551(5)	Pt(1)–Cl(1)	2.3515(14)
Pt(1)–N(4)	2.037(4)	Pt(1)–N(3)	1.952(5)	Pt(1)–N(1)	2.048(4)
N(4)–C(11)	1.346(8)	C(11)–C(6)	1.439(8)	C(6)–N(3)	1.367(7)
N(3)–N(2)	1.298(6)	N(2)–C(5)	1.384(7)	C(5)–N(1)	1.373(7)
N(4)–C(12)	1.419(7)				
N(1)–Pt(1)–N(3)	78.98(18)	N(3)–Pt(1)–N(4)	82.20(18)		
I(1)–Pt(1)–I(2)	178.20(2)				



Scheme 2

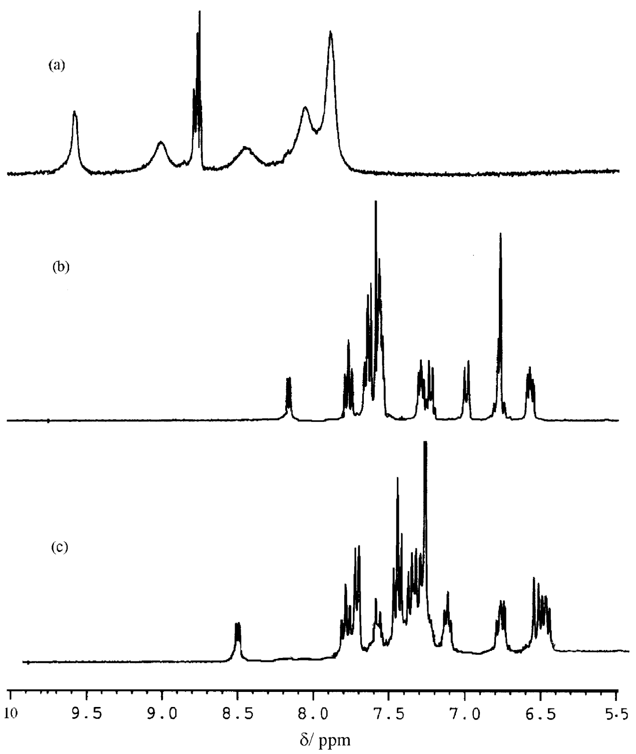


Fig. 2 ^1H NMR spectra of (a) **1a** in DMSO-d_6, (b) **2a** in $CDCl_3$ and (c) **5** in $CDCl_3$ at 300 K.

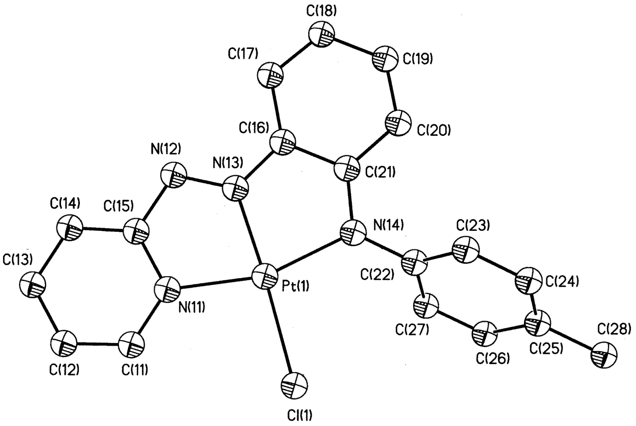


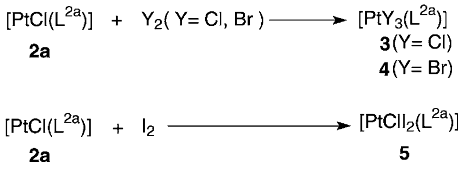
Fig. 3 ORTEP and atom numbering scheme for $[PtCl(L^{2b})]$, **2b**. Hydrogen atoms are omitted for clarity.

at electron deficient aromatic rings induced by the presence of high valent metal ions. Notably, the reference reaction of **1** with $ArNH_2$ occur only in neat amine and failed to produce any isolable products in methanol or 2-methoxyethanol even in the presence of a very high excess (10 times) of aromatic amines. Moreover, for the amine fusion reaction of the unsubstituted ligand L^{1a} the presence of air is necessary, however, the 2-chloro substituted ligand L^{1c}, reacts also in an oxygen-free atmosphere. This is not surprising since hydrogen substitution in a typical nucleophilic aromatic substitution (S_NAr) reaction needs an oxidizing agent to rearomatize[15] the intermediate. Coordination geometry of the platinum atom is distorted square planar, deviation from the idealized geometry is primarily due to geometric constraints imposed by the tridentate ligand. The Pt–N lengths showed expected variation with that to the middle nitrogen (N(13)) being shorter than those to the other two terminal nitrogens *viz.* N(11) and N(14). The chelate bite angles are in agreement[16] with those of the previously reported complexes of $[L^2]^-$ and the Pt–N and Pt–Cl lengths are similar to related[17] platinum complexes of tridentate nitrogenous ligands. Furthermore, the elongation of the diazo length, N(12)–N(13), 1.303(4) Å in this compound is attributed to extensive delocalisation[4c] of charge along the ligand backbone. A packing view of **2b** (Fig. S2, ESI†) reveals the arrangement of the molecules in an antiparallel fashion to form a noncovalent 1D chain (Table S1, ESI†) wherein the alternative antiparallel Pt atoms are displaced up and down from the chain axis. The complexes **2a** and **2b** showed highly resolved ^1H NMR spectra in $CDCl_3$ (Experimental section) and a representative spectrum is displayed in Fig. 2. The pyridyl protons resonated in the low field region (δ 8.0–7.0). Aromatic proton signals are assigned primarily based on substitution induced change in spin–spin coupling pattern. The complex **2b** of methyl substituted ligand $[L^{2b}]^-$ showed a sharp methyl resonance at δ 2.30. Notably the proton resonances for the complexes[4c] of the ligand $[L^2]^-$ appear high field as compared to that[1c] of the neutral ligand L^1. This may be attributed to electron delocalization along the ligand backbone of the coordinated anionic ligand $[L^2]^-$.

C: Reversible oxidative addition and reductive elimination reactions

The bivalent platinum complexes **2** are susceptible to oxidation and react with halogens, *viz.* chlorine, bromine and iodine instantaneously to produce the platinum(IV) complexes of type **3–5** almost quantitatively (>95%). In all the cases oxidative halogen addition occur with concomitant $2e^-$ oxidation of $Pt^{II} \rightarrow Pt^{IV}$ (Scheme 3). It was noted before[18] by us that the reaction of $K_2[PtCl_4]$ with the preformed HL^2 ligand in acetonitrile produces a tetravalent green complex, $[PtCl_3(L^2)]$ in a moderate yield. However, no bivalent platinum complex of type **2** could be isolated from the above reaction.

The identity of the Cl_2 oxidation product, $[PtCl_3(L^{2a})]$ (**3**) was confirmed[18] by comparing its spectra with those of the reported sample. However, formulations of its bromo and iodo analogues



$$\underset{\mathbf{2a}}{[PtCl(L^{2a})]} + Y_2(Y= Cl, Br) \longrightarrow \underset{\substack{\mathbf{3}(Y= Cl)\\ \mathbf{4}(Y= Br)}}{[PtY_3(L^{2a})]}$$

$$\underset{\mathbf{2a}}{[PtCl(L^{2a})]} + I_2 \longrightarrow \underset{\mathbf{5}}{[PtClI_2(L^{2a})]}$$

Scheme 3

were made from their X-ray structure determination (Table 1). The ORTEP and atom numbering scheme of $[PtClI_2(L^{2a})]$ (**5**) are shown in Fig. 4 and that of a closely related compound $[PtBr_3(L^{2a})]$ (**4**) are submitted as ESI (Fig. S3†).

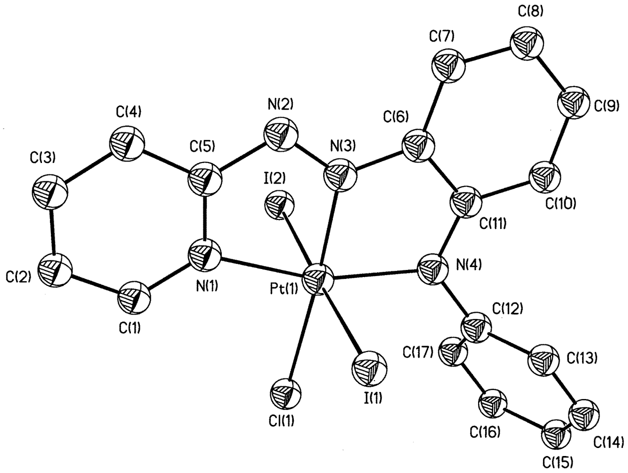


Fig. 4 ORTEP and atom numbering scheme for $[PtClI_2(L^{2a})]$, **5**. Hydrogen atoms are omitted for clarity.

The deprotonated extended tridentate N,N,N-donor in each case binds as a bis-chelating ligand and the coordination geometry around the platinum atom is distorted octahedral. Three halogen atoms occupy rest three positions. Interestingly in the mixed-halide complex **5**, the two iodine atoms occupy relative *trans*-axial positions. Of the three Pt–N bonds, the Pt–N(azo) is shortest, the N–N lengths are elongated indicating strong delocalisation of anionic charge along the ligand backbone. The Pt–Y (Y = Br, I) bond lengths[9d,19] are normal. The crystal packing of **4** reveals intermolecular Br · · · Br contacts linking the individual monomers into a 2D supramolecular network (Fig. S4, ESI†). The crystal packing of **5**, on the other hand, reveals a face-to-face π–π stacking (Fig. S5, ESI†) between the pyridine and phenyl rings.

Oxidation of $[PtCl(L^{2a})]$ (**2a**) by Br_2 has resulted in a tribromide complex, $[PtBr_3(L^{2a})]$ (**4**), while I_2 oxidation has, in contrast, resulted in a mixed-halogen complex, $[PtClI_2(L^{2a})]$ (**5**). Since platinum(IV) compounds are generally substitution inert[20] it is reasonable that substitution of Cl by Br in **2a** occurs before oxidative addition of Br_2. The chloro compound, **2a** is indeed labile and produced $[PtBr(L^{2a})]$ (**2c**) and $[PtI(L^{2a})]$ (**2d**) when reacted with aqueous solution of KBr and KI, respectively. The geometry of the mixed halide product, **5** is interesting. The compound is *trans* with respect to two coordinated iodine atoms. This suggests *trans* addition of halogen in these oxidation reactions. This is in line with widely accepted mechanism[21] of oxidative halogen addition reactions on square planar platinum(II) complexes. We wish to note here that while the complex **4** is also obtained upon oxidation of **2c** by Br_2, the corresponding triiodo complex, $[PtI_3(L^{2a})]$ could not be isolated from the reaction of **2d** and I_2 possibly due to steric crowding.

In order to assess the chemical reversibility of oxidative halogen addition in our system, the tetravalent complexes, **3**–**5** were reacted with a potential bio-reductant,[10,22] L-ascorbic acid. The reactions occurred smoothly and the parent bivalent platinum complexes, **2** were isolated in almost quantitative yields (>95%). Of the above noted reactions, the result of reduction of the mixed-halogen complex, $[PtClI_2(L^{2a})]$ (**5**) is noteworthy. In this reaction, Pt(IV)→Pt(II) occurred with the formation of $[Pt^{II}I(L^{2a})]$ indicating the elimination[10a,23] of ClI. This complex showed a ESI-MS peak at *m*/*z* 758, which indeed confirmed its formation from the above reaction.

D: Solution properties

Cyclic voltammetry of the platinum complexes reported herein are dominated by two reversible reductive responses, which are assigned[4,24] to ligand reductions (Fig. S6, ESI†). Electronic spectra of the present platinum complexes are characterized by low energy structured bands[17a] appearing in the visible-NIR range. The transitions near 600 nm in **1** may be ascribed[25] as metal to ligand (MLCT) electronic transitions. The lowest energy transitions in the complexes of the tridentate ligand, **2b** and **5** are ascribed[26] as intraligand π–π* transfer. Notably, such low energy transitions in the platinum complexes are uncommon[27] in the literature. Redox and electronic spectral data of the complexes are collected in the Experimental section. UV-visible spectra of three representative complexes are submitted as ESI (Fig. S7†).

E: Conclusion

Successful isolation and characterization of platinum complexes of 2-(arylazo)pyridine ligand together with some examples of fascinating chemical reactions *viz.* platinum promoted aromatic amine fusion, oxidative halogen addition as well as reductive dehalogenation using the bio-reductant ascorbic acid, are the main issues of the present work. The unique versatility of the chemical transformations that occur in the present complexes opens up avenues for the synthesis of new platinum–azo systems, which are scarce in the literature. Our work on the exploration of oxidative addition of other electrophiles to platinum(II) complexes for the synthesis of organometallic platinum(IV) systems is under active search.

Experimental

Materials

The starting metal salt $K_2[PtCl_4]$ was obtained from Arora-Matthey, Kolkata. Solvents and chemicals used for the syntheses were of analytical grade; 2-(arylazo)pyridine ligands, L^{1a-1c} were prepared by the published[11] procedure.

Physical measurements

A JASCO V-570 Spectrometer was used to record electronic spectra. The IR spectra were recorded with a Perkin-Elmer 783 spectrophotometer. ^1H NMR spectra were measured in $CDCl_3$ and DMSO-d_6 with a Bruker Avance DPX 300 spectrophotometer with $SiMe_4$ as an internal standard. A Perkin-Elmer 240 C elemental analyzer was used to collect microanalytical data (C,H,N). Electrochemical measurements were performed under a dry nitrogen atmosphere at 298 K on a PAR model 370-4 electrochemistry system. The potentials reported herein are referenced to the saturated Calomel electrode (SCE) and are uncorrected for junction contribution. The value for the ferrocenium–ferrocene couple under our experimental condition is 0.40 V. Tetraethylammonium perchlorate and tetrabutylammonium perchlorate were used as the supporting electrolyte. ESI mass spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer.

Synthesis of compounds

Synthesis of $[PtCl_2(L^{1a})]$ 1a. The ligand, 2-(arylazo)pyridine (L^{1a}) (45 mg, 0.24 mmol) was dissolved in 100 ml acetonitrile. To this was added an aqueous solution of $K_2[PtCl_4]$ (100 mg, 0.24 mmol) and the mixture was refluxed on a steam bath for 3 h. During this period the orange colour of the mixture slowly became reddish-orange. The reaction mixture was then cooled and filtered. It was left undisturbed for slow evaporation. After three days dark crystalline products, deposited in the reaction vessel, were collected by filtration and washed thoroughly with diethyl ether, and finally air-dried in a vacuum dessicator. Yield:

85%. Anal. Calc. for $C_{11}H_9N_3Cl_2Pt$: C, 29.4; H, 2.0; N, 9.3. Found: C, 29.6; H, 1.9; N, 9.8%. ^{1}H NMR (DMSO-d$_6$): δ: pyridyl protons: 9.53 (d), 8.88 (br), 8.62 (t), 8.24 (br); aromatic protons: 7.81–7.63 (br). IR (KBr): ν 1610 (C=N), 1380 (N=N) cm^{-1}. UV-vis (dimethylformamide), λ_{max}/nm (ε//M^{-1} cm^{-1}): 650sh (2495), 565 (5940), 530 (4820), 475 (4490), 375 (11500), 340sh (9255), 275 (11490). Cyclic voltammetric data (acetonitrile, scan rate 50 mV s^{-1}): reduction, $E_{1/2}$/V (ΔE_p/mV): −0.22 (70), −1.10 (100).

The compounds [PtCl$_2$(L^{1b})] **1b** and [PtCl$_2$(L^{1c})] **1c** were synthesized similarly following the above procedure using 2-(*m*-tolylazo)pyridine (L^{1b}) and 2-(*o*-chlorophenylazo)pyridine (L^{1c}), respectively, in place of 2-(phenylazo)pyridine.

1b. Yield: 80%. Anal. Calc. for $C_{12}H_{11}N_3Cl_2Pt$: C, 31.1; H, 2.4; N, 9.1. Found, C, 31.2; H, 2.3; N, 9.1%. ^{1}H NMR (DMSO-d$_6$): δ: pyridyl protons: 9.50 (d), 8.85 (br), 8.59 (t), 8.21 (br); aromatic protons: 7.75–7.45 (br); 2.4 (aryl CH$_3$). IR (KBr): ν 1600 (C=N), 1385 (N=N) cm^{-1}. UV-vis (dimethylformamide), λ_{max}/nm (ε/M^{-1} cm^{-1}): 630sh (2325), 540 (5985), 470 (4480), 375 (10840), 265 (11265), 220 (7250). Cyclic voltammetric data (acetonitrile, scan rate 50 mV s^{-1}): reduction, $E_{1/2}$/V (ΔE_p/mV): −0.26 (80), −1.17 (80).

1c. Yield: 85%. Anal. Calc. for $C_{11}H_8N_3Cl_3Pt$: C, 27.3; H, 1.7; N, 8.7. Found: C, 27.5; H, 1.5; N, 8.8%. ^{1}H NMR (DMSO-d$_6$): δ: pyridyl protons: 9.55 (d), 9.01 (br), 8.67 (t), 8.38 (br); aromatic protons: 7.78–7.51 (br). IR (KBr): ν 1615 (C=N), 1395 (N=N) cm^{-1}. UV-vis (dimethylformamide), λ_{max}/nm (ε//M^{-1} cm^{-1}): 635sh (2490), 570 (5900), 445 (4370), 375 (10975), 275 (11355), 235 (7010). Cyclic voltammetric data (acetonitrile, scan rate 50 mV s^{-1}): reduction, $E_{1/2}$/V (ΔE_p/mV): −0.19 (80), −1.16 (90).

Amination reactions

Synthesis of [PtCl(L^{2a})] 2a. A mixture of [PtCl$_2$(L^{1a})] **1a** (85 mg 0.19 mmol) and aniline (1 ml) was heated on a steambath for 1 h. The initial reddish brown colour of the mixture gradually became dark brown. The mixture was cooled and washed thoroughly with diethyl ether several times. Further purification was made by repeated fractional crystallization of the crude mass from dichloromethane–hexane solvent mixture. Yield: 80%. Anal. Calc. for $C_{17}H_{13}N_4ClPt$: C, 40.5; H, 2.6; N, 11.1. Found: C, 40.7; H, 2.7; N, 10.7%. MS: *m*/*z* 504. ^{1}H NMR (CDCl$_3$): δ: pyridyl protons: 7.92 (d), 7.46 (t), 7.34 (d), 7.32 (t); aromatic protons: 7.23 (m), 6.92 (t), 6.84 (d), 6.58 (d), 6.33 (d), 6.09 (m). IR (KBr): ν 1600 (C=N), 1310 (N=N) cm^{-1}. UV-vis (dichloromethane), λ_{max}/nm (ε/M^{-1} cm^{-1}): 1235 (2295), 1065 (4330), 945 (4045), 830sh (2410), 475 (8235), 425 (7650), 360 (18100), 285 (19065), 230 (20195). Cyclic voltammetric data (dichloromethane, scan rate 50 mV s^{-1}): oxidation, $E_{1/2}$/V: 1.09; reduction, $E_{1/2}$/V (ΔE_p/mV): −0.54 (140), −1.26 (150).

Similarly [PtCl(L^{2b})] **2b** was synthesized following the above procedure using *p*-toluidine (1 g) in place of aniline (1 ml).

2b. Yield: 85%. Anal. Calc. for $C_{18}H_{15}N_4ClPt$: C, 41.8; H, 3.1; N, 10.8. Found: C, 41.8; H, 3.3; N, 10.6%. ^{1}H NMR (CDCl$_3$): δ pyridyl protons: 7.89 (d), 7.44 (t), 7.11 (br); aromatic protons: 6.89 (t), 6.83 (d), 6.55 (d), 6.31 (d), 6.08 (m); 2.3 (aryl CH$_3$). IR (KBr): ν 1600 (C=N), 1315 (N=N) cm^{-1}. UV-vis (dichloromethane), λ_{max}/nm (ε/M^{-1} cm^{-1}): 1260 (2340), 1075 (4495), 945 (4260), 835sh (2500), 475 (8285), 430 (8390), 360 (18470), 265 (22870), 230 (24230). Cyclic voltammetric data (dichloromethane, scan rate 50 mV s^{-1}): oxidation, $E_{1/2}$/V: 1.07; reduction, $E_{1/2}$/V (ΔE_p/mV): −0.54 (140), −1.29 (130).

We however, note that the reactions of amines, aniline and *p*-toluidine, with [PtCl$_2$(L^{1c})] **1c** were faster, over in 30 min and produced identical compounds [PtCl(L^{2a})] **2a** and [PtCl(L^{2b})] **2b**, respectively.

Oxidative halogen addition reactions

Synthesis of [PtCl$_3$(L^{2a})] 3. A gentle stream of dichlorine was bubbled through a deep brown colour solution of complex [PtCl(L^{2a})] **2a** (105 mg, 0.21 mmol) in dichloromethane (30 ml). The colour of the solution immediately changed from dark brown to deep green. A crystalline dark green compound was obtained by the slow diffusion of hexane into the above green solution in dichloromethane. Finally the product was crystallized from a dichloromethane–acetonitrile solvent mixture. Yield: 90%. Anal. Calc. for $C_{17}H_{13}N_4Cl_3Pt$: C, 35.5; H, 2.3; N, 9.8. Found: C, 35.3; H, 2.5; N, 9.6%. MS: *m*/*z* 575. ^{1}H NMR (CDCl$_3$): δ pyridyl protons: 8.42 (d), 8.21 (t), 7.93 (d), 7.54 (m); aromatic protons: 7.44 (m), 7.28 (d), 7.10 (d), 7.04 (t), 6.69 (t), 6.54 (d). IR (KBr): ν 1605 (C=N), 1330 (N=N) cm^{-1}. UV-vis (dichloromethane), λ_{max}/nm (ε/M^{-1} cm^{-1}): 1065sh (1720), 850 (4560), 790 (7170), 720 (6380), 435 (5640), 330sh (10975), 235 (33515). Cyclic voltammetric data (dichloromethane, scan rate 50 mV s^{-1}): reduction, $E_{1/2}$/V: −0.67, −1.40.

Similarly, the compounds [PtBr$_3$(L^{2a})] **4** and [PtClI$_2$(L^{2a})] **5** were synthesized by the oxidation of **2a** in dichloromethane (30 ml) with Br$_2$ and I$_2$, respectively. Their yields and analytical data are as follows.

4. Yield: 95%. Anal. Calc. for $C_{17}H_{13}N_4Br_3Pt$: C, 28.9; H, 1.8; N, 7.9. Found: C, 29.1; H, 1.6; N, 8.3%. MS: *m*/*z* 708. ^{1}H NMR (CDCl$_3$): δ pyridyl protons: 8.62 (d), 8.15 (m), 7.92 (d); aromatic protons: 7.43 (m), 7.31 (d), 7.00 (t), 6.67 (m), 6.39 (d). IR (KBr): ν 1600 (C=N), 1325 (N=N) cm^{-1}. UV-vis (dichloromethane), λ_{max}/nm (ε/M^{-1} cm^{-1}): 1075sh (1900), 875 (4670), 785 (6890), 715 (5945), 430 (7040), 350sh (11290), 255 (42215), 230 (37805). Cyclic voltammetric data (dichloromethane, scan rate 50 mV s^{-1}): reduction, $E_{1/2}$/V: −0.71, −1.43.

5. Yield: 90%. Anal. Calc. for $C_{17}H_{13}N_4ClI_2Pt$: C, 26.9; H, 1.7; N, 7.4. Found: C, 26.8; H, 1.3; N, 7.2%. MS: *m*/*z* 758. ^{1}H NMR (CDCl$_3$): δ pyridyl protons: 8.50 (d), 7.79 (t), 7.72 (d), 7.59 (t); aromatic protons: 7.44 (t), 7.32 (m), 7.11 (t), 6.77 (t), 6.53 (d), 6.47 (t). IR (KBr): ν 1600 (C=N), 1325 (N=N) cm^{-1}. UV-vis (dichloromethane), λ_{max}/nm (ε/M^{-1} cm^{-1}): 1070sh (1815), 860 (4385), 780 (5435), 715 (4585), 430 (10560), 355sh (13880), 285 (33920), 235 (28650). Cyclic voltammetric data (dichloromethane, scan rate 50 mV s^{-1}): reduction, $E_{1/2}$/V: −0.71, −1.42.

Reductive dehalogenation reaction by L-ascorbic acid

Reduction of all the platinum(IV) complexes was achieved by L-ascorbic acid following a general procedure. Specific details are given below for the reduction, [PtCl$_3$(L^{2a})] **3** → [PtCl(L^{2a})] **2a**.

To a green dichloromethane solution of [PtCl$_3$(L^{2a})] **3** (110 mg, 0.19 mmol), an aqueous solution of L-ascorbic acid (35 mg, 0.20 mmol) was added and the mixture was stirred at a room temperature. The colour of the solution changed from green to brown in about 15 min. The resulting brown solution was extracted by dichloromethane, washed thoroughly with water and finally dried over anhydrous Na$_2$SO$_4$. Evaporation of the dichloromethane solution resulted the crude [PtCl(L^{2a})] **2a**. It was then recrystallized from a dichloromethane-acetonitrile solvent mixture. Yield: 95%.

The compounds [PtBr(L^{2a})] **2c** and [PtI(L^{2a})] **2d** were obtained similarly from the reductions of [PtBr$_3$(L^{2a})] **4** and [PtClI$_2$(L^{2a})] **5** with L-ascorbic acid, respectively. The spectral properties of **2a** from the above reduction corresponded exactly to the authentic sample. Yields and analytical data of **2c** and **2d** are as follows.

2c. Yield: 95%. Anal. Calc. For $C_{17}H_{13}N_4BrPt$: C, 37.2; H, 2.4; N, 10.2. Found: C, 37.5; H, 2.7; N, 10.4%. MS: *m*/*z* 548. ^{1}H NMR (CDCl$_3$): δ pyridyl protons: 8.13 (d), 7.45 (t), 7.36 (m); aromatic protons: 7.22 (m), 6.89 (t), 6.84 (d), 6.60 (d), 6.34 (t), 6.20 (d), 6.09 (m). IR (KBr): ν 1595 (C=N), 1305 (N=N) cm^{-1}

Table 2 Crystallographic data

	1c	**2b**	**4**	**5**
Empirical formula	$C_{11}H_8Cl_3N_3Pt$	$C_{18}H_{15}ClN_4Pt$	$C_{17}H_{13}Br_3N_4Pt$	$C_{17}H_{13}ClI_2N_4Pt$
M_r	483.64	517.88	708.13	757.65
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	7.3352(3)	6.7696(3)	12.1865(9)	9.6500(7)
b/Å	19.9225(12)	16.4559(8)	8.5286(6)	14.2218(10)
c/Å	9.3996(12)	14.7526(7)	18.5423(13)	14.8154(10)
α/°	90	90	90	90
β/°	96.766(9)	91.1020(10)	105.1650(10)	108.4540(10)
γ/°	90	90	90	90
V/Å^3	1364.0(2)	1643.13(13)	1860.1(2)	1928.7(2)
Z	4	4	4	4
D_c/Mg m^{-3}	2.355	2.093	2.529	2.609
Crystal dimens./mm	0.60 × 0.15 × 0.10	0.39 × 0.09 × 0.08	0.13 × 0.14 × 0.17	0.10 × 0.15 × 0.19
θ Range for data collect./°	3.34–27.98	1.85–28.00	2.28–28.29	2.24–28.29
λ/Å	0.71073	0.71073	0.71073	0.71073
Reflns. collected	3866	10140	12039	12549
Unique reflns.	3289	3858	4579	4729
Abs. correction	Psi-scans	SADABS	SADABS	SADABS
$\Delta\rho_{\max,\min}$/e Å^{-3}	0.969, −0.995	1.006, −0.761	2.22, −2.13	3.45, −2.99
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0240$ $wR_2 = 0.0544$	$R_1 = 0.0239$ $wR_2 = 0.0355$	$R_1 = 0.0364$ $wR_2 = 0.0930$	$R_1 = 0.0339$ $wR_2 = 0.0844$

UV-vis (dichloromethane), $\lambda_{\max}$/nm (ε/M^{-1} cm^{-1}): 1270 (2120), 1065 (3210), 940 (3060), 830sh (2340), 480 (6345), 435 (6645), 360 (17260), 280 (20425), 230 (22250). Cyclic voltammetric data (dichloromethane, scan rate 50 mV s^{-1}): oxidation, $E_{1/2}$/V: 1.11, reduction, $E_{1/2}$/V (ΔE_p/mV): −0.57 (130), −1.29 (140).

2d. Yield: 90%. Anal. Calc. For $C_{17}H_{13}N_4IPt$: C, 34.3; H, 2.2; N, 9.4. Found: C, 34.8; H, 2.1; N, 9.6%. MS: *m/z* 595. ^{1}H NMR (CDCl$_3$): δ: pyridyl protons: 8.47 (d), 7.44 (t), 7.34 (m); aromatic protons: 7.17 (m), 6.85 (m), 6.65 (d), 6.35 (t), 6.07 (m). IR (KBr): ν 1595 (C=N), 1305 (N=N) cm^{-1}. UV-vis (dichloromethane), $\lambda_{\max}$/nm (ε/M^{-1} cm^{-1}): 1235 (2075), 1070 (2730), 865 (3340), 780 (3230), 710 (2455), 430 (8145), 360 (18315), 285 (21865), 235 (22495). Cyclic voltammetric data (dichloromethane, scan rate 50 mV s^{-1}): oxidation, $E_{1/2}$/V: 1.05; reduction, $E_{1/2}$/V (ΔE_p/mV): −0.56 (120), −1.26 (110).

Crystallography

Crystallographic data for the compounds **1c**, **2b**, **4** and **5** are collected in Table 2.

[PtCl$_2$(L^{1c})] 1c. X-Ray quality crystals (0.60 × 0.15 × 0.10 mm) of **1** were obtained by slow evaporation of a concentrated acetonitrile solution of the compound. The data were collected at 293 K on an Enraf-Nonius CAD4 automatic diffractometer[28] equipped with Mo-Kα radiation (λ = 0.71073 Å), and data were corrected for Lorentz-polarization effects.[29] A total of 3866 reflections were collected, of which 3289 were unique ($R_{\text{int}} = 0.0215$). A semi-empirical absorption correction (psi-scans) was made.[30] The structure was solved by Patterson and Fourier methods[31] and refined by full-matrix least squares on F^2 using SHELXL-97.[32] The Cl(3) atom is disordered over three positions; the occupancy factor for each was refined, resulting in a value of 0.57(7) for Cl(3A), 0.10(3) for Cl(3B) and 0.33(8) for Cl(3C).

[PtCl(L^{2b})] 2b. X-Ray quality crystals (0.39 × 0.09 × 0.08 mm) of **2b** were obtained by slow diffusion of acetonitrile into a chloroform solution of the compound. The data were collected at 173(2) K on a Bruker SMART CCD 1000 diffractometer equipped with Mo-Kα radiation (λ = 0.71073 Å). The data were processed with SAINT[33] and the SADABS absorption corrections were applied.[34] A total of 10140 reflections were collected out of which 3858 were unique ($R_{\text{int}} = 0.0329$). The structure was solved by direct methods using the program SHELXS-97[31] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97.[32]

[PtBr$_3$(L^{2a})] 4. X-Ray quality crystals (0.13 × 0.14 × 0.17 mm^3) of **4** were obtained by slow diffusion of acetonitrile into a dichloromethane solution of the compound. The data were collected at 100(2) K on a Bruker SMART APEX CCD diffractometer equipped with Mo-Kα radiation (λ = 0.71073 Å). A total of 12039 reflections were collected out of which 4579 were unique ($R_{\text{int}} = 0.0573$). The structure was solved by direct methods using the program SHELXS-97[31] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97.[32]

[PtClI$_2$(L^{2a})] 5. X-Ray quality crystals (0.10 × 0.15 × 0.19) of **5** were obtained by slow diffusion of acetonitrile into a dichloromethane solution of the compound. The data were collected as noted before for **4**. A total of 12549 reflections were collected out of which 4729 were unique ($R_{\text{int}} = 0.0354$). The structure was solved by direct methods using the program SHELXS-97[31] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97.[32]

CCDC reference numbers 258038–258041.

See http://www.rsc.org/suppdata/dt/b4/b418470j/ for crystallographic data in CIF or other electronic format.

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