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Isolation and characterization of iridium(III) and iridium(V) complexes of 2-(arylazo)pyridine and studies of amine fusion reactions at the coordinated diazo-ligand⁺

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The reaction of IrCl₃·3H₂O with 2-(arylazo)pyridine (HL¹) in boiling methanol has afforded [Ir^{III}Cl₂(L¹)(HL¹)] (1) and [Ir^VCl₄(HL¹)]Cl (2). In complex 1, one of the two ligands [L¹]⁻ is orthometallated *via* coordination of an *ortho*-carbon of the aryl ring of [L¹]⁻ and one of the two azo nitrogens to form a five-membered chelate. X-Ray crystal structures of the two representative complexes, *viz.* **1a** and **2a**, have been solved. Notably, the Ir–N length (2.140(3) Å) *trans* to the Ir–C bond in **1a** is appreciably longer than the other three Ir–N lengths present in the same molecule. The N–N lengths in these two compounds lie close to that observed in the uncoordinated ligand. Thorough NMR studies were made to authenticate the carbon-bonded structure of compound **1a**. In its ¹³C NMR spectrum, the resonance near δ 148 is assigned to the carbon bonded to the iridium metal center. UV-visible spectra along with the redox properties of these complexes are reported. The iridium(v) complex, **2** showed a reversible response near 1.40 V, presumably due to the iridium(v)–iridium(v1) couple. Several reductive responses at cathodic potentials, due to ligand reductions, were also observed. Metal promoted aromatic ring amination reactions at the coordinated HL¹ ligand in complexes **1** and **2** were investigated. The products were characterized using X-ray diffraction.

Introduction

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Platinum group metal complexes of 2-(arylazo)pyridine (abbreviated as HL1) ligand systems1 have been the subject of considerable interest because of their rich redox and spectroscopic behaviour,² catalytic activities and isomerization reactions.^{1h,3} During recent years, much activities in these systems have been concentrated around unusual types of metal mediated chemical transformations of the coordinated HL1 ligand via C-H activation. The first reports on ruthenium and osmium complexes of HL¹ were published^{1e,g,h} about two decades ago. Subsequently, hydroxylation,⁴ and thiolation⁵ reactions at platinum group metal coordinated HL1 were noted. In the recent past we have been engaged in the study⁶ of the aromatic ring amination reactions on coordinated HL¹. More insights into the regioselectivity of the aforesaid amination reactions were achieved by the use of substitutionally inert rhodium(III) complexes of HL1. As a logical continuation of our ongoing work in this area of chemistry, we have been in search of suitable iridium-HL1 substrates for carrying out metal mediated reactions. Literature survey has revealed that there exist only two reports on iridium-HL1 complexes. The first one7 was on FAB mass spectral analysis of [IrCl₂(HL¹)₂]⁺; its synthesis and properties, however, was not available. The more recent report⁸ is on the synthesis and characterization of some mixed ligand iridium(I) complexes, whose compositions and structures are similar9 to those of the rhodium(I) congeners.

In this work we have investigated iridium complexes that are obtained from the reaction of hydrated iridium(III) chloride and HL^1 . The reaction yielded a brown mixture from which a chloro bis-chelated complex of iridium(III) and a mixed-ligand iridium(V) complex were isolated. Interestingly, one of the two coordinated ligands in the trivalent iridium complex coordinates as an anionic C,N-donor. This coordination mode of the reference ligand was not

observed before.¹⁻³ In the C,N-coordination mode, the ligand is deprotonated and its pyridyl nitrogen remains uncoordinated. This is in contrast with the neutral N,N-coordination mode wherein the pyridyl nitrogen as well as one of the two azo nitrogens take part in coordination to form a five-membered chelate (Chart 1).



The most notable part of the present reaction is the formation of a pentavalent iridium complex. The ease with which it is formed is unprecedented in the literature. We wish to note¹⁰ here that the most common oxidation states exhibited by iridium complexes are I and III. Examples of iridium(V) complexes, on the other hand, are scanty.11 The majority of these are organometallic complexes and mostly contain hydride as a coligand. As far as we are aware the flouro complexes, $[Ir^{V}F_{6}]A$ (A = Na, K, Ag) that were reported¹² in 1954 are the best characterized non-organometallic pentavalent iridium complexes. However, the X-ray structure of none of these is available in the literature. During recent years there has been an upsurge in the chemistry of iridium(v) complexes because of their involvement13 in iridium(III) mediated catalytic C-H activation processes. Having been successful in the isolation of Ir-HL1 complexes, we have investigated amine fusion reactions on the aryl ring of the coordinated ligands in the above complexes. Isolation and complete characterization of the products follow the reactions.

[†] Electronic supplementary information (ESI) available: Fig. S1: ¹H NMR spectra of **1a** and *tcc*-[RuCl₂(HL^{1a})₂] in CDCl₃. Inset: Methyl resonances of **1b**. Fig. S2: ¹³C NMR spectra of **1a** and *tcc*-[RuCl₂(HL^{1a})₂] in CDCl₃. Fig. S3: Cyclic voltammogram of **1a** in CH₃CN. Fig. S4: Cyclic voltammogram of **2a** in CH₃CN. See http://www.rsc.org/suppdata/dt/b4/b407209j/

Fable 1 Selected bond lengths (Å)							
$1a \cdot CH_2Cl_2$							
Ir-N(1)	2.052(3)	C(5)–N(2)	1.414(5)				
Ir-N(3)	2.140(3)	N(2)–N(3)	1.263(5)				
Ir-N(5)	2.040(3)	N(3)-C(6)	1.436(5)				
Ir-C(22)	2.021(4)	C(17)–N(6)	1.396(5)				
Ir–Cl(1)	2.3552(11)	N(6)–N(5)	1.258(5)				
Ir–Cl(2)	2.3470(11)	N(5)–C(16)	1.447(5)				
2a							
Ir–N(1)	2.013(6)	Ir-Cl(4)	2.331(2)				
Ir-N(3)	2.010(6)	C(5) - N(2)	1.384(10)				
Ir-Cl(1)	2.361(2)	N(2)–N(3)	1.260(9)				
Ir-Cl(2)	2.3820(19)	N(3)-C(6)	1.443(9)				
Ir–Cl(3)	2.3751(19)						
3·CH₂Cl₂·0.5CH	H ₃ OH						
Ir-N(4)	2.028(4)	N(5)–N(6)	!.299(6)				
Ir-N(6)	2.019(4)	N(6)-C(17)	1.404(7)				
Ir-N(2)	2.025(5)	C(5)–N(2)	1.451(7)				
Ir-C(11)	1.983(5)	N(2)–N(3)	1.284(6)				
Ir–Cl(1)	2.4610(13)	N(3)-C(6)	1.385(7)				
Ir–Cl(2)	2.3545(14)	C(20)–N(7)	1.357(7)				
C(16)–N(5)	1.384(7)	N(7)–C(23)	1.435(8)				
4							
Ir-N(1)	2.013(9)	N(2)–N(3)	1.292(12)				
Ir-N(3)	2.034(9)	N(3)-C(6)	1.422(14)				
Ir-N(5)	2.092(9)	N(5)–C(18)	1.456(13)				
Ir-N(6)	2.089(8)	N(6)-C(24)	1.441(14)				
Ir–Cl(1)	2.368(3)	C(9) - N(4)	1.406(15)				
Ir–Cl(2)	2.341(3)	N(4)-C(12)	1.49(2)				
C(5)–N(2)	1.356(14)	N(4)–C(12')	1.33(4)				

Results and discussion

The reaction of HL^1 with hydrated $IrCl_3$ (2:1 molar proportion) in boiling methanol produced a brown mixture in about 4 h. The crude mass, so obtained, upon evaporation of the solvent produced a mixture of several products. Two pure brown compounds have thus far been separated on a preparative TLC plate. There are many small overlapping bands, which could not be isolated in the pure state and we do not consider these any further. While the compound, obtained from the first brown band (brown I, 1) was soluble in common organic solvents, the second polar brown band yielded a cationic complex (brown II, 2), which was soluble only in polar solvent such as acetonitrile, alcohols *etc.* Notably, the reaction is solvent such as acetonitrile.

A. Brown I, 1

A brown band was first eluted with chloroform. A dark compound (1) was obtained by evaporation of the chloroform eluate in ca. 20% yield.

Fig. 1 shows the ORTEP and atom numbering scheme of a representative **1a** ($HL^1 = HL^{1a}$) and selected bond lengths are collected in Table 1. In this complex the central iridium(III) is surrounded by a distorted octahedral coordination environment by two *trans*-chloride ligands, one bidentate neutral HL^{1a} ligand (N,N) and an anionic $[L^{1a}]^-$ ligand (C,N). The asymmetric unit also contains one CH_2Cl_2 molecule as a solvent of crystallization. The ligand, $[L^{1a}]^-$ is orthometallated and coordinates to iridium(III) using the *ortho*-carbon, C(22) of the phenyl ring and the azonitrogen N(5) so as to form a five-membered chelate. Notably, the pyridyl nitrogen N(4) of this ligand remains unused. We wish to note here that such a coordination mode of the reference ligand *via* C–H dissociation has not been observed previously. However, examples of orthometallated¹⁴ iridium(III) complexes are numerous. In the present structure the chelate bite angle of the anionic ligand

[L^{1a}]⁻, 76.66(15)°, is marginally larger than that of the neutral ligand, HL^{1a}, 74.40(13)°. Notably, the Ir-N(3) length (2.140(3) Å) trans to the Ir-C(22) bond is appreciably longer than the other two Ir-N lengths (av. 2.046(3) Å) present in this molecule. Lengthening of the Ir-N distance trans to Ir-C is in fact a diagnostic feature14h,15 in orthometallated iridium(III) complexes. The Ir-C(22) length, 2.021(4) Å is comparable¹⁵ to that observed in related iridium(III) orthometallated complexes. The two N-N lengths in 1a are similar in their average value (1.261(5) Å) and lie close to the N-N length observed¹⁶ (1.258(5) Å) in the perchlorate salt of the protonated ligand [H₂L^{1a}]ClO₄. Notably, these N–N lengths are appreciably shorter⁸ than that observed in the Ir(1)-HL¹ complexes (>1.30 Å). This may be attributed to the absence of any significant $Ir(d\pi)$ $azo(p\pi)$ interaction in the present trivalent iridium complexes. The central metal atom in this structure sits in a plane formed by three coordinating nitrogens viz N(1), N(3) and N(5) together with C(22) with no atom deviating by >0.02 Å. Notably, far IR spectra of complexes 1a and 1b ($HL^1 = HL^{1b}$) displayed an intense, sharp and single band near 325 cm⁻¹ confirming¹ the presence of a trans-MCl₂ grouping.



Fig. 1 ORTEP representation of the molecular complex [IrCl₂(L^{la})-(HL^{la})] 1a.

It was necessary to examine the NMR[‡] of the compounds for further authentication of carbon-bonded structure in **1** since the X-ray data would not permit differentiation of a carbon from a nitrogen atom.

¹H NMR of 1. The ¹H NMR spectrum of 1a is shown in Fig. 2. The spectral data of a closely related ruthenium compound, 1g,h,17 tcc-RuCl₂(HL^{1a}-N,N)₂ is used for comparison. In the ruthenium complex, the two HL1a ligands coordinate as neutral HL1a (N,N donor). Its geometry is trans with respect to two chlorides but is cis with respect to the pyridyl and azo pairs of nitrogens. There exists a twofold axis of symmetry and the two ligands in the ruthenium complex are equivalent. Thus the spectrum (Fig. S1, ESI⁺) is simple and showed seven resonances as expected.¹⁸ In contrast, the spectrum of 1a is complex and indicates that the two ligands in it are different. With the *trans*-MCl₂ grouping for a $[MCl_2L_2]^{n+}$ complex, this can happen only if the two coordinated ligands are different. Thus the 1H NMR confirms the different coordination modes of the two ligands in 1a. Moreover, the appearance of two methyl resonances in the ¹H NMR spectrum of 1b(R = Me) (Fig. S1, inset, ESI[†]) also supports this conclusion. The methyl resonance at δ 2.53 is assigned to the coordinated C-bonded (L1b, C,N) ligand. The other methyl signal for normal HL1b (N, N) coordination appears at δ 2.25, which is similar18 to that observed in other M-HL1b complexes.

 ^{13}C NMR of 1. The C-bonded coordination of one of the two HL^{1a} ligands in 1 was finally confirmed by the analysis of ^{13}C NMR

‡ The atom numbering scheme used in this section is as shown in Chart I.



Fig. 2 ¹H NMR spectra of (a) $[IrCl_2(L^{1a})(HL^{1a})]$ 1a in CDCl₃ and (b) $[IrCl_4(HL^{1a})]Cl$ 2a in CD₃CN.

spectra of the compounds. The ¹³C NMR spectrum of 1a consists of 20 distinct resonances (Fig. 3). The spectrum of 1a is compared with that of *tcc*-RuCl₂(HL^{1a}-N,N)₂ for identification of the resonances (Fig. S2, ESI⁺). In the ruthenium complex there are only 9 resonances, two of which at δ 122.91 and 128.19 are more intense. We assign these to two overlapping resonances of C⁸, C¹¹ and C⁹, C¹¹. Two relatively small intensity resonances at δ 165.88 and 157.99 are assigned to C² and C⁷, respectively. Since there exists a two-fold axis of symmetry in the ruthenium complex, the two coordinated ligands are equivalent. Consequently, the resonances for only one coordinated HL^{1a} (R = H) were observed. In contrast, the iridium complex lacks any symmetry element. Moreover, due to orthometallation, the degeneracy of C⁸ and C¹²; C⁹ and C^{11} resonances are lost in the orthometallated $[L^{1a}]^-$ ligand. As a result, in [L^{1a}]⁻ (C,N-coordination) all eleven carbons are dissimilar and gave rise to 11 signals.



Fig. 3 ^{13}C NMR spectra of (a) $[IrCl_2(L^{1a})(HL^{1a})]$ 1a in CDCl₃ and (b) $IrCl_4(HL^{1a})]Cl$ 2a in CD₃CN.

The remaining 9 resonances are from the neutral HL^{1a} (N,Ncoordination). There are five non-hydrogen carbons in **1a**, which are absent in the DEPT spectrum. Four of these nonprotonated carbons resonate at the low-field end of the spectrum (δ 154.95–167.88) near the chemical shift of the 2- and 7-carbons of *tc*-RuCl₂(HL^{1a})₂. We assign the fifth nonprotonated carbon, which resonates at δ 148.31 to C bonded to the iridium metal center. We note here that the chemical shift¹⁹ of the carbon of 2,2'-bipyridine bonded to iridium(III) in [Ir(bpy-*N*,*N*)(bpy-*C*,*N*)]²⁺ appears at δ 139.5.

B. Brown II, 2

A second brown band was eluted with chloroform–acetonitrile (3:2) solvent mixture from the crude mixture. Its perchlorate salt can be prepared by the addition of an aqueous NaClO₄ solution to a solution of the chloride salt in acetonitrile. The yield of this product (*ca.* 25%) is relatively higher than the other product of the same reaction. Compound **2** is a 1:1 electrolytic in CH₃CN and its elemental analysis and FAB mass spectrum matched well with

a iridium(v) complex of composition [IrCl₄(HL¹)]Cl. A survey of literature indicated that isolable non-organometallic iridium(v) complexes are limited and no X-ray structures are available. Hence there has been interest in the structure of such compounds. We could grow X-ray quality crystals of 2a (HL¹ = HL^{1a}) by the diffusion of its acetonitrile solution into toluene. A view of the molecule is shown in Fig. 4. The structural analysis of 2a has confirmed its formulation. The six-coordinate iridium centre in the cationic complex has a distorted octahedral geometry surrounded by four chloride ions and a HL1a ligand. The ligand binds using its normal N,N-coordination mode. The complex as a whole is monocationic, and the crystallographic asymmetric unit also contains a chloride as a counter anion. It is noticed that the chloride anion is surrounded by four iridium coordinated chlorides with short Cl...Cl contacts (2.74, 2.82, 2.92 and 3.12 Å). This is due to the cation-anion interactions. The chelate bite angle, N(1)-Ir-N(3) is 77.9(3)°. The Ir-N lengths in this compound are systematically shorter than those in 1a. This may be attributed to stronger metal-nitrogen interactions due to the higher charge of the central metal ion. The N-N lengths in 2a are 1.258(5) Å signifying the retention of its double bond character in the coordinated ligand.



Fig. 4 ORTEP representation of the complex [IrCl₄(HL^{1a})]Cl 2a.

The IR spectrum of each of these complexes (2a, 2b (HL = HL^{1b})) showed four strong v_{Ir-CI} stretches at 335, 310, 300 and 285 cm⁻¹, indicating the presence of four Ir–Cl bonds. In addition, the complexes showed all other characteristic stretches of the coordinated HL¹ ligand. For example, the $v_{N=N}$ and $v_{C=N}$ vibrations appeared^{1h} near 1385 and 1585 cm⁻¹, respectively. Like the trivalent iridium complexes (1a and 1b) these are also diamagnetic¹¹ and showed resolved NMR spectra. The ¹H NMR spectrum is simple and indicated the presence of only one HL¹ in these complexes (Fig. 2). One of the four pyridyl proton resonances of 2a overlapped with the aromatic proton signals.

The ¹³C NMR spectrum of **2a** (Fig. 3) showed 9 resonances confirming N,N (neutral) coordination of the ligand HL^{1a} (*vide supra*).

The above synthetic reactions were attempted in two different types of solvents *viz*. common alcohols (ethanol and methanol) and acetonitrile. While the reaction proceeded smoothly in alcohols, it did not occur at all in acetonitrile. This indicates that a hydroxylic solvent favors the synthetic reaction. The mechanism of this chemical reaction is complex and we refrain from making any speculation on this aspect.

C. Cyclic voltammetry and absorption spectra of 1 and 2

The free ligand HL^{1a} is known^{1g} to undergo two-step reductions at -1.31 and -1.57 V. The iridium complexes, **1** and **2** displayed reversible responses at -0.49 and -0.57 V, respectively. These are followed by irreversible cathodic responses that occur at higher cathodic potentials. To have further insight into the nature of orbitals involved during the reduction processes, we recorded

					Cyclic voltammetry ^c	
	$IR(KBr) (\nu/cm^{-1})$				Oxidn.	Redn.
Compound	$v_{c=c+c=N}$	$v_{\rm N=N}$	$v_{\rm Ir-Cl}$	Abs. ^{<i>a</i>} [λ_{max} /nm (ϵ /M ⁻¹ cm ⁻¹)]	$\overline{E_{_{1/2}}/\mathrm{V}~(\Delta E_\mathrm{p}/\mathrm{mV})^d}$	$\overline{E_{\frac{1}{2}}/\mathrm{V}\left(\Delta E_{\mathrm{p}}/\mathrm{mV} ight)^{d}}$
1a	1580	1380,	325	620 (670), 490 (2215), 350 (8540), 250 (7590) ^b	1.58 ^e	0.49 (90), 0.99; ^{<i>f</i>}
1b	1585	1300 1380, 1300	325	$620 (660), 490 (3260), 350 (9235), 255 (9445)^{b}$	1.50 ^e	0.50 (150), 1.04, ^f 1.23 ^f
2a	1585	1375	335, 310, 300, 280	755 (650), 505 (3520), 340 (9800), 290 (8260)	1.38 (70)	0.57 (100), 1.25
2b	1590	1360	330, 315, 300, 285	760 (785), 500 (3035), 335 (10755), 285 (8450)	1.38 (90)	0.60 (150), 1.35 ^f
3	1585	1305 1370	325, 310	590 (22215), 315 (16690), ^b 245 (19300) ^b	1.23 ^e	0.46, ^f 0.83, ^f 1.11 ^f
4	1590	1300 1370	325, 315	595 (14300), 420 (2500), ^b 245 (11920) ^b	1.16 ^e	0.35, 1.20

^{*a*} Solvent, CH₃CN. ^{*b*} Shoulder. ^{*c*} Conditions: solvent CH₃CN; supporting electrolyte NEt₄ClO₄ (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration, *ca.* 10⁻³ M; scan rate, 50 mV s⁻¹. ^{*d*} $E_{\gamma_2} = \frac{1}{2}(E_{pa} + E_{pc})$; $\Delta E_p = (E_{pa} - E_{pc})$. ^{*e*} Irreversible value corresponds to E_{pa} . ^{*f*} Irreversible value corresponds to E_{pc} .

ESR spectra of electrogenerated $[1a]^-$ and [2a] at 77 K by constant potential bulk electrolysis of the respective complexes. Each of the above two reduced products showed a symmetric and sharp ESR signal with a 'g' value near 2.0, confirming the free radical nature of the reduced species. These results strongly suggest that the unpaired electrons in both $[1a]^-$ and [2a] are localized in ligand orbitals.

In addition, the iridium(III) complex, 1 showed an irreversible response with no cathodic counterpart near 1.60 V. The anodic potential response, however, in the case of 2 is reversible and occurs near 1.40 V. With reference to previously reported M-HL¹ complexes, the anodic potential response in the iridium(III) complexes is assigned as an $Ir(III) \rightarrow Ir(IV)$ process while that in the iridium(v) complexes is ascribed as an $Ir(v) \rightarrow Ir(vI)$ couple. We attempted to record the ESR spectrum of the oxidized complex $[2a]^{2+}$; the oxidized complex was, however, ESR silent. The colour of the solution of the oxidized complex was brown and showed a reductive wave at 1.40 V. This voltammogram (initial scan cathodic) is superimposable on that of the corresponding complex $[2a]^+$ (initial scan anodic) showing that the redox process under consideration is chemically reversible. We wish to note here that iridium being a 5d-element, spin-orbit coupling of it is substantial,20 which may be responsible21 for ESR inactivity of the electrogenerated Ir(vi)-complex. Cyclic voltammograms of representative compounds 1a and 2a are shown as Figs. S3 and S4, respectively (ESI[†]).

The UV-Vis absorption spectral data in the range 800-300 nm are collected in Table 2. The trivalent complexes 1a and 1b showed an intense absorption band near 350 nm (ε of the order of 10000 M⁻¹ cm⁻¹) with two weak transitions at ca. 450 and ca. 620 nm. Electronic spectra of 1a and 2a are shown in Fig. 5. Visible range transitions in the iridium(III) complexes may be attributed²² to metal to ligand charge transfer. Since the two chelating ligands are different, multiple charge transfer transitions in 1 are as expected. The spectra of the iridium(v) complexes consisted of a weak absorption (ε , 650 M⁻¹ cm⁻¹) near 750 nm, and a strong absorption (ε , 3520 M⁻¹ cm⁻¹) near 505 nm. In addition, multiple charge transfer transitions occur in the UV-region (<350 nm), which are ascribed as ligand based transitions. The strong absorption near 505 nm is due to allowed metal to ligand charge transfer, while the weak transition near 750 nm may be due to a spin forbidden transition within the t₂⁴-orbitals. Notably, electrochemical behavior of these complexes also supports the assignment of the MLCT transition. We further note here that low energy weak bands were noted before²⁰ in Cs[IrF₆].

D. Amination reactions and products

To examine the amination reaction⁶ of coordinated 2-(phenylazo)pyridine two representative iridium complexes, *viz.* **1a**



Fig. 5 Electronic absorption spectra for 1a (---), 2a (---), 3 (---) and 4 (···) in CH₃CN. Inset: Spectrum of 2a in the range 900–600 nm.

and 2a were reacted with neat PhNH₂. The initial brown solution of 1a in PhNH₂ was heated at 120 °C on an oil-bath for an hour. The mixture gradually became blue-violet. The crude product, after initial work up, was purified by repeated crystallization from a dichloromethane-hexane solvent mixture. A dark crystalline compound (3) was isolated in 50% yield. Suitable X-ray quality crystals of it were obtained by diffusion of a dichloromethane solution of 3 into heptane. The structure analysis of 3 has revealed the fusion of PhNH₂ to the para-carbon of the coordinated neutral HL^{1a} ligand (N,N-donor). The asymmetric unit contains a molecule of complex, 3, a disordered dichloromethane molecule and half a disordered methanol molecule, which is located at a center of inversion; O1 and C30 are at the same position with half occupancy. Notably, the second ligand viz. ortho-metallated [L1a]- (C,N-donor) remains unaffected (Scheme 1). Fig. 6 shows the ORTEP and atom numbering scheme for the product 3. Para-fusion of PhNH₂ in this case seems reasonable since there was no dissociation of any ligand during the course of the reaction. It has been shown before^{6b} that availability of vacant or labile coordination site(s) at the metal centre is an essential prerequisite for an ortho fusion reaction at the phenyl ring of HL1. Furthermore, we wish to note that the above fusion reaction is associated with geometrical isomerization of the compound. Thus the two chlorides in 3 are cis and the orthometallated carbon (C(11)) bonded to iridium is *trans* to a chloride ligand (Cl(1)). As a consequence, the Ir-Cl(1) bond (2.4610(13) Å) is appreciably elongated relative to the other Ir-Cl(2) (2.3545(14) Å) length due to a strong trans effect.

Similar amination reaction of the iridium(v) complex, 2a is sluggish and occurs only at a higher temperature (140 °C), after 2 h,



Fig. 6 ORTEP representation of the molecular complex [IrCl_2(L^{1a})-(HL^2)] 3.

a blue mixture was obtained that contained several overlapping blue bands in the TLC plate. Only one major band could be isolated so far from an alumina TLC plate in 20% yield. The resultant compound, 4 was finally obtained as a crystalline chloride salt by slow diffusion of its acetonitrile solution into toluene. The X-ray structure of 4 revealed that the aromatic amine fusion reaction occurred at the para carbon of the pendent phenyl ring of the coordinated HL^{1a} ligand. This organic transformation is associated with substitution of two Cl⁻ by two PhNH₂ groups. In this reaction the starting metal ion, Ir(v) underwent two-electron reduction to yield an Ir(III) system. A view of the molecule is shown in Fig. 7. In it, the iridium(III) center is surrounded in a distorted-octahedral coordination environment by two cis-chloride ligands, two trans PhNH₂ and an extended N,N donor formed due to para fusion of PhNH₂ at the coordinated HL^{1a} ligand, in 2a. The complex as a whole is monocationic and the crystallographic asymmetric unit also contains one chloride as a counter ion. The phenyl ring bonded to N(4) is disordered. In this compound, the Ir-N bond lengths of the neutral chelate viz. Ir-N(1) and Ir-N(3) are shorter than the other two Ir-N bonds. A similar trend was noted²³ before in a mixed ligand ruthenium(II) complex [Ru(PhNH₂)₂Cl₂(diim)]. In fact, the Ir-N(5) and Ir-N(6) lengths in the present iridium complex are similar to the Ru-N(PhNH₂)



Fig. 7 ORTEP representation of the complex [IrCl₂(HL²)(PhNH₂)₂]Cl 4.

lengths in the above noted ruthenium complex. It is believed that prior *para*-amination of coordinated HL^{1a} ligand in the pentavalent iridium complex is followed by chloride substitution and reduction of the intermediate complex.

The positive ion FAB mass spectra of the two compounds **3** and **4** showed a peak at m/z 684 and 723, respectively. These complexes are diamagnetic (Ir^{III}, t₂⁶). While the cationic complex **4** is a 1:1 electrolyte, complex **3** is a non-electrolyte in CH₃CN. Both of them showed complex ¹H NMR spectra with overlapping of proton signals. Like all other complexes of 2-[(4-(arylamino)phenyl)azo]-pyridine, HL², these iridium complexes are also blue and their electronic spectra are dominated^{6a,b} by intense transition(s) in the range 590–620 nm (Fig. 5). This transition(s) is (are) ascribed as intra-ligand charge transfer from the amine donor to the azo acceptor function.

E. Conclusion

The isolation and characterization of two ortho-metallated complexes of iridium(III) along with two rare examples of iridium(V) complexes are one of the main issues of this report. The normal coordination mode of the ligand, 2-(arylazo)pyridine (HL¹) is neutral (N,N); C,N-coordination as in the present iridium(III) complexes, has not been observed previously. In the C,N-coordination mode, the ligand binds as an anionic ligand, $[L^1]^-$ and its two nitrogens (a pyridyl and an azo nitrogen) remain unused. Hence, it may be anticipated²⁴ that like azobispyridine (abpy), the ligand [L1]⁻ is potentially a bridging ligand. Aromatic ring amination of the coordinated ligand in these iridium systems yielded intense blue complexes. Notably, the resultant para-aminated ligand in compounds 3 and 4 bears an uncoordinated donor amine function, which is separated from the coordinated acceptor azofunction by a conjugated spacer. Low energy transitions in these systems originate due to intra-ligand charge excitation. Examples of such systems are scarce in the literature. Our work in this area is ongoing; some of these systems might turn out to be useful photoactive materials.6b

Experimental

Materials

IrCl₃:xH₂O was obtained from Arora Matthey and was digested twice with concentrated HCl before use. Solvents and chemicals used for syntheses were of analytical grade and used as received. Supporting electrolyte (TEAP) and solvents for electrochemical work were obtained as before.^{2c} 2-(Arylazo)pyridines were prepared following the reported procedure.²⁵

Physical measurements

A Shimadzu UV2100 UV/VIS spectrophotometer was used to record electronic spectra. The IR spectra were recorded with a Perkin-Elmer 783 spectrophotometer. A Perkin-Elmer 240 C elemental analyzer was used for microanalyses. ¹H and ¹³C NMR spectra were measured with a Bruker Avance DPX300 spectrometer.

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Table 3 Crystallographic data

	$1a \cdot CH_2Cl_2$	2a	$3{\cdot}\mathrm{CH}_{2}\mathrm{Cl}_{2}{\cdot}0.5\mathrm{CH}_{3}\mathrm{OH}$	4
 Empirical formula	C ₂₃ H ₁₉ Cl ₄ N ₆ Ir	C ₁₁ H ₉ Cl ₅ N ₃ Ir	C _{29 50} H ₂₆ Cl ₄ N ₇ O _{0 50} Ir	C ₂₉ H ₂₈ Cl ₃ N ₆ Ir
M	713.44	552.66	820.57	759.12
T/K	295(2)	295(2)	150(1)	150(1)
Crystal system	Triclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P\overline{1}$	$Pca2_1$	$P\overline{1}$	$P2_{1}/c$
a/Å	10.6393(5)	13.1574(5)	10.4245(5)	14.3247(7)
b/Å	11.0054(5)	16.6804(6)	10.9234(5)	8.5842(4)
c/Å	12.3368(6)	7.1069(3)	13.0744(6)	23.3471(11)
a/°	102.928(1)	90	95.667(1)	90
B/°	113.200(1)	90	92.225(1)	103.431(1)
v/°	97.590(1)	90	91.641(1)	90
$V/Å^3$	1254.34(10)	1559.76(10)	1479.61(12)	2792.4(2)
$D_c/Mg m^{-3}$	1.889	2.353	1.842	1.806
Z	2	4	2	4
Cryst. dimens./mm	$0.36 \times 0.20 \times 0.05$	$0.50 \times 0.10 \times 0.06$	$0.30 \times 0.10 \times 0.06$	$0.33 \times 0.12 \times 0.02$
GOF	1.019	1.131	1.071	1.303
Reflections collected	16229	14933	17193	20774
Unique reflections	5736	3565	6772	6405
Rinal <i>R</i> indices	R1 = 0.0315	R1 = 0.0286	R1 = 0.0378	R1 = 0.0802
	wR2 = 0.0639	wR2 = 0.0798	wR2 = 0.0912	wR2 = 0.1596

Electrochemical measurements were performed under a dry nitrogen atmosphere on a PAR 370–4 electrochemistry system. All potentials in this work are referenced to the saturated calomel electrode (SCE) and are uncorrected for junction contribution. The value for the ferrocenium–ferrocene couple under our experimental conditions was 0.42 V.

Syntheses of $[IrCl_2(L^{1a})(HL^{1a})]$ 1a and $[IrCl_4(HL^{1a})]Cl$ 2a

100 mg (0.28 mmol) IrCl₃·3H₂O and 110 mg (0.60 mmol) 2-(phenylazo)pyridine were taken in 100 ml methanol. The mixture was refluxed on a steam bath. The yellowish-brown colour of the mixture slowly became dark brown. The reflux was continued for 4 h and then the mixture was cooled and filtered. The brown filtrate was evaporated to dryness. The crude residue was extracted with dichloromethane. The extract, which contained mainly the compound **1a**, was further purified on a preparative TLC (silica gel) plate using chloroform as eluent. A yellowish band of unreacted 2-(phenylazo)pyridine moved first followed by a major brown band of compound **1a**, which was collected and recrystallized from a dichloromethane–hexane mixture. A few minor and overlapping brown bands were observed in the plate and could not be purified.

The residue from the dichloromethane extract was dissolved in acetonitrile and loaded on a TLC (silica gel) plate and was eluted with a 3:2 chloroform–acetonitrile mixture. A major reddish brown band was collected and recrystallized from acetonitrile–toluene. Some minor overlapping brown and pink bands were observed near the spot, which however could not be isolated. Yields and analyses of **1a** and **2a** are as follows:

2a. Yield: 40 mg. 25%. Anal. Calc. for $C_{11}H_9N_3Cl_3Ir$: C, 23.90; H, 1.64; N, 7.60. Found: C, 23.98; H, 1.62; N, 7.73%. ¹³C NMR (CD₃CN): δ 150.31, 142.11, 132.24, 128.07, 126.75, 126.21, 126.11, 117.66 (2 C). MS: *m/z*: 517 [M – Cl⁻]⁺

The compounds **1b** and **2b** were synthesized similarly following the above procedure using 2-(*m*-tolylazo)pyridine in place of 2-(phenylazo)pyridine.

1b. Yield: 18%. Anal. Calc. for $C_{24}H_{21}N_6Cl_2Ir$: C, 43.90; H, 3.22; N, 12.80. Found: C, 43.83; H, 3.15; N, 13.92%. ¹³C NMR (CDCl₃): δ 168.29, 167.46, 161.89, 155.66, 152.06, 149.07, 144.46, 142.06,

139.35, 137.39, 135.86, 133.72, 133.13, 132.83, 129.02, 128.44, 127.28, 127.20, 124.76, 123.89, 120.35, 118.75, 21.68, 20.99.

2b. Yield: 22%, Anal. Calc. for $C_{12}H_{11}N_3Cl_5Ir$: C, 25.89; H, 1.99; N, 7.55. Found: C, 25.82; H, 2.03; N, 7.51%. ¹³C NMR (DMSO-d⁶): δ 171.90, 154.58, 150.72, 142.44, 137.81, 133.17, 128.03, 126.79, 126.65, 126.11, 124.59, 21.72.

Amination reactions

A. Synthesis of $[IrCl_2(L^{1a})(HL^2)]$ 3. A mixture of $[IrCl_2(L^{1a})(HL^{1a})]$ (100 mg, 0.12 mmol) and PhNH₂ (0.5 ml) was heated on an oil-bath at 120 °C for 1 h. The initial brown colour of the mixture gradually became dull violet. The mixture was cooled and washed thoroughly with diethyl ether several times. Further purification was made by repeated recrystallization of the crude mass from a dichloromethane–hexane mixture. Finally the product was purified by slow diffusion of a dichloromethane solution of the compound into hexane.

Yield: 57 mg, 50%. Anal. Calc. for $C_{29.5}H_{26}N_7Cl_4O_{0.5}Ir: C, 43.18;$ H, 3.19; N, 11.95. Found: C, 42.65; H, 3.49; N, 11.35%. MS: *m/z*: 684 [M – Cl[–]]⁺.

B. Synthesis of $[IrCl_2(HL^2)(PhNH_2)_2]Cl 4$. A mixture of $[IrCl_4(HL^{1a})]Cl (100 mg, 0.13 mmol) and PhNH_2 (0.5 ml) was heated at 140 °C on an oil-bath for 2 h. The resultant greenish-blue mixture was cooled and washed with diethyl ether several times. The crude mass was then purified on a preparative TLC (neutral alumina) plate using a 1:1 chloroform–acetonitrile mixture as the eluent. A major bright blue band was collected and other minor blue and brown bands were discarded. The blue compound was recrystallized from an acetonitrile–toluene solvent mixture.$

Yield: 27 mg, 20%. Anal. Calc. for $C_{29}H_{28}N_6Cl_3Ir$: C, 45.88; H, 3.72; N, 11.07. Found: C, 45.67; H, 3.75; N, 11.25. MS: *m/z*: 723 [M - Cl⁻]⁺.

Crystallography

Suitable X-ray quality crystals of **1a** were obtained by slow diffusion of a dichloromethane solution of the compound into hexane while those of **3** were obtained by slow diffusion of a dichloromethane solution of the compound into heptane. Suitable X-ray quality crystals of **2a** and **4** were grown by slow diffusion of an acetonitrile solution of the respective compounds into toluene. Intensity data for the above compounds **1a**, **2a**, **3** and **4** were measured on a Bruker SMART diffractometer (Mo-K α radiation, $\lambda = 0.71073$ Å) and data were corrected for Lorentz-polarisation effects. The structures were solved by employing the SHELXS-97²⁶ program package and refined by full-matrix least squares based on F^2 (SHELXL-97).²⁷ All the hydrogen atoms were added in the calculated positions. All the relevant data are given in Table 3.

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See http://www.rsc.org/suppdata/dt/b4/b407209j/ for crystallographic data in CIF or other electronic format.

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