Journal of Organometallic Chemistry 694 (2009) 3401–3408

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Reactions of 2-(arylazo)aniline with ruthenium substrates: Isolation, characterizations and reactivities of delocalized diazoketiminato and orthometallated Ru(II) chelates

Jahar Lal Pratihar, Shantanu Bhaduri, Poulami Pattanayak, Debprasad Patra, Surajit Chattopadhyay *

Department of Chemistry, University of Kalyani, Kalyani 741 235, India

ARTICLE INFO

Article history:
Received 30 April 2009
Received in revised form 22 June 2009
Accepted 26 June 2009
Available online 1 July 2009

Keywords:
2-(Arylazo)aniline
Ruthenium
Cycloruthenation
Redox
Hydrogen transfer reaction

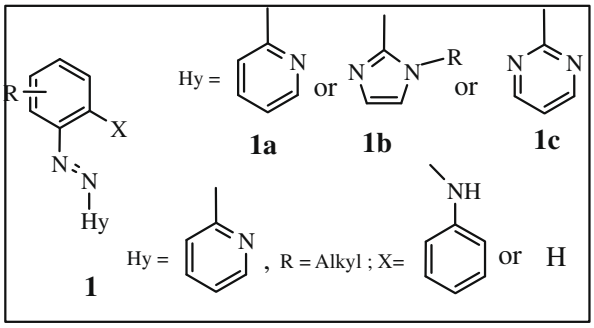
ABSTRACT

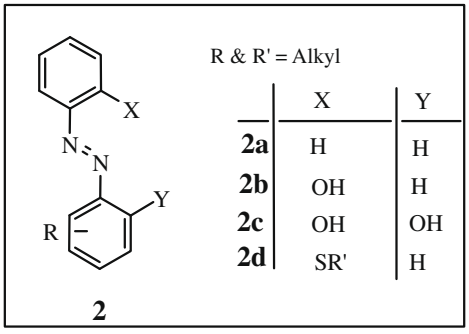
Reactions of 2-(arylazo)aniline, HL-NH_2 [H represents the dissociable protons upon complexation and HL-NH_2 is *p*-$RC_6H_4N{=}NC_6H_4$-NH_2; R = H for HL^1-NH_2; CH_3 for HL^2-NH_2 and Cl for HL^3-NH_2] with Ru(H)(CO)$(PPh_3)_3Cl$ and $Ru(CO)_3(PPh_3)_2$ afforded products of compositions [(HL-NH)Ru(CO)Cl$(PPh_3)_2$] and [(L-NH)Ru$(PPh_3)_2$(CO)], respectively. All the complexes were characterized unequivocally. The X-ray structures of the complexes **4c** and **5c** have been determined. The cyclic volatammograms exhibited one reversible oxidative response in the range of 0.56–0.16 V versus SCE for [(L-NH)Ru$(PPh_3)_2$(CO)] and a quasi reversible oxidative response within 0.56–0.70 V versus SCE for [(HL-NH)Ru(CO)Cl$(PPh_3)_2$]. The conversion of ketones to corresponding alcohols has been studied in presence of newly synthesized ruthenium complexes.

1. Introduction

Research in the area of coordination chemistry of ruthenium incorporating various kinds of ligands has upsurged in recent years due to the fascinating reactivities exhibited by the resultant complexes [1–4]. Studies on the chemistry of ruthenium complexes with azo ligands have been ongoing and several interesting results, related to electron transfer reaction [5–26], metal–carbon bond formation [14,22,23,25,26], aromatic ring amination [16–18], isomerism [7,8,24], cytotoxicity toward cancer cells [5–11] and application in catalytic transformations [25,26], were reported. The π-acidic nature of azo (–N=N–) function was indicated to be one of the reasons for fascinating properties of such ruthenium complexes [5–26]. As a consequence we expected that the appropriately designed azo ligands can dictate the properties of ruthenium complexes to originate new and more attractive results.

In general, the azo ligand systems may be divided into two categories: (i) arylazo heterocycles, **1** and (ii) associates of azobenzene moiety, **2**. Among these ligands most widely studied system is 2-arylazo pyridine (AAP), **1a**. AAP ligands bind to the ruthenium center in bidentate fashion (N,N) affording different types of isomeric complexes [7,8]. It was also reported that the metal mediated aryl ring amination of AAP ligand lead to the formation of tridentate (N,N,N) ligands [16–18], Aryl ring thiolation was studied in ruthenium complexes of AAP to obtain new complexes where the ligands bind with tridentate (N,N,S) mode [20], Several studies



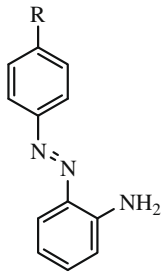


* Corresponding author. Tel.: +91 33 24149725; fax: +91 33 25828282.
E-mail address: scha8@rediffmail.com (S. Chattopadhyay).

0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2009.06.038

related to electron transfer behavior [5–26], optical properties [12,13] and cytotoxic behavior of ruthenium AAP complexes [5–11] are worthwhile to mention. Isomerism and redox behavior of ruthenium complexes of aryl azo imidazole, **1b**, ligands were studied to a considerable extent [24].

Chemistry of ruthenium complexes with azobenzene and related ligands was not studied as much as that of arylazo heterocycle complexes. A few ruthenium complexes of azobenzene and related ligands were prepared and have been described to have interesting properties. The complexes of 2-arylazo phenols, **2b**, were demonstrated to exhibit C–H activation [22,23,25,26], C–C activation [23], C–C coupling [22] and catalytic hydrogen transfer reactions [25,26]. Viewing this, we intended to study the chemistry of ruthenium with new azobenzene related ligands. For the present purpose, we have utilized 2-(arylazo)aniline, HL-NH_2, **3**, ligand for the preparation of different types of ruthenium chelates.



R= H for HL^1-NH_2 (**3a**); CH_3 for HL^2-NH_2 (**3b**); Cl for HL^3-NH_2 (**3c**)

3

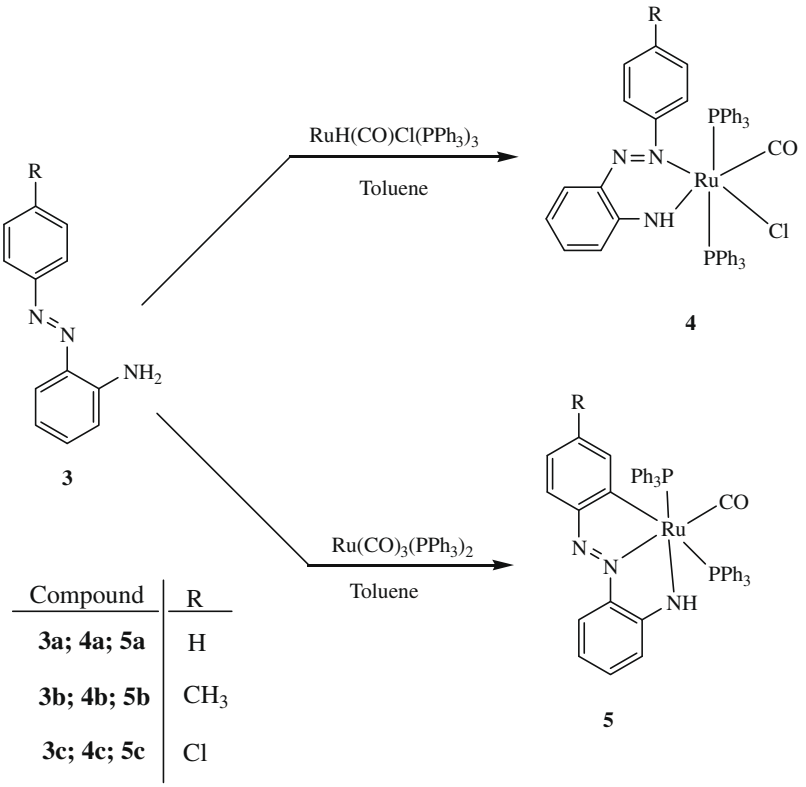
Herein we report the reaction of 2-(arylazo)aniline, **3**, with two ruthenium substrates. It has been shown that the different products were formed upon varying the ruthenium substrates. Orthometallated ruthenium (II) complexes were obtained from Ru(0) substrate. The products were characterized unequivocally. Redox properties and conversion of ketones in presence of new ruthenium complexes have been described.

2. Results and discussion

2.1. Complex formation

Reactions of HL-NH_2 with $RuH(CO)Cl(PPh_3)_3$ in refluxing toluene in anaerobic condition afforded a blue complex. Dissociation of one amino proton of HL-NH_2 and one hydride from $RuH(CO)Cl(PPh_3)_3$ gave rise to the formation of blue and non conducting complex $[(HL\text{-}NH)Ru(CO)Cl(PPh_3)_2]$, **4** (Scheme 1). The anionic $[HL\text{-}NH]^-$ ligand coordinated the metal center forming a six membered diazoketiminato chelate. Therefore, formally the elimination of one equivalent of hydrogen ($H^+ + H^- \rightarrow H_2$) in addition to dissociation of a PPh_3 ligand was believed to be the essential criterion to form the complex **4.** Previously, we reported that the reaction of HL-NH_2 with $RhCl(PPh)_3$, where oxidative addition of the ligand led to the formation of cyclometallated Rh(III) complex [27]. By analogy we considered that an oxidative addition on ruthenium center may also afford the cyclometallated complex.

Hence, we assumed that a Ru(0) substrate may bind with HL-NH_2 giving rise to Ru–C bond formation. Indeed, reactions of the ligand system 2-(arylazo)aniline, with $Ru(CO)_3(PPh_3)_2$, afforded the cyclometallated complexes as given in **5**. The $[(L\text{-}NH)Ru(PPh_3)_2(CO)]$, **5**, complexes are a new family of orthometallated complexes of Ru(II) [Eq. (1)]. Besides the elimination of one of the amino protons, an aryl proton of HL-NH_2 was dissociated from the pendant aryl ring during orthometallation. Two electron oxidation of Ru(0) center and concomitant dissociation of two protons from the ligand is formally consistent with the release of $2H^+ - 2e^-$. Reactions of HL-NH_2 with $Ru(CO)_3(PPh_3)_2$ in inert condition or in



Compound	R
3a; 4a; 5a	H
3b; 4b; 5b	CH_3
3c; 4c; 5c	Cl

Scheme 1.

presence of air afforded the identical product which was anticipated to occur either by releasing H_2 or H_2O, respectively.

$$HL\text{-}NH_2 + [Ru^0] \rightarrow [(L\text{-}NH)Ru^{II}] + 2H^+ + 2e \quad (1)$$

2.2. Spectral characterization

The UV–Vis spectra of [(HL-NH)Ru(CO)Cl(PPh_3)$_2$] **4** and [(L-NH)Ru(CO)(PPh_3)$_2$] **5** exhibited low energy absorption band near 600 nm and 800 nm, respectively. The low energy absorptions in metal complexes have been reported to occur due to electronic transition either from or to the energy levels containing substantial ligand character [27–32]. The representative UV–Vis spectra of complexes are shown in Fig. 1. The UV–Vis spectra of all the complexes are given in Supplementary material (Figs. S1–S6) and data are collected in Section 3.

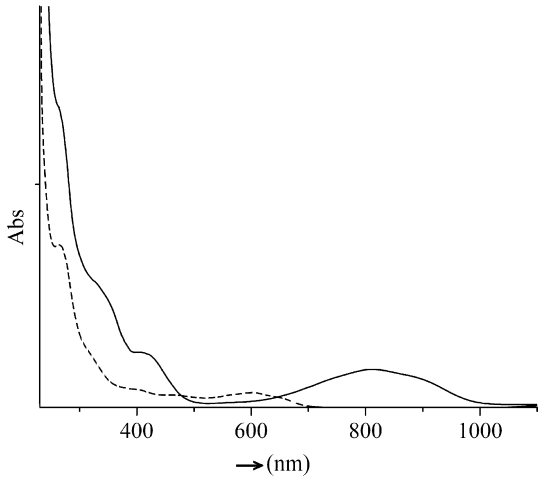


Fig. 1. A representative UV–Vis spectra of [(HL^1-NH)RuCOCl(PPh_3)$_2$] (- - -) and [(L^1-NH)RuCO(PPh_3)$_2$] (—).

All the complexes **4** and **5** exhibited sharp singlet ν_{NH} stretches within the range 3330–3353 cm^{-1}. This is consistent with the dissociation of an amino proton of HL-NH_2 since ν_{NH_2} of free ligands appear as a twin band near 3455 and 3380 cm^{-1} [30,31]. For the complexes the $\nu_{N=N}$ (1333–1432 cm^{-1}) shifted to lower energy than the $\nu_{N=N}$ (1458–1474 cm^{-1}) of the free ligands [27–32] indicating the coordination of azo nitrogen. The ν_{CO} of [(HL-NH)Ru(-CO)Cl(PPh_3)$_2$] and [(L-NH)Ru(CO)(PPh_3)$_2$] appeared as a singlet within the range 1910–1930 cm^{-1}. The IR spectra of all the complexes are given in Supplementary material (Figs. S7–S12) and data are collected in Section 3.

The ^{1}H NMR spectra of [(HL-NH)Ru(CO)Cl(PPh_3)$_2$], **4**, complexes exhibited N–H resonance as a broad singlet in the range δ 5.37−5.57 for one equivalent proton signifying the dissociation of one of the amino protons of HL-NH_2 during complexation [27,29–31]. A singlet near δ 6.7 in the ^{1}H NMR spectra of [(L^2-NH)Ru(CO)(PPh_3)$_2$] and [(L^3-NH)Ru(CO)(PPh_3)$_2$] signified ortho-metallation [27]. The N–H resonance has been overlapped by the signals of other protons and therefore could not be identified unequivocally even when the spectra drawn after shaking with D_2O. Only one N–H hydrogen could be located during X-ray structure determination of [(L^3-NH)Ru(CO)(PPh_3)$_2$] (see below) is consistent with the dissociation of one of the amino protons in the complex.

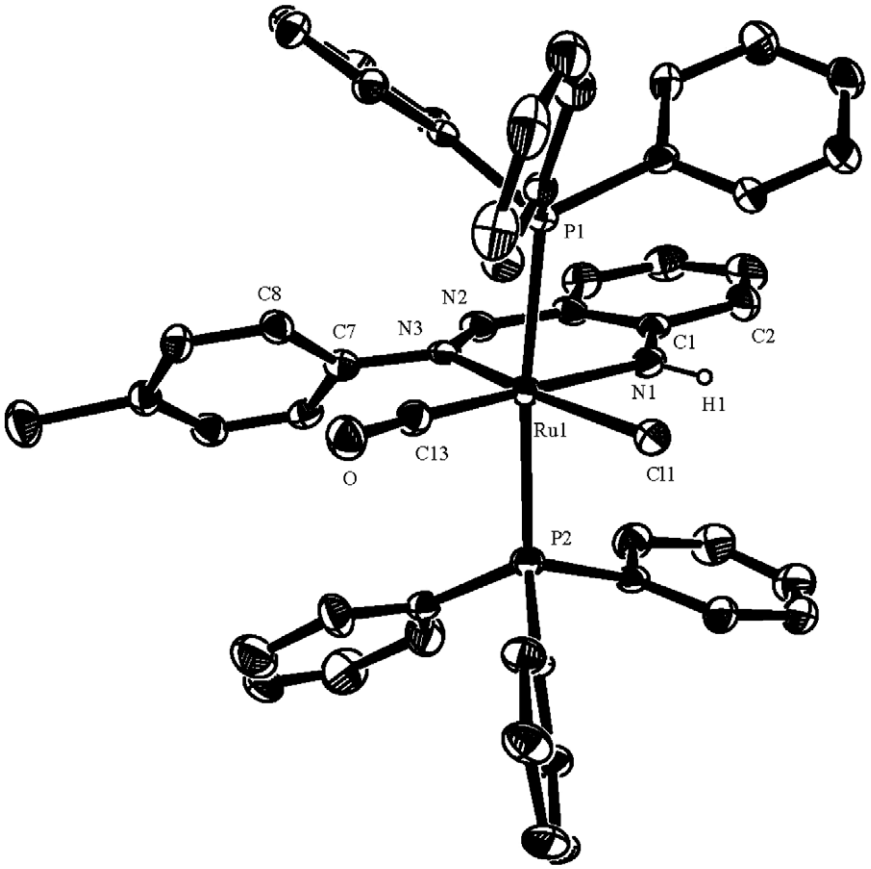


Fig. 2. Molecular structure of [(HL^3-NH)Ru(CO)Cl(PPh_3)$_2$] with atom numbering scheme. The hydrogen atoms excepting on N(1) of the amino groups have been omitted for clarity.

2.3. Crystal and molecular structure of $[(HL^3\text{-}NH)Ru(CO)Cl(PPh_3)_2]$ and $[(L^3\text{-}NH)Ru(CO)(PPh_3)_2]$

2.3.1. $[(HL^3\text{-}NH)Ru(CO)Cl(PPh_3)_2]$

Suitable crystals of $[(HL^3\text{-}NH)Ru(CO)Cl(PPh_3)_2]$ **4c** were grown by slow diffusion of dichloromethane solution into petroleum ether with few drops of benzene. A perspective view of the molecule is shown in Fig. 2 and selected bond distances and angles are collected in Table 1. The $[(HL^3\text{-}NH)Ru(CO)Cl(PPh_3)_2]$ **4c** coordination sphere has distorted octahedral geometry. The monoanionic $(HL\text{-}NH)^-$ ligands bind to the metal in an N,N-bidentate fashion forming diazoketiminato chelate. One chloride, one CO and two *trans* PPh_3 ligands are present in the coordination sphere of $[(HL^3\text{-}NH)Ru(CO)Cl(PPh_3)_2]$. There is half benzene molecule per asymmetric unit in the crystal lattice. The Ru–Cl, Ru–CO and Ru–P bond lengths of $[(HL^3\text{-}NH)Ru(CO)Cl(PPh_3)_2]$ **4c** are within the normal range [22,23]. Only one hydrogen [H(1)] atom on N(1) could be located from difference Fourier mapping, signifying dissociation of the other amino proton consistent with the ^1H NMR data (*vide infra*). The C(1)–N(1) bond (1.30 Å) is shorter than C(7)–N(3) single bond (1.43 Å) in the same molecule and similar to a imine (–C=N–) length as a result of delocalization [30,31]. The ruthenium center is closer to azo nitrogen N(3) (2.09 Å) and the N(2)–N(3) distance (1.30 Å) is longer than the azo (–N=N–) distance (−1.25 Å) in free azo molecules [27]. These observations are in support of backbone conjugation within the coordinated ligand [27]. The quinonoid distortion in the phenyl ring (C1–C6) adjacent to the chelate ring with four longer (∼1.42 Å) and two shorter (∼1.35 Å) bonds, like other coordinated arylimines [30,31], is consistent with delocalization [29–31]. The packing of the molecules **4c** in crystals do not show any significant interaction either amongst each other or with the benzene solvents molecules. The solvents of crystallization, i.e. benzene are situated in the void spaces of the lattice formed by the complex, **4c** molecules. The views of packing diagrams are given in Fig. S19 (Supplementary material).

Table 1
Selected bond distances (Å) and angles (°) for $[(HL^3\text{-}NH)Ru(CO)Cl(PPh_3)_2]$ and $[(L^3\text{-}NH)Ru(CO)(PPh_3)_2]$.

$[(HL^3\text{-}NH)Ru(CO)Cl(PPh_3)_2]$			
Distances (Å)			
Ru1–P1	2.430(2)	N2–N3	1.303(10)
Ru1–P2	2.415(2)	Ru1–N3	2.091(5)
Ru1–N1	2.055(6)	C4–C5	1.354(15)
Ru1–Cl1	2.4330(18)	C5–C6	1.428(13)
N1–C1	1.307(11)	O–C13	1.129(10)
N2–C6	1.354(12)	C3–C4	1.394(18)
C1–C2	1.445(13)	N3–C7	1.431(10)
C2–C3	1.348(15)	C1–C6	1.448(14)
Ru1–C13	1.856(8)		
Angles (°)			
P1–Ru1–P2	173.90(7)	Ru1–N3–N2	127.3(5)
P1–Ru1–N1	85.78(19)	N3–Ru1–C13	96.0(3)
P1–Ru1–N3	94.25(18)	N3–N2–C6	126.1(6)
N1–Ru1–Cl1	82.8(2)	N2–N3–C7	109.2(5)
P1–Ru1–C13	93.1(2)	P2–Ru1–N1	90.52(19)
P2–Ru1–N3	90.41(18)	Cl1–Ru1–C13	94.1(2)
N1–Ru1–C13	176.8(3)	N1–Ru1–N3	87.1(3)
P2–Ru1–C13	90.3(2)	N2–C6–C1	127.0(8)
$[(L^3\text{-}NH)Ru(CO)(PPh_3)_2]$			
Distances (Å)			
Ru1–P1	2.3642(11)	Ru1–Cl2	2.063(4)
Ru1–P2	2.3624(12)	Ru1–N1	2.164(4)
Ru1–N2	2.064(3)	C4–C5	1.376(8)
Ru1–C13	1.859(3)	C5–C6	1.407(6)
N1–C1	1.326(6)	O–C13	1.155(5)
N2–C6	1.379(5)	N2–N3	1.286(5)
C1–C2	1.442(7)	N3–C7	1.399(5)
C2–C3	1.359(7)	C1–C6	1.419(7)
C3–C4	1.388(10)		
Angles (°)			
P1–Ru1–P2	178.40(3)	Ru1–N2–N3	121.7(2)
P1–Ru1–N1	89.31(11)	Ru1–N2–C6	117.8(3)
P1–Ru1–N2	90.08(12)	N3–N2–C6	120.5(3)
P1–Ru1–C12	91.01(12)	N2–N3–C7	110.1(3)
P1–Ru1–C13	89.89(13)	P2–Ru1–N1	91.49(11)
P2–Ru1–N2	91.45(12)	N2–C6–C1	113.3(3)
P2–Ru1–C12	88.89(12)	N1–C1–C6	119.1(4)
P2–Ru1–C13	88.55(13)	N2–Ru1–C12	77.04(13)
N1–Ru1–N2	76.26(14)	N2–Ru1–C13	176.29(15)
N1–Ru1–C12	153.30(13)	C12–Ru1–C13	99.25(15)
N1–Ru1–C13	107.45(15)		

2.3.2. $[(L^3\text{-}NH)Ru(CO)(PPh_3)_2]$

Suitable crystals of $[(L^3\text{-}NH)Ru(CO)(PPh_3)_2]$ **5c** were grown by slow diffusion of dichloromethane solution into petroleum ether. A perspective view of the molecule is shown in Fig. 3 and selected bond distances and angles are collected in Table 1.

The $Ru(CNN)(CO)(P)_2$ coordination sphere has distorted octahedral geometry. The dianionic $(L^3\text{-}NH)^{2-}$ ligand coordinates the Ru(II) in a tridentate (C, N, N) fashion along with two mutually *trans* PPh_3 and a CO ligand. There is a CH_2Cl_2 molecule per asymmetric unit in the crystal lattice. The Ru–C (aryl), Ru–C (carbonyl) and Ru–P bond lengths of **5c** are within the normal range [22,23]. Only one hydrogen [H(1)] atom could be located on N(1) from difference Fourier mapping, signifying dissociation of the other amino proton. The C(1)–N(1) bond (1.32 Å) is shorter than C(6)–N(2) single bond (1.37 Å) in the same molecule and similar to a imine (>C=N–) length as a result of delocalization [30,31]. The quinonoid distortion in the phenyl ring (C1–C6) adjacent to the five membered chelate with two shorter (av. ∼1.35 Å) and four longer (av. ∼1.40 Å) bonds is also in accordance with the delocalization and imine formation [27]. Thus in **5** the formation of five membered azoimine chelate has been inferred. The packing of the molecules **5c** in crystals do not show any significant interaction. The view of packing diagram is given in Figs. S20 (Supplementary material).

2.4. Electrochemistry

$[(HL\text{-}NH)Ru(CO)Cl(PPh_3)_2]$, **4**, complexes exhibited one electron quasireversible oxidative cyclic voltammetric responses with the $E_{1/2}$ in the range of 0.56–0.70 V versus SCE in dichloromethane solution. On the other hand $[(L\text{-}NH)Ru(CO)(PPh_3)_2]$, **5**, complexes displayed reversible oxidative couples within 0.05–0.16 V versus SCE in dichloromethane–acetonitrile mixed solvent. The oxidations have been assigned according to the couple of Eqs. (2) and (3), where $[(L\text{-}NH)Ru(CO)(PPh_3)_2]^+$ and $[(HL\text{-}NH)Ru(CO)Cl(PPh_3)_2]^+$ are the Ru(III) analogs of $[(L\text{-}NH)Ru(CO)(PPh_3)_2]$ and $[(HL\text{-}NH)Ru(CO)Cl(PPh_3)_2]$. Representative cyclic voltammograms of $[(L^1\text{-}NH)Ru(CO)(PPh_3)_2]$ and $[(HL^1\text{-}NH)Ru(CO)Cl(PPh_3)_2]$ is shown in Fig. 4 and all other cyclic voltammograms are given in Supplementary material (Figs. S21–S24). Further the relative positions of MLCT absorptions in low energy region, ∼800 nm and ∼600 nm for $[(L\text{-}NH)Ru(CO)(PPh_3)_2]$ and $[(HL\text{-}NH)Ru(CO)Cl(PPh_3)_2]$, respectively, were consistent with the metal oxidation potentials.

$$[(L\text{-}NH)Ru(CO)(PPh_3)_2] - e \rightarrow [(L\text{-}NH)Ru(CO)(PPh_3)_2]^+ \quad (2)$$

$$[(HL\text{-}NH)Ru(CO)Cl(PPh_3)_2] - e \rightarrow [(HL\text{-}NH)Ru(CO)Cl(PPh_3)_2]^+ \quad (3)$$

2.5. Transformation of ketones to 2^0 – alcohols via hydrogen transfer reactions

Homogenous hydrogenation of organic compounds via catalytic hydrogen transfer reactions have been under investigation in recent years using Ruthenium catalyst [25,26]. This information

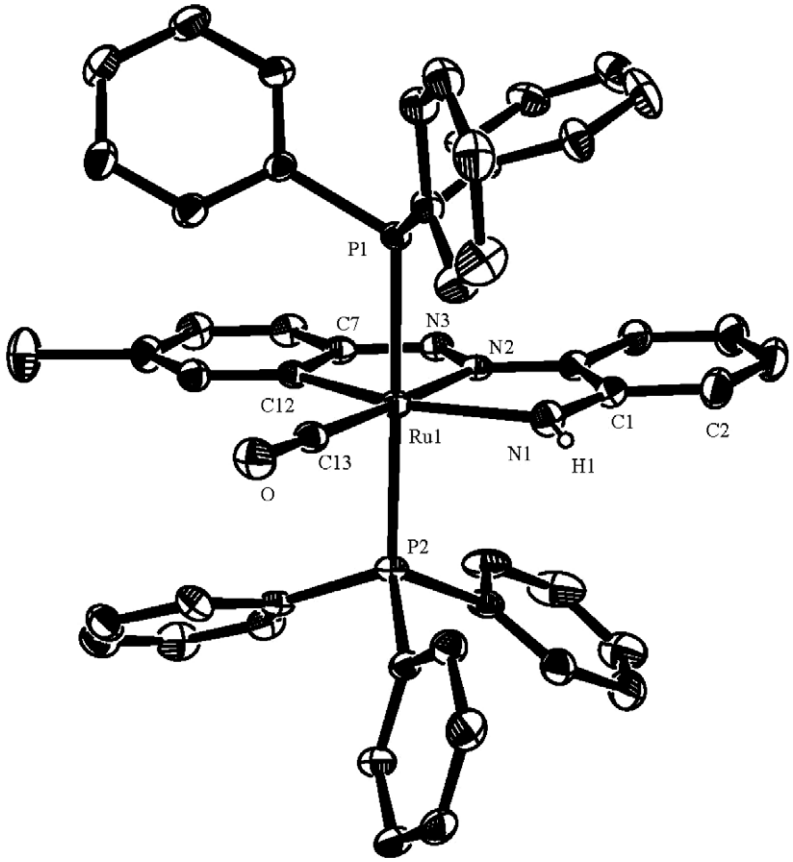


Fig. 3. Molecular structure of [(L^3-NH)Ru(CO)(PPh_3)$_2$] with atom numbering scheme. The hydrogen atoms excepting on N(1) of the amino groups have been omitted for clarity.

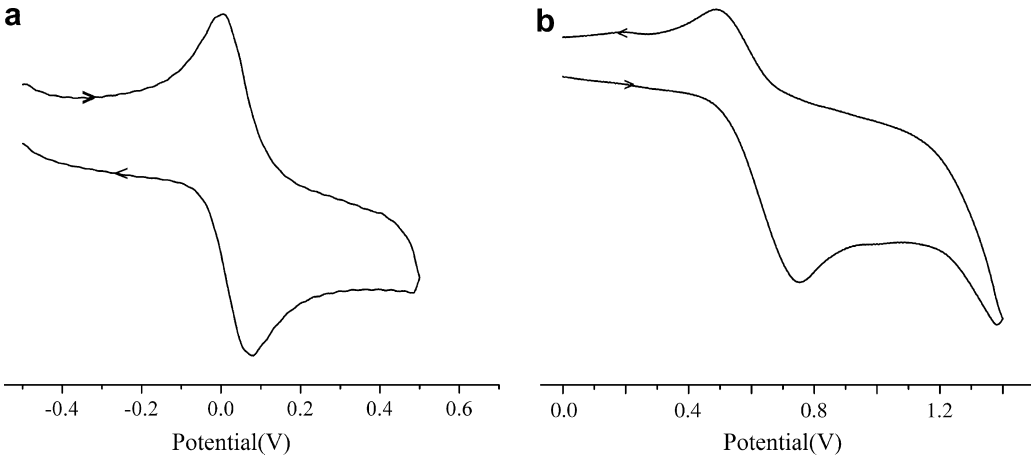
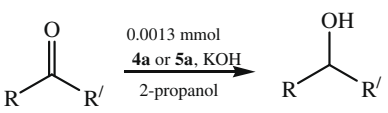


Fig. 4. Cyclic voltammograms of [(L^1-NH)Ru(CO)(PPh_3)$_2$] (a) and [(HL^1-NH)Ru(CO)Cl(PPh_3)$_2$] (b).

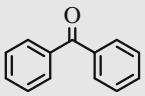
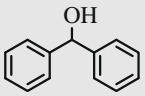
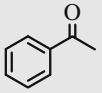
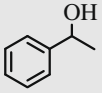
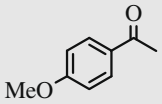
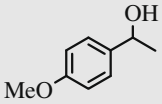
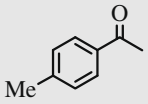
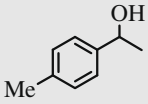
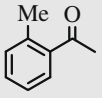
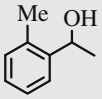
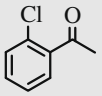
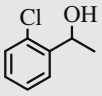
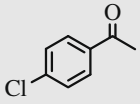
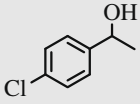
encouraged us to study the activity of [(L-NH)Ru(CO)(PPh_3)$_2$] and [(HL-NH)Ru(CO)Cl(PPh_3)$_2$] toward the transfer hydrogenation of representative aliphatic and aromatic ketones in presence of KOH and isopropyl alcohol promoters.

The conversion of ketones to corresponding alcohols were studied adding small amount of [(L^1-NH)Ru(CO)(PPh_3)$_2$], **5a**, or [(HL^1-NH)Ru(CO)Cl(PPh_3)$_2$], **4a**, in the reaction mixture Eq. (4). The results of transformations are given in Table 2. However, at the end of each reaction neither we could isolate the original ruthenium complexes (**4a** or **5a**) nor did we obtain only one complex as the major one suitable for characterization. Since the formation of species other than **4a** or **5a** could not be excluded during the transformations, the original complexes (**4a** and **5a**) were not considered to be the only catalytically active species. The ^{1}H NMR and IR spectra of the residues obtained after catalytic reactions were identical signifying formation of identical catalytically active species in both the cases.



(4)

Table 2
Transformation of ketones to 2^0 – alcohols via hydrogen transfer reactions for $[(HL^1\text{-}NH)Ru(CO)Cl(PPh_3)_2]$ and $[(L^1\text{-}NH)Ru(CO)(PPh_3)_2]$.

Entry	Substrate	Product	Time (h)	Isolated yield (%)	
				Complex **4a**	Complex **5a**
1			1	90	90
2			1.5	82	70
3			1.5	75	75
4			1.5	78	75
5			1.5	70	65
6			1.5	73	71
7			1.5	68	65
8			1.5	45	43
9			1.5	42	44

All the reactions were carried out in ambient condition unlike the reported reactions using other ruthenium orthometallated complexes, incorporating azo ligands, as catalyst [25,26]. A series of blank reactions were carried out in absence of complex **4a** and **5a** and in presence of only ligand or $RuCl_3{\cdot}3H_2O$. This ascertained the necessity of the complex during the reaction. The yields of the alcohols obtained from all the ketones were determined after isolation.

3. Experimental

3.1. Materials

The solvents used in the reactions were of reagent grade (E. Marck, Kolkata, India) and were purified and dried by reported procedure [33]. Ruthenium trichloride was purchased from Johnson Matthey, India. $Ru(CO)_3(PPh_3)_2$ and $RuH(CO)Cl(PPh_3)_3$ were synthesized following the reported procedure [34]. The ligands 2-(phenylazo)aniline ($HL^1\text{-}NH_2$), 2-(*p*-tolylazo)aniline ($HL^2\text{-}NH_2$), and 2-(*p*-chlorophenylazo)aniline ($HL^3\text{-}NH_2$) were prepared following the reported procedures [30,31].

3.2. Physical measurements

Microanalysis (C, H, N) was performed using a Perkin–Elmer 240C elemental analyzer. Infrared spectra were recorded on a Perkin–Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer. ^1H NMR spectra were obtained on Brucker DPX 400 and Brucker 500 RPX NMR spectrometers in $CDCl_3$ using TMS as the internal standard. Electrochemical measurements were made under dinitrogen atmosphere using a PAR model VARSASTAT-II potentiostat. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. Electrochemical data were collected at 298 K and are uncorrected for junction potentials.

3.3. Synthesis of complexes

3.3.1. $[(HL^1\text{-}NH)Ru(CO)Cl(PPh_3)_2]$

$HL^1\text{-}NH_2$ (0.043 g, 0.22 mmol) was dissolved in toluene (40 mL) and to it were added $RuH(CO)Cl(PPh_3)_3$ (0.021 g, 0.22 mmol). The mixture was then refluxed for 3 h, when a bluish solution was obtained. Evaporation of these solutions afforded a dark solid which was washed with hexane several times to remove excess ligands. The blue solid, obtained upon evaporation of the solvent, was recrystallized from dichloromethane–petroleum ether to afford $[(HL^1\text{-}NH)Ru(CO)Cl(PPh_3)_2]$ as a crystalline dark solid. Isolated yield: 0.117 g (60%). Anal. Calc. for $RuC_{49}H_{40}N_3ClOP_2$ (885.46): C, 66.46; H, 4.55; N, 4.75. Found: C, 66.62; H, 4.42; N, 4.68%. UV–Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 600 (3300), 400

(3750), 320 (11 175), 265 (34 360). IR (KBr): ν = 3335 (NH), 1934 (C=O), 1615 (C=N), 1432 (N=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.35–7.40 (m, 12H), 7.24–7.27 (m, 6H), 7.15–7.19 (m, 12H), 6.98 (d, 1H), 6.87 (t, 1H), 6.71 (t, 2H), 6.47 (t, 1H), 6.01 (t, 2H), 5.63 (d, 1H), 5.47 (s, NH). $E_{1/2}$ [V]: 0.56.

3.3.2. [(HL^2-NH)Ru(CO)Cl(PPh_3)$_2$] and [(HL^3-NH)Ru(CO)Cl(PPh_3)$_2$]

Complex [(HL^2-NH)Ru(CO)Cl(PPh_3)$_2$] and [(HL^3-NH)Ru(CO)-Cl(PPh_3)$_2$] were prepared and purified by following a similar procedure as described for [(HL^1-NH)Ru(CO)Cl(PPh_3)$_2$] using ligand HL^2-NH_2 and HL^3-NH_2 in place of HL^1-NH_2. Isolated yield: 0.119 g, (60%) and 0.131 g (65%), respectively.

Anal. Calc. for $RuC_{50}H_{42}N_3OClP_2$ (899.49): C, 66.76; H, 4.70; N, 4.68. Found: C, 66.61; H, 4.552; N, 4.78%. UV–Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 600 (3030), 400 (4200), 325 (10 600), 265 (34 600). IR (KBr): ν = 3333 (NH), 1928 (C=O), 1615 (C=N), 1432 (N=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.35–7.40 (m, 12H), 7.23–7.28 (m, 6H), 7.15–7.19 (m, 12H), 6.97 (d, 1H), 6.45–6.52 (m, 3H), 6.00 (t, 2H), 5.89 (d, 2H), 5.64 (d, 1H), 5.37 (s, NH), 2.17 (s, 3H). $E_{1/2}$ [V]: 0.62.

Anal. Calc. for $RuC_{49}H_{39}N_3OClP_2$ (919.91): C, 63.97; H, 4.27; N, 4.58. Found: C, 64.18; H, 4.21; N, 4.68%. UV–Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 600 (3130), 400 (3140), 325 (11 150), 270 (30 400). IR (KBr): ν = 3330 (NH), 1933 (C=O), 1614 (C=N), 1433 (N=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.41–7.44 (m, 12H), 7.25–7.28 (m, 6H), 7.15–7.20 (m, 12H), 6.95 (d, 1H), 6.64 (d, 2H), 6.46 (t, 1H), 6.02 (t, 1H), 5.97 (d, 2H), 5.57 (s, NH). $E_{1/2}$ [V]: 0.70.

3.3.3. [(L^1-NH)Ru(CO)(PPh_3)$_2$]

HL^1-NH_2 (0.043 g, 0.22 mmol) was dissolved in toluene (40 mL) and to it were added $Ru(CO)_3(PPh_3)_2$ (0.0156 g, 0.22 mmol). The mixture was then refluxed for 4 h, when a green solution was obtained. Evaporation of these solutions afforded a dark solid which was washed with hexane several times to remove excess ligands, and then it was purified by thin layer chromatography on silica plate with toluene:acetonitrile (90:10) as the eluent. A yellowish pink band separated and the complex was extracted from it with methanol turns to green solution. The pure green crystals, obtained upon evaporation of the solvent, was recrystallized from dichloromethane–petroleum ether to afford [(L^1-NH)Ru(CO)(PPh_3)$_2$] as a crystalline green solid. Isolated yield: 0.093 g (50%). Anal. Calc. for $RuC_{49}H_{39}N_3OP_2$ (849): C, 69.32; H, 4.62; N, 4.96. Found: C, 69.15; H, 4.53; N, 5.12%. UV–Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 800 (3430), 410 (4830), 340 (10 520), 270 (26 030). IR (KBr): ν = 3333 (NH) 1919 (C=O), 1598 (C=N), 1434 (N=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.44 (b, 12H), 7.27 (t, 6H), 7.21 (t, 12H), 6.75 (d, 1H), 6.71 (d, 1H), 6.38 (d, 1H), 6.08 (t, 1H), 5.91 (d, 1H), 5.40 (d, 1H), 5.33 (d, 1H). $E_{1/2}$ [V]: 0.05.

3.3.4. [(L^2-NH)Ru(CO)(PPh_3)$_2$ and (L^3-NH)Ru(CO)(PPh_3)$_2$]

Complex [(L^2-NH)Ru(CO)(PPh_3)$_2$] and [(L^3-NH)Ru(CO)(PPh_3)$_2$] were prepared and purified following a similar procedure as described for [(L^1-NH)Ru(CO)(PPh_3)$_2$] using ligand HL^2-NH_2 and HL^3-NH_2 in place of HL^1-NH_2. Yield: 0.114 g, (60%) and 0.101 g (55%), respectively.

Anal. Calc. for $RuC_{50}H_{41}N_3OP_2$ (863.03): C, 69.58; H, 4.78; N, 4.88. Found: C, 69.62; H, 4.62; N, 4.75%. UV–Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 800 (3850), 420 (6780), 340 (12 360), 270 (29 100). IR (KBr): ν = 3353 (NH), 1910 (C=O), 1596 (C=N), 1433 (N=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.38–7.45 (m, 12H), 7.23–7.28 (m, 6H), 7.18–7.22 (m, 12H), 6.81 (d, 1H), 6.63 (s, 1H), 6.25 (d, 1H), 6.09 (t, 1H), 5.86 (d, 1H), 5.42 (d, 1H), 5.28 (b, 1H), 1.88 (s, 3H). $E_{1/2}$ [V]: 0.10.

Anal. Calc. for $RuC_{49}H_{38}N_3ClOP_2$ (883.45): C, 66.61; H, 4.33; N, 4.76. Found: C, 66.73; H, 4.42; N, 4.62%. UV–Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 800 (4680), 420 (6380), 350 (13 410), 270 (32 020). IR (KBr): ν = 3352 (NH), 1920 (C=O), 1598 (C=N), 1433 (N=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40–7.44 (m, 12H), 7.28–7.31 (m, 6H), 7.22–7.25 (m, 12H), 6.75 (d, 1H), 6.71 (s, 1H), 6.38 (d, 1H), 6.08 (t, 1H), 5.91 (d, 1H), 5.40 (d, 1H), 5.33 (d, 1H). $E_{1/2}$ [V]: 0.15.

3.4. Transformation of ketones to 2^0 – alcohols via hydrogen transfer reactions

A mixture containing ketones (0.071 g, 3.9 mmol), the ruthenium complex (0.0012 g, 0.0013 mmol) and (0.0036 g, 0.0625 mmol) of KOH was heated to reflux in 10 mL of *i*-PrOH for appropriate period of time as mentioned in Table 2. The complex was removed as precipitate from the reaction mixture by the addition of diethyl ether followed by filtration and subsequent neutralization with 5 mL of 1 (M) HCl. Then the ether layer was passed through a short path of silica gel and purified by preparative chromatography. The hydrogenated products were characterized by matching the UV–Vis and IR spectra of authentic samples.

Table 3
Crystallographic data for [(HL^3-NH)Ru(CO)Cl(PPh_3)$_2$] and [(L^3-NH)Ru(CO)(PPh_3)$_2$].

	[(HL^3-NH)Ru(CO)Cl-(PPh_3)$_2$]	[(L^3-NH)Ru(CO)(PPh_3)$_2$]
Chemical formula	$C_{49}H_{39}Cl_2N_3OP_2Ru{\cdot}0.5(C_6H_6)$	$C_{49}H_{38}ClN_3OP_2Ru{\cdot}CH_2Cl_2$
Formula weight	958.80	968.21
Space group	$P2_1/n$	$P\bar{1}$
Crystal system	monoclinic	triclinic
a (Å)	12.3751(16)	12.2334(6)
b (Å)	20.948(3)	13.1599(7)
c (Å)	17.946(2)	17.3881(9)
α (°)	90	68.127(3)
β (°)	106.849(4)	89.056(3)
γ (°)	90	62.302(3)
λ (Å)	0.71073	0.71073
V (Å^3)	4452.5(10)	2257.9(2)
Z	4	2
Temperature (K)	293	293
D_{calc} (g cm^{-3})	1.430	1.424
μ (mm^{-1})	0.587	0.636
R_1	0.0393	0.0510
wR_2	0.1051	0.1621
Unique reflections [$I > 2\sigma(I)$]	3406/2550	11 005/7853
Goodness-of-fit (GOF)	1.06	1.02

4. Crystallography

The suitable X-ray crystals of [(L^3-NH)Ru(CO)(PPh_3)$_2$] and [(HL^3-NH)Ru(CO)Cl(PPh_3)$_2$] were obtained by slow diffusion of a dichloromethane solution into petroleum ether with few drop of benzene at 298 K. Data were collected by ω-scan technique on a Bruker Smart CCD diffractometer with Mo Kα radiation monochromated by graphite crystal. Structure solution was done by direct method with SHELXS-97 program [35,36]. Full matrix least square refinements on F^2 were performed using SHELXL-97 program [35,36]. All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. All hydrogens were included at calculated positions excepting H1 for both the complexes. These were located by difference Fourier mapping and refined isotropically. The data collection parameters and relevant crystal data are collected in Table 3.

Acknowledgments

We are thankful to the DST (New Delhi) for funding under DST-SERC project (SR/S1/IC-0026/2007). J.P. is thankful to the CSIR (New Delhi) for his fellowship (No. 09/106(0097)2K8-EMR-I). The necessary laboratory and infrastructural facility are provided by the Department of Chemistry, University of Kalyani. The support of DST under FIST and UGC SAP program to the Department of Chemistry, University of Kalyani is acknowledged.

Appendix A. Supplementary material

CCDC 724146 and 724145 contain the supplementary crystallographic data for [(HL^3-NH)Ru(CO)Cl(PPh_3)$_2$] (**4c**) and [(L^3-NH)Ru(CO)(PPh_3)$_2$] (**5c**). These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.06.038.

References

[1] P.H. Dixneuf, C. Bruneau, Ruthenium Catalysts and Fine Chemistry, Topics in Organometallic Chemistry, vol. 11, Springer-Verlag, Berlin, Heidelberg, New York, 2004.
[2] R. Abbel, K. Abdur-Rashid, M. Faatz, A. Hadzovic, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 127 (2005) 1870–1882.
[3] S.H. Hong, M.W. Day, R.H. Grubbs, J. Am. Chem. Soc. 126 (2004) 7414–7415.
[4] T. Ren, Chem. Rev. 108 (2008) 4185–4207.
[5] A.H. Velders, K. van der Schilden, A.C.G. Hotze, J. Reedijk, H. Kooijman, A.L. Spek, Dalton Trans. (2004) 448–455.
[6] S.J. Dougan, M.M.A. Habtemariam, S. Parsons, P.J. Sadler, Inorg. Chem. 45 (2006) 10882–10894.
[7] A.C.G. Hotze, A.H. Velders, F. Ugozzoli, M. Biagini-Cingi, A.M. Manotti-Lanfredi, J.G. Haasnoot, J. Reedijk, Inorg. Chem. 39 (2000) 3838–3844.
[8] A.C.G. Hotze, M. Bacac, A.H. Velders, B.A.J. Jansen, H. Kooijman, A.L. Spek, J.G. Haasnoot, J. Reedijk, J. Med. Chem. 46 (2003) 1743–1750.
[9] A.H. Velders, H. Kooijman, A.L. Spek, J.G. Haasnoot, D. de Vos, J. Reedijk, Inorg. Chem. 39 (2000) 2966–2967.
[10] A.C.G. Hotze, E.P.L. van der Geer, S.E. Caspers, H. Kooijman, A.L. Spek, J.G. Haasnoot, J. Reedijk, Inorg. Chem. 43 (2004) 4935–4943.
[11] A.C.G. Hotze, H. Kooijman, A.L. Spek, J.G. Haasnoot, J. Reedijk, New J. Chem. 1 (2004) 565–569.
[12] J. Otsuki, N. Omokawa, K. Yoshiba, I. Yoshikawa, T. Akasaka, T. Suenobu, T. Takido, K. Araki, S. Fukuzumi, Inorg. Chem. 42 (2003) 3057–3066.
[13] H.-Y. Ye, F.-R. Dai, L.-Y. Zhang, Z.-N. Chen, Inorg. Chem. 46 (2007) 6129–6135.
[14] A.K. Mahapatra, S. Datta, S. Goswami, M. Mukherjee, A.K. Mukherjee, A. Chakravorty, Inorg. Chem. 25 (1986) 1715–1721.
[15] G.K. Lahiri, S. Bhattacharya, M. Mukherjee, A.K. Mukherjee, A. Chakravorty, Inorg. Chem. 26 (1987) 3359–3365.
[16] C. Das, A.K. Ghosh, C.-H. Hung, G.-H. Lee, S.-M. Peng, S. Goswami, Inorg. Chem. 41 (2002) 7125–7135.
[17] C. Das, A. Saha, C.-H. Hung, G.-H. Lee, S.-M. Peng, S. Goswami, Inorg. Chem. 42 (2003) 198–204.
[18] S. Samanta, P. Singh, J. Fiedler, S. Záliš, W. Kaim, S. Goswami, Inorg. Chem. 47 (2008) 1625–1633.
[19] B. Sarkar, S. Patra, J. Fiedler, R.B. Sunoj, D. Janardanan, G.K. Lahiri, W. Kaim, J. Am. Chem. Soc. 130 (2008) 3532–3542.
[20] S. Maji, B. Sarkar, S.M. Mobin, J. Fiedler, W. Kaim, G.K. Lahiri, Dalton Trans. (2007) 2411–2418.
[21] S. Kar, B. Pradhan, R.K. Sinha, T. Kundu, P. Kodgire, K.K. Rao, V.G. Puranik, G.K. Lahiri, Dalton Trans. (2004) 1752–1760.
[22] S. Halder, R. Acharyya, S.-M. Peng, G.-H. Lee, M.G.B. Drew, S. Bhattacharya, Inorg. Chem. 45 (2006) 9654–9663.
[23] S. Nag, P. Gupta, R.J. Butcher, S. Bhattacharya, Inorg. Chem. 43 (2004) 4814–4816.
[24] T.K. Misra, D. Das, C. Sinha, P. Ghosh, C.K. Pal, Inorg. Chem. 37 (1998) 1672–1678.
[25] S. Kannan, R. Ramesh, Y. Liu, J. Organomet. Chem. 692 (2007) 3380–3391.
[26] G. Venkatachalam, R. Ramesh, Tetrahedron Lett. 46 (2005) 5215–5218.
[27] J. Pratihar, D. Patra, S. Chattopadhyay, J. Organomet. Chem. 690 (2005) 4816–4821.
[28] J.L. Pratihar, N. Maiti, S. Chattopadhyay, Inorg. Chem. 44 (2005) 6111–6114.
[29] J.L. Pratihar, B. Shee, P. Pattanayak, D. Patra, A. Bhattacharyya, V.G. Puranik, C.H. Hung, S. Chattopadhyay, Eur. J. Inorg. Chem. 1 (2007) 4272–4281.
[30] N. Maiti, S. Pal, S. Chattopadhyay, Inorg. Chem. 40 (2001) 2204–2205.
[31] N. Maiti, B.K. Dirghangi, S. Chattopadhyay, Polyhedron 22 (2003) 3109–3113.
[32] P. Pattanayak, J.L. Pratihar, D. Patra, A. Burrows, M. Mohan, S. Chattopadhyay, Eur. J. Inorg. Chem. (2007) 4263–4271.
[33] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, third ed., Pergamon, New York, 1988.
[34] G.W. Parshall, Inorg. Synth. XV (1974) 48 and 50.
[35] G.M. Sheldrick, SHELXS-97, University of Göttingen, Göttingen, Germany, 1990.
[36] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystals Structures from Diffraction Data, University of Göttingen, Göttingen, Germany, 1997.