Inorg. Chem. **2005**, *44*, 6111–6114

Inorganic Chemistry
Article

Reactions of 2-(Arylazo) Aniline with $\mathrm{RhCl_3}$: Synthesis and Structure of New Cyclometalated Complexes of Rh(III) and Recognition of $\mathrm{RhCl_3}$ Assisted Azo (−N=N−) Cleavage

Jahar lal Pratihar, Nilkamal Maiti, and Surajit Chattopadhyay*

Department of Chemistry, University of Kalyani, Kalyani 741235, India

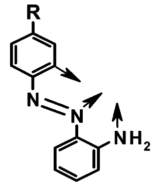
Received April 9, 2005

The reactions of 2-(arylazo) anilines, HL (**1**) [where HL is 2-($\mathrm{ArN{=}N}$)$\mathrm{C_6H_4NH_2}$; Ar is $\mathrm{C_6H_5}$ (for $\mathrm{HL^1}$, **1a**) and *p*-$\mathrm{MeC_6H_4}$ (for $\mathrm{HL^2}$, **1b**); H of HL represents the proton of Ar which gets dissociated upon orthometalation] with $\mathrm{RhCl_3}$ in methanol afforded new orthometalated complexes of composition $\mathrm{(L)(HL)Rh^{III}Cl_2}$ (**2**) and $\mathrm{(L)(ArNH_2)Rh^{III}Cl_2}$ (**3**). The anionic $\mathrm{L^-}$ binds the metal in tridentate (C, N, N) manner in both the complexes, while HL and $\mathrm{ArNH_2}$ bind the metal of **2** and **3** in monodentate fashion through the amino nitrogen. The $\mathrm{ArNH_2}$ of **3** was formed in situ due to cleavage of azo (−N=N−) function of monodentate HL of **2**. The scission of N=N has been authenticated.

Introduction

Rhodium complexes have been exploited a great deal as efficient catalysts in homogeneous catalysis.[1] The most notable example in this regard is Wilkinson's catalyst, $\mathrm{Rh(PPh_3)_3Cl}$. Rhodium complexes are useful to mediate organic transformations primarily due to the affinity of rhodium to form Rh−C bond, accessibility to variable oxidation states (+I, +III), and coordination numbers (4, 6). Transition metal complexes incorporating azo ligands have displayed several interesting properties related to electron-transfer reactions,[2] photolumunescence[3], liquid crystals,[4] photochromism,[5] and organic transformation via metal carbon bond formation.[6]

Our interest to explore the chemistry of transition metal complexes with new azo ligands prompted us to study the chemistry of Rh(III) complexes incorporating 2-(arylazo) aniline ligand. Herein we report the reaction of 2-(arylazo) aniline, HL (**1**), with $\mathrm{RhCl_3}$ yielding new cyclometalated complexes of Rh(III) of composition $\mathrm{(L)(HL)Rh^{III}Cl_2}$ and $\mathrm{(L)(ArNH_2)Rh^{III}Cl_2}$. The new binding mode (C, N, N) of **1** (shown by the arrows in the structure below) has been described for the first time. The products obtained upon reaction between $\mathrm{RhCl_3}$ and **1** indicated the cleavage of azo (−N=N−) bond of HL. The reaction of $\mathrm{(L)(HL)Rh^{III}Cl_2}$ with $\mathrm{RhCl_3}$ has been examined to rationalize the reaction route toward the formation of $\mathrm{(L)(ArNH_2)Rh^{III}Cl_2}$ as a result of azo cleavage.



1

Results and Discussion

Synthesis and Azo Cleavage. Reaction of one equiv of rhodium (III) chloride with two equiv of 2-(arylazo) aniline

---

* To whom correspondence should be addressed. E-mail: scha8@rediffmail.com.

[1] Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999.

[2] (a) Ray, U.; Banerjee, D.; Mostafa, G.; Lu, T. H.; Sinha, C. *New. J. Chem*. **2004**, *28*, 1437. (b) Kar, S.; Pradhan, B.; Sinha, R. K.; Kundu, T.; Kodgire, P.; Rao, K. K.; Puranic, V. G.; Lahiri, G. K. *J. Chem. Soc., Dalton Trans.* **2004**, 1752. (c) Sanyal, A.; Banerjee, P.; Lee, G. H.; Peng, S. M.; Hung, C. H.; Goswami, S. *Inorg. Chem*. **2004**, *43*, 7456.

[3] Marquez, F.; Marti, V.; Palomares, E.; Garcia, H.; Adam, W. *J. Am. Chem. Soc.* **2002**, *124*, 7264.

[4] (a) Kurihara, S.; Nomiyama, S.; Nonaka, T. *Chem. Mater*. **2001**, *13*, 1992. (b) Inoue, K.; Takeuchi, H.; Konaka, S. *J. Phys. Chem. A* **2001**, *105*, 671. (c) Yamamoto, T.; Ohashi, A.; Yoneyama, S.; Hasegawa, M.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Phys. Chem. B* **2001**, *105*, 2308.

[5] (a) Rau, H. In *Photochromism: Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Studies in Organic Chemistry, 40; Elsevier: Amsterdam, 1990; p 165. (b) Janus, K.; Sworakowski, J. *J. Phys. Chem. B* **2005**, *109*, 93. (c) Kume, S.; Kurihara, M.; Nishihara, H. *Chem. Commun.* **2001**, 1656. (d) Ruslim, C.; Ichimura, K. *J. Mater. Chem.* **2000**, 2704.

[6] (a) Chattopadhyay, S.; Sinha, C.; Basu, A.; Chakravorty, A. *Organometallics*. **1991**, *10*, 1135, and references therein. (b) Nag, S.; Gupta, P.; Butcher, J. R.; Bhattacharya, S. *Inorg. Chem.* **2004**, *43*, 4814. (c) Acharyya, R.; Bsuli, F.; Wang, R.-Z.; Bhattacharya, S. *Inorg. Chem.* **2004**, *43*, 704.

10.1021/ic050551w CCC: $30.25

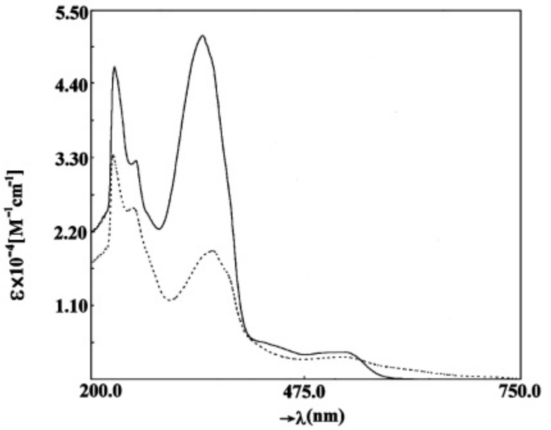
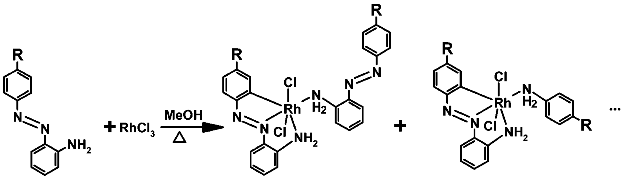


Figure 1. UV-vis spectra of **2a** (—) and **3a** (- - -).

in refluxing methanol afforded two dark brown products, **2** and **3**, in ~40% and ~15% yields, respectively (eq 1) after 4 h. The specific ligands used and the products obtained are shown in eq 1.

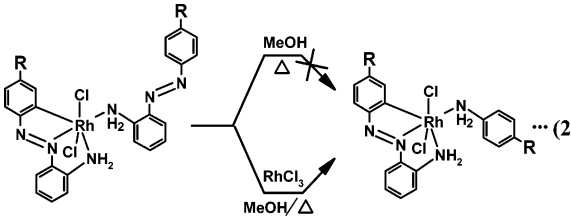


... (1)

1 2 3

R = H for **1a**, **2a** & **3a** ; R = Me for **1b**, **2b** & **3b**.

The monodentate p-$RC_6H_4NH_2$ ligand of **3** is formed during the syntheses as a result of cleavage of —N=N— bond of coordinated HL in **2**. The N=N cleavage could be recognized unequivocally by characterizing **3b** (the coordinated p-$MeC_6H_4NH_2$), obtained on treating **1b** with $RhCl_3$ (^1H NMR, see below). However, complex **2** did not undergo any transformation on boiling in methanol for 6 h, whereas, in the presence of excess $RhCl_3$, **3** was obtained from **2** upon refluxing in methanol or ethanol (eq 2). Therefore, possibly, a transient Rh(I) species, formed on boiling $RhCl_3$ in alcohol, is acting as reducing agent for the reductive cleavage of azo function of monodentate HL of **2** to afford **3**.



... (2)

Spectral Characterization. The compounds **2** and **3** are soluble in common organic solvents furnishing orange-brown and brown-red solutions. The complexes displayed characteristic UV—vis spectra; representative spectra for **2a** and **3a** are shown in Figure 1. The UV—vis spectral data are given in the Experimental Section.

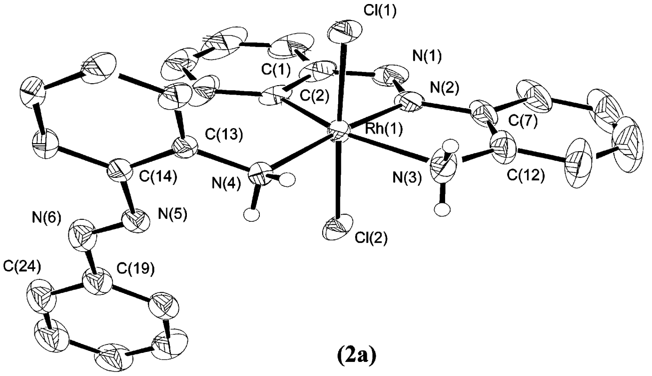
The IR spectra of the complexes (Figures S1—S4 in the Supporting Information) in solid KBr support exhibited several overlapping ν_{N-H} absorptions within the ranges 3177—3268 cm^{-1} and 3190—3280 cm^{-1} for **2** and **3**, respectively, indicating the presence of more than one amino group. The ν_{Rh-Cl} that appeared near 330 cm^{-1} as split bands may be due to the site effect in the solid state since the Cl—Rh—Cl angles are very close to 180° (X-ray structure, see below) and the asymmetric stretch is unlikely to be observed. The IR data are collected in the Experimental Section.

The compositions of **2** and **3** matched well with the C,H,N analytical data and ^1H NMR spectral data. The ^1H NMR spectra (Figures S5—S8) of the complexes were recorded in $CDCl_3$. The amino protons appeared as broad singlets within δ 4.58—4.59 and δ 6.63—6.67 for **2**, while for **3** these were observed in the ranges of δ 4.30—4.32 and δ 5.50—5.60 for two equivalent proton counts for each resonance. This is consistent with the formulation having two amino (—NH_2) groups in each of the two types of complexes, **2** and **3**. The total count of aromatic protons (δ 7.114—8.236) matched well with the composition of the complexes (Experimental Section and Figures S5—S8). The spectra of **2b** displays two resonances for R = Me at δ 2.394 and δ 2.543 for the L^2 and HL^2. The complex **3b** also displays two methyl resonances for R = Me at δ 2.395 and δ 2.509 for L^2 and p-$MeC_6H_4NH_2$ signifying the cleavage of the —N=N— bond of **1b** unequivocally.

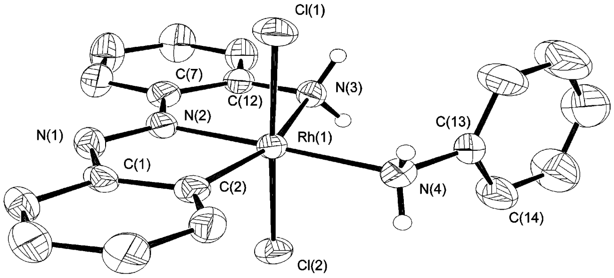
X-ray Structures. After separation and purification, **2a** and **3a** were crystallized by slow diffusion of petroleum ether (60—80° C) into the dichloromethane solutions. Suitable crystals were picked for X-ray studies. The crystals of **2a** are monoclinic with the space group $C2/c$ whereas crytals of **3a** are triclinic with the space group $P\bar{1}$. The molecular structures of **2a** and **3a** are given in Figure 2. with the atom numbering scheme. The selected bond distances and angles are given in Tables 1 and 2 for **2a** and **3a**, respectively. In both the complexes (**2a** and **3a**), Rh(III) forms the cyclometalated chelate with a 2-(phenylazo) aniline ligand which is tridentate (C,N,N) and uninegative. Two chloride ligands are held in trans positions occupying the other two coordinating sites. A second molecule of 2-(phenylazo) aniline binds in a monodentate fashion through the amino nitrogen at the sixth position of hexacoordinated Rh(III) in **2a**, while in **3a** the amino nitrogen of aniline (obtained upon —N=N— scission) binds at the sixth position of hexacoordinated Rh(III). The geometries about Rh(III), for both the complexes, are distorted octahedral where the chloride ligands are mutually trans with Cl—Rh—Cl angle being equal to 176.28(3)° and 178.04(5)° for **2a** and **3a**, respectively. The Rh—N(azo) length (1.942(3)Å) of **2a** is shorter than the Rh—N(amine) lengths [Rh—N(3), 2.213(3); Rh—N(4), 2.150(2)Å] of the same molecule as a result of stronger Rh → N(azo) back-bonding.[7] The Rh—N(3) [2.213(3)Å] bond, trans to Rh—C, is longer than the Rh—N(4) distance [2.150(2)Å] of **2a** due to stronger trans effect of aryl carbon.[6a] Similar trends in Rh—N bond distances have been observed for **3a** also: Rh—N(azo) [1.960(3)Å] < Rh—N(amine) [Rh—N(3), 2.255(4)Å; Rh—N(4), 2.143(3)Å]; Rh—N(3)

---

[7] Whuler, P. A.; Brouty, C.; Spinat, P.; Herpin, P. *Acta Crystallogr. Sect. B* **1976**, *32*, 2576.



(2a)



(3a)

Figure 2. Views of molecular structures of **2a** and **3a** with atom numbering scheme. The hydrogen atoms, except those of the amino groups, have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compound **2a**

	distances		
Rh−Cl(1)	2.3314(8)	N(3)−C(12)	1.439(5)
Rh−Cl(2)	2.3481(8)	N(1)−N(2)	1.264(4)
Rh−N(3)	2.213(3)	N(2)−C(7)	1.415(5)
Rh−N(2)	1.942(3)	N(1)−C(1)	1.410(5)
Rh−N(4)	2.150(2)	N(4)−C(13)	1.439(4)
Rh−C(2)	1.994(3)	N(5)−N(6)	1.227(5)
	angles		
Cl(1)−Rh−Cl(2)	176.28(3)	Cl(2)−Rh−C(2)	92.02(8)
Cl(1)−Rh−N(3)	89.65(7)	N(3)−Rh−N(2)	81.53(10)
Cl(1)−Rh−N(2)	90.35(7)	N(3)−Rh−N(4)	94.09(10)
Cl(1)−Rh−N(4)	91.84(6)	N(3)−Rh−C(2)	161.15(12)
Cl(1)−Rh−C(2)	91.69(8)	N(2)−Rh−N(4)	175.09(10)
Cl(2)−Rh−N(2)	90.48(7)	N(2)−Rh−C(2)	79.66(12)
Cl(2)−Rh−N(4)	87.06(6)	N(4)−Rh−C(2)	104.65(12)

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound **3a**

	distances		
Rh(1)−Cl(1)	2.357(3)	N(3)−C(12)	1.466(5)
Rh(1)−Cl(2)	2.367(3)	N(1)−N(2)	1.290(4)
Rh(1)−N(3)	2.255(4)	N(2)−C(7)	1.435(5)
Rh(1)−N(2)	1.960(3)	N(1)−C(1)	1.439(5)
Rh(1)−N(4)	2.143(3)	N(4)−C(13)	1.459(5)
Rh(1)−C(2)	2.014(4)		
	angles		
Cl(1)−Rh(1)−Cl(2)	178.04(5)	Cl(2)−Rh(1)-C(2)	92.21(14)
Cl(1)−Rh(1)−N(3)	89.48(9)	N(2)−Rh(1)−N(3)	80.47(11)
Cl(1)−Rh(1)−N(2)	91.64(11)	N(3)−Rh(1)−N(4)	101.34(11)
Cl(1)−Rh(1)−N(4)	88.76(10)	N(3)−Rh(1)−C(2)	161.71(13)
Cl(1)−Rh(1)−C(2)	89.32(13)	N(2)−Rh(1)−N(4)	178.16(13)
Cl(2)−Rh(1)−N(2)	89.81(10)	N(2)−Rh(1)−C(2)	81.32(14)
Cl(2)−Rh(1)−N(4)	89.84(10)	N(4)−Rh(1)−C(2)	96.88(13)

[2.255(4)Å] > Rh−N(4) [2.143(3)Å] as a result of $d\pi-p\pi$ back-bonding and stronger trans influence of aryl carbon, respectively. One of the important features in the structures of **2a** and **3a** are the longer C(aryl)−N(amine) distances [**2a**, N(3)−C(12), 1.439(5)Å; N(4)−C(13), 1.439(4)Å; **3a**, N(3)−C(12), 1.466(5) Å; N(4)−C(13), 1.459(5) Å] than that in the azoimine (N, N) chelates of **1**, where it is shorter (av. ∼1.34Å) and similar to imine length due to dissociation of an amino proton followed by delocalization.[8] This is again consistent with the ^{1}H NMR spectral data (vide supra) of **2** and **3** where it was noticed that the Rh(III) was coordinated by the amino nitrogen rather than imino nitrogen.

Concluding Remarks

The reaction of 2-(arylazo) aniline with RhCl$_3$ afforded new cyclometalated complexes of Rh(III), **2** and **3**. Further, the formation of **2** and **3** indicated azo (−N═N−) bond cleavage of 2-(arylazo) aniline. The reaction of **2** with RhCl$_3$ in methanol exhibited that the scission of azo function occurs after coordination of 2-(arylazo) aniline to Rh(III) in a monodentate fashion via amino nitrogen. It is believed that the reductive cleavage of azo function has been promoted by a transient Rh(I) species that formed in situ upon boiling RhCl$_3$ in methanol.

Experimental Section

Materials. RhCl$_3$ was obtained from Arora-Mathey, India, and used as it was received. All the solvents were purified and distilled after receipt from Merck India. Silical gel G with binder was used for thin-layer chromatography. 2-(Arylazo) aniline ligands were prepared according to the procedure described earlier.[8a]

Physical Measurements. UV−vis spectra were recorded with a Shimadzu UV-2401 PC spectrophotometer. IR spectra were taken on a Perkin-Elmer L120-00A FT IR spectrophotometer (4000−225 cm^{-1}) on KBr pellets. C, H, N analyses were performed on a Perkin-Elmer 240C elemental analyzer. NMR spectra were drawn on Brucker Avance RPX 500 MHz and Brucker Avance DPX 300 spectrometers.

Syntheses of compounds. (L^1)(HL^1)RhCl$_2$ (2a) and (L^1)-(C$_6$H$_5$NH$_2$)RhCl$_2$ (3a). 2-(Phenylazo) aniline, **1a**, (150 mg, 0.76 mmol) was dissolved in methanol (40 mL), and to the mixture RhCl$_3$ (100 mg, 0.38 mmol) was added. The mixture was then heated to reflux for 4 h to afford a dark brown solution. Evaporation of the solvent gave a brown residue, which was introduced for purification by thin-layer chromatography on silica gel. Two deep brown bands separated in toluene−acetonitrile (90:10, V/V) mixed solvent. From the first and second bands **2a** and **3a**, respectively, were isolated in pure form upon extracting with acetonitrile. Yield: 40% (for complex **2a**) and 15% (for complex **3a**). Complex **2a** calcd: C, 50.79%; H, 3.70%; N, 14.81%. Found: C, 50.68%; H, 3.67%; N, 14.75%. IR (KBr disk): ν_{NH2} = 3268, 3226, 3177 cm^{-1}, $\nu_{N=N}$ 1389, 1485 cm^{-1}, ν_{Rh-Cl} 339, 325 cm^{-1}. ^{1}H NMR (CDCl$_3$): 4.59(s, NH$_2$, 2H), 6.67(s, NH$_2$, 2H), 7.278(d, 1H), 7.319−7.399(m, 4H), 7.419−7.473(m, 5H), 7.554 (t, 1H), 7.75(d, 1H), 7.938(d, 1H), 7.986(t, 2H), 8.203 (d, 1H), 8.236(d, 1H). Electronic spectral data in dichloromethane solution: (λ, nm, (ϵ, M^{-1}, cm^{-1})): 520 (6550), 340 (66480), 250 (49000), 230 (73000).

Complex **3a** calcd: C, 45.65%; H, 3.67%; N, 12.09%. Found: C, 45.57%; H, 3.60%; N, 12.00%. IR (KBr disk): ν_{NH2} = 3285,

---

(8) (a) Maiti, N.; Pal, S.; Chattopadhyay, S. *Inorg. Chem.* **2001**, *40*, 2204. (b) Maiti, N.; Dirghangi, B. K.; Chattopadhyay, S. *Polyhedron* **2003**, *22*, 3109. (c) Maiti, N.; Chattopadhyay, S. *Ind. J. Chem.* **2003**, *42A*, 2327.

3244, 3187 cm^{-1}, $\nu_{N=N}$ 1386, cm^{-1}, ν_{Rh-Cl} 339, 328 cm^{-1}. ^{1}H NMR ($CDCl_3$): 4.30(s, NH_2, 2H), 5.60(s, NH_2, 2H), 7.270−7.324 (m, 2H), 7.349−7.439(m, 5H), 7.466−7.521(m, 3H), 7.628(s, 1H), 8.223(d, 2H). Electronic spectral data in dichloromethane solution: (λ, nm,(ϵ, M^{-1}, cm^{-1})): 525 (4800), 370 (21900), 270 (30000), 245 (27650), 230 (47630).

(L^2)(HL^2)$RhCl_2$ (2b) and (L^2)(*p*-$MeC_6H_4NH_2$)$RhCl_2$ (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 was toluene−acetonitrile (95:5 V/V) mixed solvent. Yield: 46% (for complex **2b**) and 12% (for complex **3b**). Complex **2b** calcd: C, 52.42%; H, 4.23%; N, 14.12%. Found: C, 52.32%; H, 4.12%; N, 14.02%. IR (KBr disk): ν_{NH2} = 3300, 3225, 3150 cm^{-1}, $\nu_{N=N}$ 1380, 1384 cm^{-1}, ν_{Rh-Cl} 329 cm^{-1}. ^{1}H NMR ($CDCl_3$): 4.586(s, NH_2, 2H), 6.630(s, NH_2, 2H), 2.394 (s, *p*-CH_3, 3H), 2.543 (s, *p*-CH_3, 3H), 7.132(d, 1H), 7.230−7.281 (m, 4H), 7.325−7.423(m, 3H), 7.523(t, 1H), 7.542 (s, 1H), 7.898−7.927(m, 2H), 7.969(d, 1H), 8.107(d, 1H), 8.176 (d, 1H). Electronic spectral data in dichloromethane solution: (λ, nm (ϵ, M^{-1}, cm^{-1})): 520 (9000), 360 (64200), 260(48043), 230 (67700).

Complex **3b** calcd: C, 48.88%; H, 4.27%; N, 11.40%. Found: C, 48.42%; H, 4.18%; N, 11.20%. IR (KBr disk): ν_{NH2} = 3313, 3240,3175 cm^{-1}, $\nu_{N=N}$ 1395 cm^{-1}, ν_{Rh-Cl} 321 cm^{-1}. ^{1}H NMR ($CDCl_3$): 4.319(s, NH_2, 2H), 5.506(s, NH_2, 2H), 2.395 (s, *p*-CH_3, 3H), 2.509 (s, *p*-CH_3, 3H), 7.114(d, 1H), 7.203 (d, 2H), 7.287(d, 1H), 7.347(t, 1H), 7.404−7.430 (m, 4H), 8.101(d, 1H), 8.186(d, 1H). Electronic spectral data in dichloromethane solution: (λ, nm (ϵ, M^{-1}, cm^{-1})): 525 (4800), 370 (21900), 270 (29800), 230 (47630).

Reaction of 2a with $RhCl_3$. $RhCl_3 \cdot 3H_2O$ (9 mg, 0.035 mmol) was added to a methanolic (10 mL) solution of **2a** (20 mg, 0.035 mmol), and refluxed for 0.5 h. The solid mass obtained upon evaporation of methanol was introduced on a thin-layer chromatographic plate prepared by silica gel. **3a** was separated almost exclusively using toluene−acetonitrile (95:5 V/V) mixed solvent. The pure **3a** was isolated from the TLC plate. Yield: 90%. The product obtained was characterized by matching the UV−vis spectrum.

X-ray Crystallography. Data were collected on a Brucker SMART CCD diffractometer using a Mo Kα monochromator (λ = 0.71043). Structure solutions were performed using the Shelx 97 PC version program. The full matrix least-squares and anisotropic refinements were performed on all the atoms. Hydrogen atoms were included at calculated positions. The data collection parameters and relevant crystal data are collected in Table 3.

Table 3. Crystal Data for Complexes **2a** and **3a**

param	**2a**	**3a**
formula	$C_{24}H_{21}N_6RhCl_2$	$(C_{18}H_{17}N_4Rh\ Cl_2)_2$,O
M	567.28	942.33
space group	monoclinic, *C*2/*c*	triclinic, $P\bar{1}$
a/Å	27.216(3)	12.251(1)
b/Å	10.299(8)	12.438(1)
c/Å	20.577(1)	13.836(1)
α/deg	90.000(0)	91.210(2)
β/deg	122.024(4)	98.510(2)
γ/deg	90.000(0)	101.850(3)
λ/Å	0.71073	0.71073
V/Å^3	4890.2(8)	2038(3)
Z	8	2
T/K	273	273
D/mg/m^{-3}	1.541	1.536
μ/mm^{-1}	0.941	1.111
R(all data)	0.036	0.039
wR2[c] [$I > 2\sigma(I)$]	0.088	0.102
R1[a]/GOF[b]	0.97	1.02

[a] Observation criterion: $I > 2\sigma(I)$. R1 = $\Sigma||F_o| - |F_o||/\Sigma|F_o|$. [b] GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. [c] wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/\ \sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2\ F_c^2)/3$.

Acknowledgment. We are thankful to the DST (New Delhi) for funding and fellowship to J.P. under the DST-SERC project. The necessary laboratory and infrastructural facility are provided by the Department of Chemistry, University of Kalyani. The support of DST under FIST program to the Department of Chemistry, University of Kalyani is acknowledged. We acknowledge Prof. Jui-Hsien Huang, National Changhua University of Education, Changhua, Taiwan for X-ray studies. We are thankful to Prof. Biswanath Chakraborty, Department of Chemistry, University of Kalyani, for donating some costly metal salts.

Supporting Information Available: Figures S1−S8 (pdf) and crystallographic details for complexes **2a** and **3a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC050551W