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Reactions of 2-(arylazo)aniline with iridium trichloride: Synthesis, characterization and structure of new cyclometallated complexes of iridium(III)

Jahar Lal Pratihar^a, Poulami Pattanayak^a, Debprasad Patra^a, Rajendra Rathore^b, Surajit Chattopadhyay^{a,*}

^a Department of Chemistry, University of Kalyani, Kalyani 741235, India ^b Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, WI 53201, USA

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1. Introduction

Facile coordination of azo (-N=N-) nitrogen of multidentate ligands, to heavier transition metal ions, are well documented [1-26]. Most of these ligands are bidentate or tridentate. A few tetradentate ligands have been reported recently [8–12]. Reactions of tridentate azo ligands with the appropriate substrates of heavier transition metal ions afforded complexes with metal-carbon bond [1-7,20-23]. These metal-carbon bonded complexes exhibited interesting reactivities and redox properties [1-7,20-23]. Often it was stated that the types of complexes formed are very much dependent of metal substrates.

Among the heavier transition metal ions, reactions of iridium substrates with azo ligands have been studied scarcely [20,24-26]. Reports on reactions of IrCl₃·3H₂O with azo ligands are limited [24-26]. Further, the reaction of 2-(arylazo)aniline, HL, 1, with RhCl₃ in methanol enabled us to recognize the reductive cleavage of -N=N- bond [1,2]. These interesting results prompted us to study the reaction of $IrCl_3 \cdot 3H_2O$ with 2-(arylazo)aniline.



* Corresponding author. Tel.: +91 33 25828750; fax: +91 33 25828282. E-mail address: scha8@rediffmail.com (S. Chattopadhyay).

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ABSTRACT

Reactions of 2-(arylazo)aniline, HL (H represents the dissociable protons upon orthometallation and HL is $p-RC_6H_4N=NC_6H_4-NH_2$; R=H for HL¹; CH₃ for HL² and Cl for HL³) with IrCl₃ in methanol afforded orthometallated complexes of composition $(L)(HL)IrCl_2$ (2) and $(L)(MeOH)IrCl_2$ (3), respectively. Complex (L)(MeOH)IrCl₂ (**3**) converted into (L)(CH₃CN)IrCl₂ (**4**) upon refluxing in acetonitrile. The X-ray structure of the complexes $(L^1)(HL^1)IrCl_2$ (2a) and $(L^3)(CH_3CN)IrCl_2$ (4c) have been determined and characterized unequivocally. The anionic L⁻ binds the metal in tridentate (C, N, N) manner for all the complexes. © 2011 Elsevier B.V. All rights reserved.

> Herein, we report the reaction of 2-(arylazo)aniline, HL(1), with IrCl₃ yielding cyclometallated complexes of Ir(III) of composition (L)(HL)IrCl₂, (L)(MeOH)IrCl₂ and (L)(MeCN)IrCl₂. All the complexes were characterized unequivocally. The X-ray structures of the complexes $(L^1)(HL^1)IrCl_2$ (**2a**) and $(L^3)(CH_3CN)IrCl_2$ (**4c**) have been determined.

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2. Results and discussion

2.1. Synthesis

Reaction of iridium(III) chloride with 2-(arylazo)aniline in 1:2 stoichiometric ratio afforded two products (L)(HL)IrCl₂, (2) and (L)(MeOH)IrCl₂ (**3**) in \sim 10% and \sim 60% yields, respectively upon boiling in methanol for 3 h (Eq. (1)). The ligands used and the products obtained are shown in Eq. (1). Complex (L)(MeOH)IrCl₂ (3) converted into (L)(CH₃CN)IrCl₂ (4) upon refluxing in acetonitrile (Eq. (2)).

In contrast to the reaction of RhCl₃ with HL, herein, the reductive cleavage of -N=N- could not be identified. The reduction of azo (-N=N-) bond, in the case of RhCl₃, was reported to occur by Rh(I) species which formed in situ in boiling methanol [1,2]. Although, the mention regarding the formation of such Rh(I) species in boiling methanol has been included in the text books [1,2,27] but the formation of Ir(I) species upon boiling IrCl₃ in methanol has not been indicated. Conversion of RhCl₃ and IrCl₃ into Rh(I) and Ir(I) species, respectively were compared and reported elsewhere [28]. It was described that IrCl₃ afforded Ir^{III}(H)Cl₂(PPh₃)₃ rather than Ir^I(PPh₃)₃Cl upon reaction with PPh₃ in boiling ethanol or methanol [28]. Whereas Rh(PPh₃)₃Cl could be prepared at ease upon reaction of RhCl₃ with PPh₃ in boiling





Fig. 1. UV–Vis spectra of $(L^1)(HL^1)IrCl_2$ (–), $(L^1)(MeOH)IrCl_2$ (–) and $(L^1)(CH_3CN)IrCl_2$ (…).

in ethanol or methanol [29]. Moreover, the Ir(I) compounds are more air sensitive than the corresponding Rh(I) analogues [28] indicating the difficulty of formation of appreciably stable Ir(I) species upon boiling IrCl₃ in methanol. Notably, Ir(PPh₃)₃Cl was

prepared from the Ir(I) substrates IrCl(C_8H_4)₂ [28]. This fundamental difference in the reactivities of IrCl₃ and RhCl₃ in boiling methanol has never been addressed unambiguously due to complexity in isolation and characterization of products directly. However, the noncleaveage of -N=N- by IrCl₃ upon reaction with HL is an indirect evidence regarding the intricacy in the formation of Ir(I) species in boiling methanol. As a result upon refluxing **2** with IrCl₃ in methanol did not afford the azo (-N=N-) cleaved product as in the case of RhCl₃ [1,2].





Fig. 2. Views of molecular structures of (L¹)(HL¹)IrCl₂ and (L³)(CH₃CN)IrCl₂ with atom numbering scheme. The hydrogen atoms, excepting those of the amino groups and acetonitrile solvent molecule, have been omitted for clarity.



2.2. Spectral characterization and solution structures

Solutions **2**, **3** and **4** in common organic solvents are green, greenish-brown and green, respectively. UV–Vis spectra of the complexes were recorded in dichloromethane solutions characteristic spectra for **2a**, **3a** and **4a** are shown in Fig 1. Spectra of other complexes are given in Supplementary material (Figs. S1–S9). The UV–Vis spectral data are given in the Section 4. All the complexes displayed several absorptions in the visible and ultraviolet regions. A characteristic low energy absorption band appeared near 625 nm for all the complexes.

The IR spectra of the complexes (Figs. S10–S18) in solid KBr support exhibited several overlapping v_{N-H} absorptions within the ranges 3090–3064 cm⁻¹ for **2** indicating the presence of more than one amino group. Complexes **3** and **4** exhibited v_{N-H} near 3165–3254. The $v_{N=N}$ of all the complexes shifted to lower energy (1368–1404) than the $v_{N=N}$ of the free ligands (1458–1474) indicating the coordination of azo nitrogen [17–19]. The IR data are collected in Section 4.

The composition of **2**, **3** and **4** matched well with the C, H, N analytical data and ¹H NMR spectral data. The ¹H NMR spectra (Figs. S19–S24 and S25–S27) of the complexes were recorded in CDCl₃ for **2** and CDCl₃–DMSO-*d*₆ mixed solvent for **3**. The amino protons appeared as broad singlet near δ 3.75 and δ 4.75 for **2** indicating two types of amino groups and consistent to the structure (see below). Complex **3** exhibit only one resonance for amino proton near δ 6.10. The resonances for NH₂ protons of **4** shifted marginally and appeared near δ 6.25. The total count of aromatic protons (δ 6.85– δ 8.22) matched well with the composition of the complexes (Section 4; Figs. S5–S8). The spectra of **2b** displayed two resonances for R = Me at δ 2.35 and δ 2.40. Whereas **3b** exhibited one methyl resonance for R = Me at δ 2.45. The resonances for –CH₃ protons of coordinated MeOH and CH₃CN appeared near δ 2.50 and δ 2.75 for **3** and **4**, respectively.

2.3. X-ray structures

The complexes, **2a** and **4c**, were crystallized by slow diffusion of petroleum ether (60–80 $^{\circ}$ C) into the dichloromethane and slow

Table

Selected bond distances	(Å) and angle	es (°) for com	pound (L ¹)(HL ¹)IrCl ₂
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Distances			
Ir(1)-Cl(1)	2.349(4)	N(3)-C(2)	1.42(2)
Ir(1)-Cl(2)	2.343(5)	N(1)-N(2)	1.271(19)
Ir(1) - N(1)	1.910(13)	N(2)-C(7)	1.43(3)
Ir(1)-N(3)	2.177(14)	N(1)-C(1)	1.46(2)
Ir(1)-N(6)	2.167(11)	N(4)-C(13)	1.41(2)
Ir(1)-C(12)	2.030(12)	N(4)-N(5)	1.23(2)
Angles			
Cl(1)-Ir(1)-Cl(2)	174.05(14)	Cl(2)-Ir(1)-C(12)	92.7(4)
Cl(1)-Ir(1)-N(3)	85.8(4)	N(3)-Ir(1)-N(1)	82.7(5)
Cl(1)-Ir(1)-N(1)	92.3(4)	N(3)-Ir(1)-N(6)	93.5(4)
Cl(1)-Ir(1)-N(6)	86.5(3)	N(3)-Ir(1)-C(12)	161.15(12)
Cl(1)-Ir(1)-C(12)	93.1(4)	N(2)-Ir(1)-N(4)	160.2(5)
Cl(2)-Ir(1)-N(1)	90.1(4)	N(1)-Ir(1)-C(12)	77.6(6)
Cl(2)-Ir(1)-N(6)	90.7(3)	N(6)-Ir(1)-C(12)	106.2(5)

Table 2 Selected bond distan	ces (Å) and angles ('	²) for compound (L ³)(CH ₃ CN)IrCl ₂ .
Distances	2 2575(0)	N(2) C(2)	1 461(5

Ir(1)-CI(1) Ir(1)-CI(2) Ir(1)-N(3) Ir(1)-N(1) Ir(1)-N(1S) Ir(1)-C(12)	2.3575(9) 2.3543(9) 2.189(3) 1.945(3) 2.029(3) 1.995(3)	N(3)-C(2) N(1)-N(2) N(2)-C(7) N(1)-C(1) N(1S)-C(1S)	1.461(5) 1.279(5) 1.401(5) 1.418(5) 1.134(5)
Angles Cl(1)-lr(1)-Cl(2) Cl(1)-lr(1)-N(3) Cl(1)-lr(1)-N(1) Cl(1)-lr(1)-N(1S) Cl(1)-lr(1)-C(12) Cl(2)-lr(1)-N(1) Cl(2)-lr(1)-N(1S)	176.34(3) 88.42(8) 91.83(10) 87.13(9) 91.55(10) 89.74(9) 91.32(9)	$\begin{array}{c} Cl(2)-lr(1)-C(12)\\ N(3)-lr(1)-N(1)\\ N(1)-lr(1)-N(1S)\\ N(3)-lr(1)-C(12)\\ N(1)-lr(1)-N(3)\\ N(1)-lr(1)-C(12)\\ N(1S)-lr(1)-C(12) \end{array}$	91.99(10) 82.03(13) 178.92(13) 161.57(15) 98.20(13) 79.54(16) 100.21(15)

evaporation of acetonitrile solutions, respectively. Both the crystals of 2a and 4c are monoclinic with the space group P21/c. The molecular structures of 2a and 4c are given in Fig. 2 with atom numbering scheme. The selected bond distances and angles are given in Tables 1 and 2 for **2a** and **4c**, respectively. Since the geometry and bond parameters are similar in the two molecules in the asymmetric unit of 2a, therefore those are same molecules. In $(L^{1})(HL^{1})IrCl_{2}$ tridentate $(L^{1})^{-}$ is coordinated to Ir(III) forming cyclometallated chelate. Another HL¹ ligand binds the Ir(III) centre in monodentate fashion through amino-N. Two chloride ligands completed hexacoordination about Ir(III). A second molecule of 2-(phenylazo)aniline binds in a monodentate fashion through the amino nitrogen at the sixth position of hexacoordinated Ir(III) in 2a while in 4c the nitrogen of acetonitrile solvents binds at the sixth position of hexacoordinated Ir(III). The geometries about Ir(-III), for both the complexes, are distorted octahedral where the chloride ligands are mutually trans with Cl-Ir-Cl angle being equal to 174.05(14) and 176.34(3) for **2a** and **4c**, respectively. The Ir-C, Ir-N(azo), Ir-Cl bond distances are all quite normal [20,24-26]. The Ir-N(azo) distance (1.910(13) Å) of 2a is shorter than the Ir-N(amine) lengths [Ir-N(3), 2.177(14); Ir-N(6), 2.167(11) Å] of the same molecule consistent to stronger $Ir \rightarrow N(azo)$ back bonding [1]. The Ir-N(3) [2.177(14) Å] bond is longer than the Ir-N(6) distance [2.167(11) Å] of **2a** due to stronger *trans* effect of aryl carbon [1]. Similar trends in Ir-N bond distances have been observed for **4c** also: Ir-N(azo) [1.945(3) Å] < Ir-N(amine) [Ir-N(3), 2.189(3) Å;Ir-N(1S), 2.029(3)Å]; Ir-N(3) [2.189(3)Å] > Ir-N(6) [2.167(11)Å] as a result of $d\pi$ - $p\pi$ backbonding and *trans* influence of aryl carbon, respectively. In the structure of **2a** C(aryl)–N(amine) bond is longer [**2a**: N(3)-C(2),1.42(2) Å; N(6)-C(14), 1.43(2) Å.] than that of in the azoimine (N, N) chelates of 1, where it is shorter $(av. \sim 1.34 \text{ Å})$ and similar to imine length due to dissociation of an amino proton followed by delocalization [17–19].

3. Conclusion

The reaction of 2-(arylazo)aniline with $IrCl_3$ afforded cyclometallated complexes of Ir(III), **2** and **3**. Upon boiling **3** in CH₃CN afforded complex **4** where CH₃CN is N-coordinated. It is proposed that the reduction of $IrCl_3$ in boiling methanol to form Ir(I) species, suitable for in situ reduction of -N=N- bond does not occur.

4. Experimental

4.1. Materials

The solvents used in the reactions were of reagent grade (E. Marck, Kolkata, India) and were purified and dried by reported

procedure [30]. IrCl₃·3H₂O was obtained from Arora-Mathey, India and used as it was received. Silical gel G with binder was used for thin layer chromatography. The ligands 2-(phenylazo)aniline (HL¹), 2-(p-tolylazo)aniline (HL²), and 2-(p-chlorophenylazo)aniline (HL³) were prepared following the reported procedures [17–19].

4.2. Physical measurements

Microanalysis (C, H, N) was performed using a Perkin–Elmer 2400 C, H, N, S/O series II elemental analyzer. Infrared spectra were recorded on a Parkin-Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1800 PC spectrophotometer. ¹H NMR spectra were obtained on Brucker DPX 400 and Brucker 500 RPX NMR spectrometers in CDCl₃ or CDCl₃-DMSO- d_6 mixture using TMS as the internal standard.

4.3. Syntheses of complexes

4.3.1. (L)(HL)IrCl₂ (**2**) and (L)(CH₃OH)IrCl₂ (**3**)

The (L)(HL)IrCl₂ (**2**) and (L)(CH₃OH)IrCl₂ (**3**) complexes were obtained by following a general procedure. Specific details are given below for a particular complex.

4.3.2. (*L*¹)(*HL*¹)*IrCl*₂ (**2***a*) and (*L*¹)(*CH*₃OH)*IrCl*₂ (**3***a*)

2-(Phenylazo)aniline, 1a, (60 mg, 0.30 mmol) was dissolved in methanol (40 mL), and to it IrCl₃ (100 mg, 0.15 mmol) was added. The mixture was then heated to reflux for 4 h to afford green solution. Evaporation of the solvent gave a dark green residue, which was introduced for purification by thin layer chromatography on silica gel. Two green bands separated in toluene-methanol (90:10, V/V) mixed solvent. From the first and second bands 2a and **3a**, respectively, were isolated in pure form upon extracting with dichloromethane and methanol, respectively. Yield: 10% (for complex **2a**) and 60% (for complex **3a**). IrC₂₄H₂₁N₆Cl₂ (656): Anal. Calc. C. 43.90: H. 3.20: N. 12.80. Found: C. 43.45: H. 3.28: N. 12.65%. UV–Vis spectrum (CH₂Cl₂) λ_{max} (ϵ , M⁻¹ cm⁻¹) = 620 (780), 430 (2730), 340 (19,660), 270 (9300), 235 (18,250). IR (KBr pellets, cm⁻¹): v = 3254, 3211, 3176 (NH₂), 1372 (N=N). ¹H NMR CDCl₃: δ 8.22–8.15 (m, 1H), 8.11 (d, 1H), 7.90–7.88 (m, 2H), 7.53-7.46 (m, 3H), 7.41-7.39 (m, 4H), 7.32-7.23 (m, 5H), 7.19 (t, 1H), 4.76 (s, 2H), 3.57 (s, 2H).

(L¹)(CH₃OH)IrCl₂ (**3a**): Yield: 60 %. IrC₁₃H₁₄N₃OCl₂ (491): *Anal.* Calc. C, 31.77; H, 2.85; N, 8.55. Found: C, 31.65; H, 2.73; N, 8.74%. UV–Vis spectrum (CH₂Cl₂) λ_{max} (ε , M⁻¹ cm⁻¹) = 640 (500), 440 (1790), 360 (7100), 230 (9580). IR (KBr pellets, cm⁻¹): v = 3216, 3185 (NH₂), 1369 (N=N). ¹H NMR (CDCl₃₊ 1 drop DMSO-*d*₆, ppm): δ 8.15–8.13 (m, 1H), 8.01–7.91 (m, 2H), 7.59–7.56 (m, 1H), 7.32–7.28 (m, 2H), 7.14–7.06 (m, 1H), 6.95 (t, 1H), 6.10 (s, 2H), 2.51 (s, 3H).

4.3.3. $(L^2)(HL^2)RhCl_2$ (**2b**) and $(L^2)(CH_3OH)RhCl_2$ (**3b**)

The complexes **2b** and **3b** were prepared following the same procedure as in the cases of **2a** and **3a** using 2-(*p*-tolylazo)aniline, **1b** (160 mg, 0.76 mmol), in place of **1a**. The solvent used for thin layer chromatographic separation is toluene–methanol (90:10 V/ V) mixed solvent. Yield: 15% (for complex **2b**) and 50% (for complex **3b**). IrC₂₆H₂₅N₆Cl₂ (684): *Anal.* Calc. C, 45.61; H, 3.65; N, 12.28. Found: C, 45.45; H, 3.60; N, 12.32. UV–Vis spectrum (CH₂Cl₂) λ_{max} (ε , M⁻¹ cm⁻¹) = 620 (1593), 430 (6080), 350 (37,000), 275 (16,000), 235 (29,400). IR (KBr pellets, cm⁻¹): v = 3250, 3215, 3167 (NH₂), 1368 (N=N). ¹H NMR CDCl₃: δ 8.16–8.13 (m, 1H), 7.99 (d, 1H), 7.88–7.82 (m, 4H), 7.53–7.45 (m, 2H), 7.41–7.39 (m, 3H), 7.32–7. 20 (m, 6H), 6.94 (d, 1H), 4.75 (s, 2H), 3.56 (s, 2H), 2.53 (s, 3H), 2.40 (s, 3H).

(L²)(CH₃OH)RhCl₂ (**3b**): Yield: 60%. IrC₁₄H₁₆N₃OCl₂ (505): Anal. Calc. C, 33.26; H, 3.16; N, 8.31. Found: C, 33.35; H, 3.19; N, 8.22. UV–Vis spectrum (CH₂Cl₂) λ_{max} (ε , M⁻¹ cm⁻¹) = 630 (520), 435 (1720), 365 (6770), 270 (4700), 230 (7660). IR (KBr pellets, cm⁻¹): v = 3191 (NH₂), 1368(N=N). ¹H NMR (CDCl₃₊ 1 drop DMSO-d₆, ppm): δ 8.10–8.09 (m, 1H), 7.95–7.82 (m, 1H), 7.74 (s, 1H), 7.64–7.41 (m, 1H), 7.34–7.24 (m, 1H), 6.78 (d, 1H), 6.09 (s, 2H), 2.51 (s, 3H), 2.45 (s, 3H).

4.3.4. $(L^3)(HL^3)RhCl_2$ (**2c**) and $(L^3)(CH_3OH)RhCl_2$ (**3c**)

The complexes **2c** and **3c** were prepared following the same procedure as in the cases of **2a** and **3a** using 2-(*p*-chlorophenylazo)aniline, **1c** (160 mg, 0.76 mmol), in place of **1a**. The solvent used for thin layer chromatographic separation is toluene–methanol (90:10 V/V) mixed solvent. Yield: 10% (for complex **2c**) and 50% (for complex **3c**). IrC₂₄H₁₉N₆Cl₄ (725): *Anal*. Calc. C, 39.72; H, 2.61; N, 11.57. Found: C, 39.83; H, 2.69; N, 11.67. UV–Vis spectrum (CH₂Cl₂) λ_{max} (ε , M⁻¹ cm⁻¹) = 620 (1100), 430 (3580), 350 (23,800), 275 (10,900), 235 (19,800). IR (KBr pellets, cm⁻¹): v = 3250, 3215, 3167 (NH₂), 1373 (N=N). ¹H NMR CDCl₃: δ 8.16– 8.14 (m, 1H), 8.00 (d, 1H), 7.90–7.85 (m, 3H), 7.56–7.51 (m, 2H), 7.47–7.24 (m, 7H), 7.01 (d, 1H), 4.78 (s, 2H), 3.56 (s, 2H).

(L³)(CH₃OH)RhCl₂ (**3c**): Yield: 60%. IrC₁₃H₁₃N₃OCl₃ (525.5): *Anal.* Calc. C, 29.68; H, 2.47; N, 7.99. Found: C, 29.77; H, 2.53; N, 8.12. UV–Vis spectrum (CH₂Cl₂) λ_{max} (ε , M⁻¹ cm⁻¹) = 635 (770), 435 (2480), 380 (8970), 360 (9960), 275 (7080), 230 (11,590). IR (KBr pellets, cm⁻¹): ν = 3176 (NH₂), 1373 (N=N). ¹H NMR (CDCl₃₊ 1 drop DMSO-*d*₆, ppm): δ 8.14–8.09 (m, 1H), 7.90 (d, 1H), 7.83 (d, 1H), 7.67–7.59 (m, 1H), 7.36–7.25 (m, 2H), 6.95 (d, 1H), 6.22 (s, 2H), 2.52 (s, 3H).

4.3.5. Synthesis of $(L^{1-3})(CH_3OH)IrCl_2(4a-c)$

(L)(CH₃CN)IrCl₂ (**4**) complexes were obtained from (L)(CH₃O-H)IrCl₂ (**3**) upon refluxing in acetonitrile for 4 h to afford green solution. Slow evaporation of the solvent gave crystals of (L)(CH₃CN)IrCl₂ (**4**).

(L¹)(CH₃CN)lrCl₂ (**4a**): Yield: 85%. IrC₁₄H₁₃N₄Cl₂ (500): *Anal.* Calc. C, 33.60; H, 2.60; N, 11.20. Found: C, 33.74; H, 2.45; N, 11.02. UV–Vis spectrum (CH₂Cl₂) λ_{max} (ε , M⁻¹ cm⁻¹) = 620 (1240), 425 (3360), 360 (13,830), 265 (8550), 235 (11,250). IR (KBr pellets, cm⁻¹): v = 3254, 3209, 3191 (NH₂), 1381 (N=N). ¹H NMR (CDCl₃₊ 1 drop DMSO-*d*₆, ppm): δ 8.14 (d, 1H), 8.01 (d, 1H), 7.62–7.57 (m, 2H), 7.40 (t, 1H), 7.33 (t, 1H), 7.15 (t, 1H), 7.06 (t, 1H), 6.29 (s, 2H), 2.76 (s, 3H).

(L²)(CH₃CN)lrCl₂ (**4b**): Yield: 90%. IrC₁₅H₁₅N₄Cl₂ (514): *Anal.* Calc. C, 35.01; H, 2.91; N, 10.89. Found: C, 35.22; H, 2.98; N, 10.75. UV–Vis spectrum (CH₂Cl₂) λ_{max} (ε , M⁻¹ cm⁻¹) = 615 (990), 420 (3250), 380 (11,000), 270 (7100), 240 (10,500). IR (KBr pellets, cm⁻¹): v = 3252, 3203, 3099 (NH₂), 1380 (N=N). ¹H NMR (CDCl₃₊ 1 drop DMSO-*d*₆, ppm): δ 8.13 (d, 1H), 7.89 (d, 1H), 7.54 (d, 1H), 7.41–7.27 (m, 3H), 6.88 (d, 1H), 6.12 (s, 2H), 2.75 (s, 3H), 2.47 (s, 3H).

(L³)(CH₃CN)RhCl₂ (**4c**): Yield: 90%. $IrC_{14}H_{12}N_4Cl_3$ (534.5): *Anal.* Calc. C, 31.43; H, 2.24; N, 10.47. Found: C, 31.56; H, 2.32; N, 10.50. UV–Vis spectrum (CH₂Cl₂) λ_{max} (ε , M⁻¹ cm⁻¹) = 610 (1000), 420 (3400), 380 (9900), 265 (7050), 235 (10,950). IR (KBr pellets, cm⁻¹): ν = 3260, 3234 (NH₂), 1404 (N=N). ¹H NMR (CDCl₃+ 1 drop DMSO-*d*₆, ppm): δ 8.21 (d, 1H), 8.02 (d, 1H); 7.63 (d, 1H), 7.58–7.54 (m, 1H), 7.51–7.48 (m, 1H), 7.40 (t, 1H), 7.14–7.12 (m, 1H), 6.27 (s, 2H), 2.84 (s, 3H).

5. Crystallography

Single crystals of (L)(HL)IrCl₂ and (L)(MeCN)IrCl₂ were grown by slow diffusion of a dichloromethane solution into petroleum ether

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Crystallographic data	for (L1)(HL1)IrCl2	and (L3)(CH3CN)IrCl2.
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Complex	$(L^1)(HL^1)IrCl_2$	(L ³)(CH ₃ CN)IrCl ₂
Formula	C24H21N6IrCl2	C14H12N4IrCl3
Formula weight	656.59	534.85
Space group	$P_2 1/c$	$P_2 1/c$
Crystal system	monoclinic	monoclinic
a (Å)	20.6735(15)	13.7822(8)
b (Å)	10.2520(7)	10.2484(6)
<i>c</i> (Å)	23.7851(17)	12.3338(8)
α (°)	90.000(0)	90.000(0)
β (°)	104.867(4)	114.186(3)
γ (°)	90.000(0)	90.000(0)
λ (Å)	0.71073	0.71073
V (Å ³)	4872.4(6)	1589.17(17)
Ζ	8	4
T (K)	293	150
$D_{\text{calcd.}}$ (g cm ⁻³)	1.790	2.236
μ (mm $^{-1}$)	5.724	20.911
R_1	0.0580	0.0175
wR ₂	0.1476	0.0422
Unique reflections $[I > 2\sigma(I)]$	13,008	2412
Goodness-of-fit (GOF)	1.01	1.24

and slow evaporation of acetonitrile solution respectively at 298 K. Data were collected by ω -scan technique on a Bruker Smart CCD diffractometer with Mo K α and Cu K α radiation monochromated by graphite crystal. Structure solution was done by direct method with shelxs-97 program [31,32]. Full matrix least square refinements on F^2 were performed using shelxl-97 program [31,32]. All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. All hydrogens were included at calculated positions. The data collection parameters and relevant crystal data are collected in Table 3.

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Appendix A. Supplementary material

CCDC 741096 and 741097 contain the supplementary crystallographic data for $(L^1)(HL^1)IrCl_2$ and $(L^3)(MeCN)IrCl_2$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Figures S1–S18 show the UV–Vis and IR spectra and Figures S19–S27 the ¹H NMR spectra of all the complexes. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.12.025.

References

- [1] J.L. Pratihar, N. Maiti, S. Chattopadhyay, Inorg. Chem. 44 (2005) 6111.
- [2] J.L. Pratihar, P. Pattanayak, S. Chattopadhyay, J. Chem. Res. 10 (2006) 629.
- [3] J.L. Pratihar, B. Shee, P. Pattanayak, D. Patra, A. Bhattacharyya, V.G. Puranik, C.H. Hung, S. Chattopadhyay, Eur. J. Inorg. Chem. (2007) 4272.
- [4] J.L. Pratihar, D. Patra, S. Chattopadhyay, J. Organomet. Chem. 690 (2005) 4816.
- [5] J.L. Pratihar, S. Bhaduri, P. Pattanayak, D. Patra, S. Chattopadhyay, J. Organomet. Chem. 694 (2009) 3401.
 [6] J.L. Pratihar, P. Pattanayak, J.H. Huang, S. Chattopadhyay, Inorg. Chim. Acta 362
- (2009) 5170.
 [7] J.L. Pratihar, N. Maiti, P. Pattanayak, S. Chattopadhyay, Polyhedron 24 (2005)
- [8] P. Pattanayak, J.L. Pratihar, D. Patra, A. Burrows, M. Mohan, S. Chattopadhyay,
- Eur. J. Inorg. Chem. (2007) 4263. [9] P. Pattanayak, J.L. Pratihar, D. Patra, V.G. Puranik, S. Chattopadhyay, Polyhedron
- 27 (2008) 2209. [10] P. Pattanayak, J.L. Pratihar, D. Patra, S. Mitra, A. Bhattacharyya, H.M. Lee, S.
- Chattopadhyay, Dalton Trans. (2009) 6220. [11] P. Pattanayak, D. Patra, J.L. Pratihar, A. Burrows, M. Mohan, S. Chattopadhyay,
- Inorg. Chim. Acta (2010), doi:10.1016/j.ica. 2010.04.016. [12] P.K. Dhara, S. Pramanik, T.-H. Lu, P. Chattopadhyay, J. Coord. Chem. 58 (2005)
- 985. [13] T. Kaiya, T. Fujiwara, K. Kohda, Chem. Res. Toxicol. 13 (2000) 993.
- [13] I. Kalya, I. Fujiwala, K. Koliua, Chelli, Res. Toxicol. 15 (2000) 995
- [14] A.K. Sharma, S. Biswas, S.K. Barman, R. Mukherjee, Inorg. Chim. Acta (2010), doi:10.1016/j.ica.2010.03.056.
 [15] D. Papericio II. Pays. Scientification of Chicaga Technology and Papericio II.
- [15] D. Banerjee, U. Ray, S. Jasimuddin, J.-C. Liou, T.-H. Lu, C. Sinha, Polyhedron 25 (2006) 1299.
- [16] P. Pratihar, A.K. Dasmahapatra, C. Sinha, Polyhedron 26 (2007) 1217.
- [17] N. Maiti, S. Pal, S. Chattopadhyay, Inorg. Chem. 40 (2001) 2204.
- [18] N. Maiti, B.K. Dirghangi, S. Chattopadhyay, Polyhedron 22 (2003) 3109.
- [19] N. Maiti, S. Chattopadhyay, Indian J. Chem. 42A (2003) 2327.
- [20] R. Acharyya, F. Basuli, R.-Z. Wang, T.C.W. Mak, S. Bhattacharya, Inorg. Chem. 43 (2004) 704.
- [21] R. Acharyya, S.-M. Peng, G.-H. Lee, S. Bhattacharya, J. Chem. Sci. 121 (2009) 387.
- [22] R. Acharyya, F. Basuli, S.-M. Peng, G.-H. Lee, R.-Z. Wang, T.C.W. Mak, S. Bhattacharya, J. Organomet. Chem. 690 (2005) 3908.
- [23] S. Baksi, D.K. Seth, H. Tadesse, A.J. Blake, S. Bhattacharya, J. Organomet. Chem. (2010), doi:10.1016/j.jorganchem.2010.01.015.
- [24] M. Panda, C. Das, G.-H. Lee, S.-M. Peng, S. Goswami, Dalton Trans. (2004) 2655.
- [25] M. Panda, C. Das, C.-H. Hung, S. Goswami, J. Chem. Sci. 119 (2007) 3.
- [26] D. Sardar, P. Datta, P. Mitra, C. Sinha, Polyhedron (2010), doi:10.1016/ j.poly.2010.08.038.
- [27] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, sixth ed., John Wiley & Sons, New York, 1999.
- [28] M.A. Bennett, D.L. Milner, J. Am. Chem. Soc. 91 (1969) 6983.
- [29] J.A. Osborn, G. Wilkinson, Inorg. Synth. 10 (1967) 67.
- [30] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, third ed., Pergamon, New York, 1988.
- [31] G.M. Sheldrick, SHELXS-97, University of Göttingen, Göttingen, Germany, 1990.
- [32] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystals Structures from Diffraction Data, University of Göttingen, Göttingen, Germany, 1997.