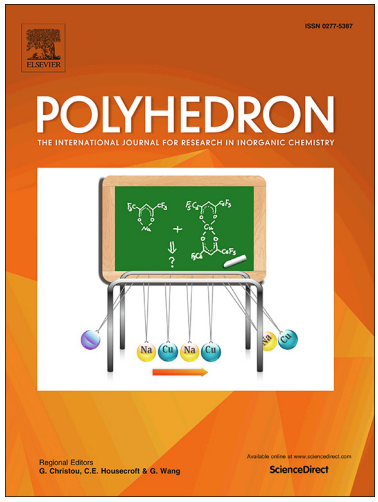
Accepted Manuscript



Arene-ruthenium complexes with 2-(arylazo)phenol as ancillary ligand: Synthesis, characterization, and utilization in catalytic transfer-hydrogenation

Jit Karmakar, Samaresh Bhattacharya

PII: S0277-5387(19)30147-0
DOI: https://doi.org/10.1016/j.poly.2019.02.046
Reference: POLY 13790

To appear in: *Polyhedron*

Received Date: 15 January 2019
Revised Date: 22 February 2019
Accepted Date: 23 February 2019

Please cite this article as: J. Karmakar, S. Bhattacharya, Arene-ruthenium complexes with 2-(arylazo)phenol as ancillary ligand: Synthesis, characterization, and utilization in catalytic transfer-hydrogenation, *Polyhedron* (2019), doi: https://doi.org/10.1016/j.poly.2019.02.046

Manuscript No.: POLY-D-19-00042

(Revised)

Arene-ruthenium complexes with 2-(arylazo)phenol as ancillary ligand: Synthesis, characterization, and utilization in catalytic transfer-hydrogenation

Jit Karmakar, Samaresh Bhattacharya*

Department of Chemistry, Inorganic Chemistry Section,
Jadavpur University, Kolkata 700 032, India

ABSTRACT

Reaction of 2-(arylazo)phenols (HL-R, where H represents the phenolic proton and, R = CH_3, H and Cl) with [{Ru(*p*-cymene)Cl_2}$_2$] in the presence of triethylamine affords a group of three reddish-brown complexes of type [Ru(*p*-cymene)(L-R)Cl] in good yields. Structure of [Ru(*p*-cymene)(L-CH_3)Cl] has been determined by X-ray crystallography. The 2-(arylazo)phenolate ligand (L-R) is coordinated to the metal center as a mono-anionic bidentate N,O-donor forming five-membered chelate ring. All the complexes are diamagnetic, and show characteristic ^{1}H NMR signals. They also show intense absorptions in the visible and ultraviolet regions, which have been analyzed by TDDFT calculations. Cyclic voltammetry on the complexes shows two successive irreversible oxidations within 1.10 - 1.40 V *vs*. SCE. The [Ru(*p*-cymene)(L-R)Cl] complexes are found to serve as efficient catalyst-precursor for the transfer-hydrogenation of aldehydes.

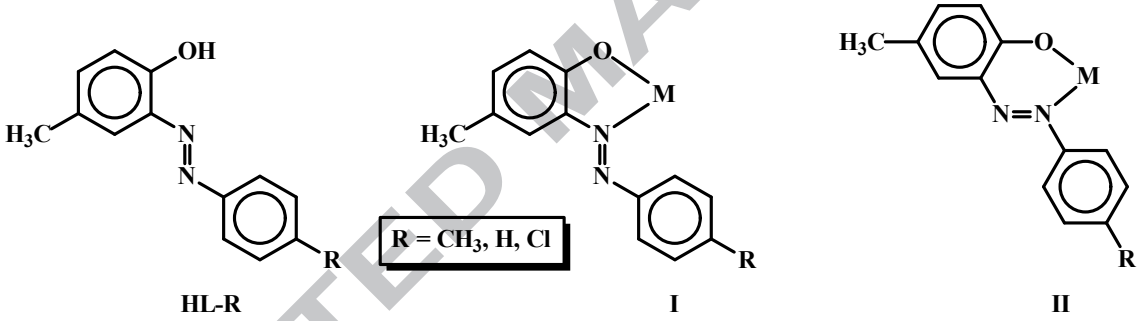
Keywords:
2-(arylazo)phenols (HL-R)
[Ru(*p*-cymene)(L-R)Cl] complexes
Crystal structure
Electronic spectra
Catalytic transfer-hydrogenation

* Corresponding author.

E-mail address: samaresh_b@hotmail.com (S. Bhattacharya).

1. Introduction

The current interest in the coordination complexes of ruthenium is largely due to their catalytic and biological applications [1-6]. Such properties are dependent primarily on the coordination environment around the metal center, and hence binding of ruthenium by ligands of selected types is of significant importance. Herein we have chosen a group of three 2-(arylazo)phenols as the principal ligand, which are abbreviated in general as HL-R, where H depicts the phenolic proton and R the *para*-substituent in the pendent phenyl ring. The three different substituents (R = CH_3, H and Cl), with different electron-withdrawing properties, have been chosen to study their influence, if any, on the redox properties of the resulting complexes. The 2-(arylazo)phenols usually bind to a metal center, via dissociation of the phenolic proton, as bidentate N,O-donors forming either five-membered (**I**) or six-membered (**II**) chelate rings [7-10]. In the



present work, which has originated from our continued interest in ruthenium complexes having targeted coordination environments, with particular reference to their possible utilization in catalysis [11-16], the primary objective has been to synthesize a family of mixed-ligand arene-ruthenium complexes incorporating the chosen 2-(arylazo)phenols, and explore their catalytic potential. In order to prepare the targeted Ru-arene-2-(arylazo)phenol complexes, [{Ru(*p*-cymene)Cl_2}$_2$] has been selected as the source of ruthenium-arene moiety because of its demonstrated ability to serve as an efficient starting material for the synthesis of mixed-ligand complexes of type [Ru(*p*-cymene)(L-L′)Cl] (L-L′ depicts a bidentate chelating ligand) [17-20]. Reaction of the selected 2-(arylazo)phenols with [{Ru(*p*-cymene)Cl_2}$_2$] has indeed afforded a group of complexes of the expected type. The chemistry of all these complexes is reported herein, with special reference to their formation, characterization, and catalytic application.

2. Experimental

2.1. Materials

Ruthenium trichloride was purchased from Arora Matthey, Kolkata, India, and α-phellandrene was procured from Sigma-Aldrich, USA. [{Ru(*p*-cymene)Cl_2}$_2$] was synthesized by following a reported procedure [21]. Aniline, *p*-toluidine, *p*-chloroaniline and *p*-cresol were purchased from S.D. Fine-Chem Limited, Mumbai, India. The 2-(arylazo)phenols were prepared by coupling respective diazotized aniline with *p*-cresol. Tetrabutylammonium hexaflurophosphate (TBHP), obtained from Aldrich, and AR grade acetonitrile, procured from Merck, India, were used for electrochemical work. All other chemicals and solvents were reagent grade commercial materials and were used as received.

2.2. Syntheses of complexes

The [Ru(*p*-cymene)(L-R)Cl] complexes were prepared by following a general procedure. Specific details are given below for a particular complex.

***[Ru(p-cymene)(L-CH_3)Cl]*:** The HL-CH_3 ligand (38 mg, 0.17 mmol) was dissolved in 30 mL of methanol, and to it was added a solution of [{Ru(*p*-cymene)Cl_2}$_2$] (50 mg, 0.08 mmol)**1** in chloroform (30 mL), followed by triethylamine (17 mg, 0.17 mmol). The reaction mixture was refluxed for 4 h. The solvents were removed under reduced pressure to yield a dark solid, which was subjected to purification by thin layer chromatography on a silica plate. With 1:5 acetonitrile-benzene as the eluant, a reddish-brown band separated, which was extracted with acetonitrile. Evaporation of the acetonitrile extract gave [Ru(*p*-cymene)(L-CH_3)Cl] as a dark crystalline solid. Yield: 78%. Anal. Calcd for $C_{24}H_{27}N_2O_1Cl_1Ru$: C, 58.12; H, 5.44; N, 5.65. Found: C, 58.06; H, 5.46; N, 5.58 %. MS (ESI), positive mode: $[M - Cl]^+$, 460. IR: 2958, 2920, 1614, 1491, 1384, 1310, 1242, 1136 and 1111 cm^{-1}. ^1H NMR:**2** 7.78 (d, 1H, *J* = 8.5 Hz), 7.60 (d, 1H, *J* = 8.0 Hz), 7.48 (s, 1H), 7.34 (d, 1H, J = 9.0 Hz), 7.17 (d, 1H, *J* = 7.0 Hz), 6.96 (d, 1H, *J* = 8.5 Hz), 6.89 (d, 1H, *J* = 8.5 Hz), 5.47 (d, 1H, *J* = 6.0 Hz), 5.12 (d, 1H, *J* = 6 Hz), 4.70 (d, 1H, *J* = 5.5 Hz), 4.07 (d, 1H, *J* = 5.5 Hz), 3.47 (q, 1H, *J* = 7.0 Hz), 2.48 (s, CH_3), 2.17 (s, CH_3), 2.00 (s, CH_3), 1.22 (m, $2CH_3$).

***[Ru(p-cymene)(L-H)Cl]*:** Yield: 72%. Anal. Calcd for $C_{23}H_{25}N_2O_1Cl_1Ru$: C, 57.32; H, 5.19; N, 5.81. Found: C, 57.05; H, 5.32; N, 5.80 %. MS (ESI), positive mode: $[M - Cl]^+$, 446. IR: 2960, 2920, 1613, 1490, 1384, 1311, 1241, 1135 and 1109 cm^{-1}. ^1H NMR: 7.91 (d, 1H, J = 8.0 Hz), 7.71 (d, 1H, J = 7.0 Hz), 7.41 (s, 1H), 7.54-7.44 (3H)*, 6.99 (d, 1H, J = 7.6 Hz), 6.89 (d, 1H, J = 8.8 Hz), 5.52 (d, 1H, J = 5.5 Hz), 5.17 (d, 1H, J = 5.7 Hz), 4.72 (d, 1H, J = 5.5 Hz), 4.16 (d, 1H, J = 5.7 Hz), 3.50 (q, 1H), 2.18 (s, CH_3), 2.03 (s, CH_3), 1.15 (m, $2CH_3$).

***[Ru(p-cymene)(L-Cl)Cl]*:** Yield: 74%. Anal. Calcd for $C_{23}H_{24}N_2O_1Cl_2Ru$: C, 53.48; H, 4.65; N, 5.42. Found: C, 53.40; H, 4.58; N, 5.39 %. MS (ESI), positive mode: $[M - Cl]^+$, 480. $[M - Cl]^+$. IR: 2924, 2854, 1575, 1496, 1429, 1273, 1141, 1083 and 516 cm^{-1}. ^1H NMR: 7.90 (d, 1H, J = 8.6 Hz), 7.70 (d, 1H, J = 8.1 Hz), 7.52 (d, 1H, J = 8.5 Hz), 7.45 (d, 1H, J = 7.4 Hz), 7.40 (s, 1H), 6.95 (d, 1H, J = 9.4 Hz), 6.88 (d, 1H, J = 8.8 Hz), 5.51 (d, 1H, J = 6.0 Hz), 5.16 (d, 1H, J = 5.6 Hz), 4.71 (d, 1H, J = 6.0 Hz), 4.15 (d, 1H, J = 6.0 Hz), 3.49 (m, 1H), 2.22 (s, CH_3), 2.18 (s, CH_3), 1.12 (m, $2CH_3$).

2.3. Physical measurements

Microanalyses (C, H, N) were performed on a Heraeus Carlo Erba 1108 elemental analyzer. Magnetic susceptibilities were measured using a Sherwood MK-1 balance. ^1H NMR spectra recorded in $CDCl_3$ solution on a Bruker Avance DPX 300 NMR spectrometer using TMS as the internal standard. IR spectra were obtained on a Perkin Elmer Spectrum Two spectrometer with samples prepared as KBr pellets. Mass spectra were recorded with a Micromass LCT electrospray (Qtof Micro YA263) mass spectrometer. Electronic spectra were recorded on a PerkinElmer LAMBDA 25 spectrophotometer. Electrochemical measurements were made using a CH Instruments model 600A electrochemical analyzer. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in the cyclic voltammetry experiments. All electrochemical experiments were performed under a dinitrogen atmosphere, and the electrochemical data were collected at 298 K. Geometry optimization by density functional theory (DFT) method and electronic spectral analysis by TDDFT calculation were performed using the Gaussian 09

(B3LYP/SDD-6-31G) package [22]. GC-MS analyses were performed using a Perkin Elmer CLARUS 680 instrument.

2.4. X-ray crystallography

Single crystals of [Ru(*p*-cymene)(L-CH_3)Cl] were obtained by slow diffusion of toluene into a chloroform solution of the complex. Selected crystal data and data collection parameters are given in **Table 1**. Data were collected on a Bruker SMART CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). X-ray data reduction and, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs [23,24]. The structures were solved by the direct methods. The structure refined fairly well, however, the azo (-N=N-) fragment was found to suffer from disorder problem.

2.5. General procedure for the catalytic transfer-hydrogenation reactions

In a typical run, an oven-dried 10 ml round-bottomed flask was charged with the aldehyde (1 mmol), a known mol percent of the catalyst, and KOH (0.5 mmol) dissolved in 2-propanol (5 ml). The flask was placed in a preheated oil bath at the required temperature. After the specified time, the flask was removed from the oil bath and water (20 ml) was added, and extracted with diethyl ether (4-10 ml). The combined organic layers were washed with water (3-10 ml), dried with anhydrous Na_2SO_4, and filtered. Diethyl ether was removed under vacuum and the residue obtained dissolved in hexane and analyzed by GC-MS.

3. Results and discussion

3.1. Synthesis and characterization

As outlined in the introduction, the initial goal of the present work was to synthesize a group of mixed-ligand arene-ruthenium complexes containing the N,O-donor 2-(arylazo)phenolate ligand. Accordingly, reactions of the chosen 2-(arylazo)phenols (HL-R) were carried out with [{Ru(*p*-cymene)Cl_2}$_2$] in the presence of triethylamine, which afforded the targeted complexes of type [Ru(*p*-cymene)(L-R)Cl] in good yields. Preliminary characterizations on the complexes were found to be consistent with their compositions. However, for an unambiguous identification of these complexes, with particular regard to coordination mode of the 2-(arylazo)phenolate ligand, structure of a selected complex, *viz*. [Ru(*p*-cymene)(L-CH_3)Cl], was determined by X-ray crystallography. The structure is shown in **Fig. 1** and some relevant bond parameters are

Fig. 1

given in **Table 2**. The structure shows that the 2-(arylazo)phenolate ligand is coordinated to ruthenium as a mono-anionic N,O-donor forming a five-membered chelate ring (**I**, M = Ru). The *p*-cymene moiety is linked to ruthenium in the usual π-fashion, and a chloride is also bound to the metal center. All the bond distances are observed to be quite usual.[3] As all three [Ru(*p*-cymene)(L-R)Cl] complexes were synthesized similarly, and they show similar properties (*vide infra*), the remaining two complexes, *viz*. [Ru(*p*-cymene)(L-H)Cl] and [Ru(*p*-cymene)(L-Cl)Cl], are assumed to have similar structure as [Ru(*p*-cymene)(L-CH_3)Cl].

3.2. Spectral studies

Magnetic susceptibility measurements show that the [Ru(*p*-cymene)(L-R)Cl] complexes are diamagnetic, which is consistent with the +2 oxidation state of ruthenium (low-spin d^6, S = 0) in them. ^{1}H NMR spectra of the [Ru(*p*-cymene)(L-R)Cl] complexes show many signals arising from the coordinated *p*-cymene and 2-(arylazo)phenolate ligands, most of which could be easily identified, while few could not be clearly detected due to overlap problem. For example, all the signals for the *p*-cymene ligand could be distinctly observed in all three complexes. The methyl group in the phenolic fragment of the 2-(arylazo)phenolate ligands is observed near 2.18 ppm in all the complexes. In the

[Ru(*p*-cymene)(L-CH_3)Cl] complex, an additional methyl signal is observed at 2.48 ppm, which is due to the methyl group in the arylazo fragment.

Infrared spectra of the [Ru(*p*-cymene)(L-R)Cl] complexes show many bands of different intensities in the 450-4000 cm^{-1} region, and assignment of the bands to specific vibrations has not been attempted. However, comparison with the spectrum of the starting [{Ru(*p*-cymene)Cl_2}$_2$] complex shows the presence of several additional bands (near 1491, 1314, 1244, 1135 and 1110 cm^{-1}), which are attributable to the coordinated 2-(arylazo)phenolate ligand. Among these bands, the one near 1491 cm^{-1} and the other one near 1110 cm^{-1} are assignable respectively to the azo (N=N) and phenolic C-O stretches. The ^{1}H NMR and infrared spectral data are therefore in good agreement with the composition of the complexes.

The [Ru(*p*-cymene)(L-R)Cl] complexes are found to be readily soluble in polar organic solvents, such as: methanol, ethanol, dichloromethane, chloroform and acetonitrile, producing intense pinkish-brown solutions. Electronic spectra of the complexes were recorded in methanol solutions. Spectral data are presented in **Table 3**. Each complex shows three absorptions spanning the visible and ultraviolet regions. The two absorptions in the visible region near 550 nm and 388 nm are believed to be due to a metal-to-ligand charge-transfer transition. The intense absorption in the ultraviolet region around 320 nm is attributable to transitions within the ligand orbitals. To have an insight into the nature of these absorptions, TDDFT calculations have been performed on all three [Ru(*p*-cymene)(L-R)Cl] complexes, using the Gaussian 09 package [21], and the results are found to be similar for all the complexes. The DFT-optimized structures of the complexes are shown in **Fig. S1** and some computed bond parameters are listed in **Table S1** (Supplementary material). The computed bond parameters for [Ru(*p*-cymene)(L-CH_3)Cl] compare well with those found in its crystal structure. The main calculated transitions for [Ru(*p*-cymene)(L-CH_3)Cl] and compositions of the molecular orbitals associated with these transitions are presented respectively in **Table 4** and **Table 5**, and contour plots of the same molecular orbitals are shown in **Fig. 2**. Similar data and

Fig. 2

diagrams for the other two [Ru(*p*-cymene)(L-R)Cl] (R = H and Cl) complexes are deposited in **Table S2-S5** and **Fig. S2-S3** (Supplementary material). Since the computed orbital and optical transition data are qualitatively similar for this group of complexes, only the results for [Ru(*p*-cymene)(L-CH_3)Cl] are discussed here as a representative case. Plots of experimental and theoretical spectra for this complex are shown in **Fig. S4** (Supplementary material). The lowest energy absorption at 547 nm is attributable primarily to a HOMO → LUMO transition, with much less HOMO-1 → LUMO, HOMO-3 → LUMO and HOMO → LUMO+2 character, and based on the nature of the participating orbitals the electronic excitation is assignable to a combination of MLCT, LMCT, LLCT and ILCT transitions. The next absorption at 388 nm has dominant HOMO-1 → LUMO character, while the third absorption at 323 nm is largely due to HOMO-3 → LUMO and HOMO-1 → LUMO+1 transitions, and both of these absorptions are again assignable to a combination of MLCT, LMCT, LLCT and ILCT transitions.

3.3. Electrochemical properties

Electrochemical properties of the [Ru(*p*-cymene)(L-R)Cl] complexes have been studied by cyclic voltammetry in acetonitrile solution (0.1 M TBHP). Each complex shows two oxidative responses on the positive side of SCE, which are found to be irreversible in nature. Cyclic voltammetric data are given in **Table 3**. The first oxidative response near 1.10 V vs SCE is assigned to Ru(II)-Ru(III) oxidation. The second oxidation, that takes place near 1.40 V vs SCE, is too close to the first Ru(II)-Ru(III) oxidation, and hence it is unlikely to be Ru(III)-Ru(IV) oxidation. Therefore this second oxidation is tentatively assigned to oxidation of the coordinated 2-(arylazo)phenolate ligand. Potential of the oxidative responses in these [Ru(*p*-cymene)(L-R)Cl] complexes does not show any significant variation with the nature of the substituent R in the 2-(arylazo)phenolate ligands.

3.4. Catalytic transfer-hydrogenation

Catalytic transfer-hydrogenation of organic substrates has been receiving considerable attention [25-28], primarily because of the green nature of the methodology. Such reactions are known to be efficiently catalyzed by a variety of ruthenium(II)

complexes [25,27,28], where the reactions usually proceed through the intermediacy of a ruthenium-hydrido species. Hence, complexes having a pre-existing Ru-H bond, or with the potential of formation of a Ru-H bond *in situ*, are suitable for trial as transfer-hydrogenation catalyst. As complexes with a Ru-X (X = halide, pseudohalide, or other anionic ligand) bond are known to provide a Ru-H fragment upon reaction with primary or secondary alcohols [12,13,15,29,30], and complexes of type [Ru(*p*-cymene)(L-L′)Cl] (L-L′ depicting a bidentate chelating ligand) are being routinely utilized for such reactions [31-42], we wanted to explore such possibility in the present group of [Ru(*p*-cymene)(L-R)Cl] complexes.

We began our study by examining the transfer hydrogenation of 4-chlorobenzaldehyde to 4-chlorobenzyl alcohol using [Ru(*p*-cymene)(L-CH_3)Cl] as the catalyst. After extensive optimization (**Table S6**; Supplementary material) it was found that 0.00001 mol% catalyst, 0.5 mol% KOH, 2-propanol as solvent, a reaction temperature of 100 °C, and a reaction time of 30 min furnished an excellent yield (97%) of the expected product (**Table 6**, entry 1). As all the three [Ru(*p*-cymene)(L-R)Cl] complexes were found to show comparable catalytic efficiency (**Table S6**; Supplementary material), only the results obtained with [Ru(*p*-cymene)(L-CH_3)Cl] as the catalyst are presented here. Using the optimized reaction conditions, transfer-hydrogenation of twelve different aldehydes have been performed (**Table 6**, entries 1-12), and the corresponding product alcohols were obtained in good to excellent yields for all the substrates (entries 1-9) except three, which have a donor site next to the -CHO group, where the product alcohols were obtained in negligible yield (entries 10-12). It is interesting to mention here that when ketones were taken as substrates, their hydrogenation to the corresponding secondary alcohol was not observed at all, which indicates that the present group of [Ru(*p*-cymene)(L-R)Cl] complexes can selectively, and efficiently, catalyze hydrogenation of alhedydes to the corresponding primary alcohols.

The observed Ru-catalyzed transfer-hydrogenation of aldehydes is believed to follow the sequences illustrated in **Scheme 1**, which are essentially drawn from those proposed earlier [31-42]. The [Ru(*p*-cymene)(L-R)Cl] catalyst-precursor, which is

depicted as (**i**) with only the Ru-Cl fragment shown, undergoes reaction with 2-propanol in the initial step to generate the intermediate (**ii**), in which the isopropoxide ion is

Scheme 1

coordinated to ruthenium through oxygen, and thus entry into the catalytic cycle takes place. This species (**ii**) then undergoes a β-hydride elimination from the coordinated isopropoxide ligand, which is quite usual [29,43-47], to afford the hydrido species (**iii**). Attachment of the aldehyde to the metal center is believed to take place next to generate species (**iv**), which is followed by insertion of the aldehyde substrate into the Ru–H bond to generate the corresponding aryloxo species (**v**). In the final step, elimination of the product alcohol takes place with simultaneous regeneration of the active catalyst (**ii**). In the light of the proposed mechanism, the negligible yield observed for the hydrogenation of pyrrole-2-aldehyde, pyridine-2-aldehyde and 2-hydroxynaphthaldehyde (entries 9-12) is probably due to catalyst deactivation through the coordination of these substrates, their potential to form chelates being well known. The absence of any catalysis for hydrogenation of ketones is attributable to the steric inhibition involved in the formation of species of type (**iv**). Though catalytic transfer-hydrogenation with [Ru(*p*-cymene)(L-L′)Cl] type complexes as pre-catalyst is precedent in the literature [31-42], the observed catalytic efficiency of the present group of [Ru(*p*-cymene)(L-R)Cl] complexes is remarkable, with particular reference to very low catalyst loading, high yield, very large turn-over number (~ 10^7), and low reaction time.

4. Conclusion

The present study shows that the 2-(arylazo)phenols (HL-R) undergo facile reaction with [{Ru(*p*-cymene)Cl_2}$_2$] in the presence of triethylamine to afford mixed-ligand complexes of type [Ru(*p*-cymene)(L-R)Cl]. This study also demonstrates that these [Ru(*p*-cymene)(L-R)Cl] complexes serve as excellent precursor for catalytic transfer-hydrogenation of aldehydes.

Acknowledgments

The authors thank the reviewers for their constructive comments, which have been very helpful in preparing the revised manuscript. Financial assistance received from the UGC-CAS program and the DST-PURSE program of the Department of Chemistry, Jadavpur University, Kolkata 700032, is gratefully acknowledged. J. K. thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, for a fellowship [grant number 09/096(0842)/2015-EMR-I]. The authors thank Prof. Saurabh Das (Department of Chemistry, Jadavpur University) for his help in recording the electronic spectra.

Appendix A. Supplementary data

CCDC 1889794 contains the supplementary crystallographic data for [Ru(*p*-cymene)(L-R)Cl]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at doi:----------.

References and footnotes

References

[1] E. Carmona, M. Paneque, L.L. Santos, V. Salazar, Coord. Chem. Rev. 249 (2005) 1729.

[2] J. Liu, X. Wu, J.A. Iggo, J. Xiao, Coord. Chem. Rev. 252 (2008) 782.

[3] T.L. Church, P.G. Andersson, Coord. Chem. Rev. 252 (2008) 513.

[4] R. Malacea, R. Poli, E. Manoury, Coord. Chem. Rev. 254 (2010) 729.

[5] S. Fantacci, F.D. Angelis, Coord. Chem. Rev. 255 (2011) 2704.

[6] N.G. Leonard, P.G. Williard, W.H. Bernskoetter, Dalton Trans. 40 (2011) 4300.

[7] F. Basuli, S.M. Peng, S. Bhattacharya, Polyhedron 18 (1999) 391.

[8] K. Sui, S.M. Peng, S. Bhattacharya, Polyhedron 19 (1999) 631.

[9] R.K. Rath, M. Nethaji, A.R. Chakravarty, J. Organomet. Chem. 633 (2001) 79.

[10] P. Gupta, S. Dutta, F. Basuli, S.M. Peng, G.H. Lee, S. Bhattacharya, Inorg. Chem. 45 (2006) 460.

[11] B.K. Dey, J. Dutta, M.G.B. Drew, S. Bhattacharya, J. Organomet. Chem. 750 (2014) 176.

[12] J. Dutta, M.G. Richmond, S. Bhattacharya, Eur. J. Inorg. Chem. (2014) 4600.

[13] P. Dhibar, P. Paul, S. Bhattacharya, J. Indian Chem. Soc. 93 (2016) 781.

[14] A. Mukherjee, P. Paul, S. Bhattacharya, J. Organomet. Chem. 834 (2017) 47.

[15] R. Kumar, P. Paul, S. Bhattacharya, J. Indian Chem. Soc. 95 (2018) 721.

[16] A. Mukherjee, D.A. Hrovat, M.G. Richmond, S. Bhattacharya, Dalton Trans. 47 (2018) 10264.

[17] R.M. Moriarty, U.S. Gill, Y.Y. Ku, J. Organomet. Chem. 350 (1988) 157.

[18] H. Le Bozec, D. Touchard, P.H. Dixneuf, Adv. Organomet. Chem. 29 (1989) 163.

[19] C. Ganter, Chem. Soc. Rev. 32 (2003) 130.

[20] P. Kumar, R.K. Gupta, D.S. Pandey, Chem. Soc. Rev. 43 (2014) 707.

[21] M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith, Inorganic Syntheses. 21 (1982) 74.

[22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida,

T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision E.01, Gaussian, Inc., Wallingford CT, (2009).

[23] G.M. Sheldrick, SHELXS-97 and SHELXL-97, Fortran programs for crystal structure solution and refinement, University of Göttingen: Göttingen, Germany, (1997).

[24] G.M. Sheldrick, Acta Crystallogr. Sect. A 64 (2008) 112.

[25] S.E. Clapham, A. Hadzovic, R.H. Morris, Coord. Chem. Rev. 248 (2004) 2201.

[26] R. Malacea, R. Poli, E. Manoury, Coord. Chem. Rev. 254 (2010) 729.

[27] D.K. Dutta, B. Deb, Coord. Chem. Rev. 255 (2011) 1686.

[28] D.A. Hey, R.M. Reich, W. Baratta, F.E. Kühn, Coord. Chem. Rev. 374 (2018) 114.

[29] R.F. Winter, F. M. Hornung, Inorg. Chem. 36 (1997) 6197.

[30] J.L. Pratihar, S. Bhaduri, P. Pattanayak, D. Patra, S. Chattopadhyay, J. Organomet. Chem. 694 (2009) 3401.

[31] W.N.O. Wylie, A.J. Lough, R.H. Morris, Organometallics 30 (2011) 1236.

[32] L.J. Hounjet, M.J. Ferguson, M. Cowie, Organometallics 30 (2011) 4108.

[33] I. Nieto, M.S. Livings, J.B. Sacci, L.E. Reuther, M. Zeller, E.T. Papish, Organometallics 30 (2011) 6339.

[34] W.B. Cross, C.G. Daly, Y. Boutadla, K. Singh, Dalton Trans. 40 (2011) 9722.

[35] F.E. Fernández, M.C. Puerta, P. Valerga, Organometallics 31 (2012) 6868.

[36] H. Ohara, W.N.O. Wylie, A. J. Lough, R. H. Morris, Dalton Trans. 41 (2012) 8797.

[37] M. Kumar, J. DePasquale, N.J. White, M. Zeller, E.T. Papish, Organometallics 32 (2013) 2135.

[38] H.S. Calik, E. Ispir, S. Karabuga, M. Aslantas, J. Organomet. Chem. 801 (2016) 122.

[39] M. Hollering, M. Albrecht, F.E. Kuhn, Organometallics 35 (2016) 2980.

[40] S. Denizaltı, B. Sen, A.G. Gokce, B. Cetinkaya, Appl. Organomet. Chem. 30 (2016) 373.

[41] L.S. Zheng, P. Phansavath, V.R. Vidal, Org. Lett. 20 (2018) 5107.

[42] S. Bauri, S. N. R. Donthireddy, P. M. Illam, A. Rit, Inorg. Chem. 57 (2018) 14582.

[43] J.J. Levison, S.D. Robinson, J. Chem. Soc. A (1970) 2947.

[44] R. Young, G. Wilkinson, Inorg. Synth. 17 (1977) 79.

[45] C. S. Yi, S. Y. Yun, I. A. Guzei, Organometallics 23 (2004) 5392.

[46] T. Li, R. Churlaud, A.J. Lough, K. Abdur-Rashid, R.H. Morris, Organometallics 23 (2004) 6239.

[47] R. Celenligil-Cetin, L. A. Watson, C. Guo, B. M. Foxman, O. V. Ozerov, Organometallics 24 (2005) 186.

Footnotes

1 The mmol calculation was been done taking [{Ru(*p*-cymene)Cl_2}$_2$] as the molecular formula.

2 Chemical shifts for all NMR data are given in ppm and the multiplicity of the signals, along with the associated coupling constant, is given in parentheses. Overlapping signals are marked with an asterisk (*).

3 Bond parameters around the azo (-N=N-) fragment, which had disorder problem, are found to be bit different than usual values.

****

Table 1

Crystal data and structure refinement parameters for [Ru(*p*-cymene)(L-CH_3)Cl].

Empirical formula	$C_{24}H_{27}N_2O_1Cl_1Ru$
Formula weight	496.00
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	12.7479 (8)
b (Å)	13.6907 (9)
c (Å)	13.0168 (9)
α (º)	90.00
β (º)	100.075 (4)
γ (º)	90.00
V (Å^3)	2236.8 (3)
Z	4
D_{calcd} (mg/m^3)	1.473
F(000)	1016
Crystal size (mm)	0.12 × 0.16 × 0.24
T (K)	296
μ (mm^{-1})	0.837
Collected reflections	31557
R_{int}	0.074
Independent reflections	5122
R_1[a]	0.0481
wR_2[b]	0.2059
GOF[c]	0.75

[a] $R_1 = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$

[b] $wR_2 = [\ \Sigma[\ w(F_o^2 - F_c^2)^2] / \Sigma\ [w(F_o^2)^2]\ ]^{1/2}$

[c] GOF = $[\Sigma[w(F_o^2-F_c^2)^2]/(M-N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

Table 2

Selected bond distances and bond angels for [Ru(*p*-cymene)(L-CH_3)Cl].

Bond distances (Å)			
Ru1-Cl1	2.4101(14)	C1-O1	1.310(7)
Ru1-O1	2.039(4)	C2-N1	1.389(8)
Ru1-N1	2.130(6)	N1-N2	1.306(11)
		N2-C8	1.427(12)
Bond angles (°)			
Cl1-Ru1-O1	84.57(12)	O1-Ru1-N1	74.0(2)
Cl1-Ru1-N1	84.55(16)		

Table 3

Electronic spectral and cyclic voltammetric data.

Complex	Electronic spectral data[a] λ_{max}, nm (ε, M^{-1} cm^{-1})	Cyclic voltammetric data[b] E, V *vs*. SCE
[Ru(*p*-cymene)(L-CH_3)Cl]	547 (2700), 388 (5000), 323 (8300)	1.11[c], 1.36[c]
[Ru(*p*-cymene)(L-H)Cl]	546 (2700), 388 (4900), 316 (10000)	1.12[c], 1.38[c]
[Ru(*p*-cymene)(L-Cl)Cl]	557 (2200), 384 (3900), 321 (7400)	1.14[c], 1.40[c]

[a] In methanol.

[b] Solvent, acetonitrile; supporting electrolyte, TBHP; scan rate, 50 mVs^{-1}.

[c] E_{pa} (anodic peak potential) value.

Table 4

Main calculated transitions for [Ru(*p*-cymene)(L-CH_3)Cl] with composition in terms of molecular orbital contribution of the transition, excitation energies, and oscillator strength in methanol.

Transi-tion No.	Nature of transition	CI	E (eV)	Oscillator strength (*f*)	λ_{theo} (nm) (λ_{exp}(nm))	Assignments
1	H-3 → L H-1 → L H → L H → L+2	-0.14270 -0.16198 0.62242 -0.15597	2.5706	0.0038	518.32 (547)	MLCT/LLCT/ILCT MLCT/LLCT/ILCT MLCT/ILCT LMCT/LLCT/MLCT
2	H-3 → L H-3 → L+1 H-2 → L+1 H-1 → L H-1 → L+1	-0.27939 -0.18172 -0.16122 0.44296 0.29659	3.1674	0.0048	391.44 (388)	MLCT/LLCT/ILCT LMCT/MLCT/LLCT LMCT/MLCT/LLCT MLCT/ILCT MLCT/LMCT/LLCT
3	H-5 → L H-3 → L H-2 → L H-1 → L H-1 → L+1 H → L+2	0.10854 0.34398 -0.28828 -0.17738 0.43232 -0.13053	3.7349	0.0256	331.96 (323)	LLCT/ILCT MLCT/LLCT/ILCT MLCT/LLCT/ILCT MLCT/ILCT MLCT/LMCT/LLCT LMCT/LLCT/MLCT

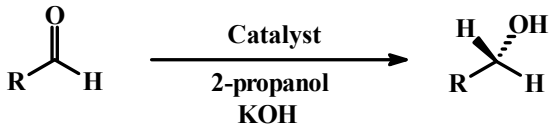
Table 5

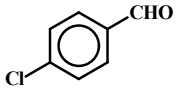
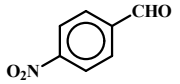
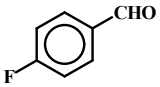
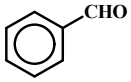
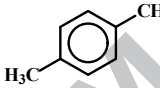
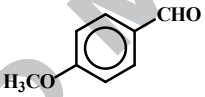
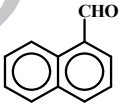
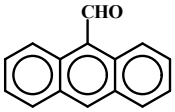
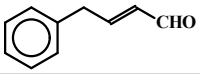
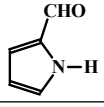
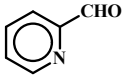
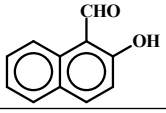
Compositions of selected molecular orbitals of [Ru(*p*-cymene)(L-CH_3)Cl].

Fragments	Contribution (%) of fragments to						
	H-3	H-2	H-1	HOMO (H)	LUMO (L)	L+1	L+2
Ru	25	30	44	13	5	52	53
L-CH_3	54	50	24	81	89	12	17
p-cymene	5	8	16	4	4	26	29
Cl	16	12	16	2	2	10	0

Table 6

Catalytic transfer-hydrogenation of aldehydes.[a]



Entry	Substrate	Yield[b] (%)
1		97
2		96
3		98
4		93
5		94
6		95
7		94
8		95
9		91
10		0
11		2
12		2

[a] Reaction conditions: aldehyde (1.0 mmol), KOH (0.5 mmol), 2-propanol (5 ml), catalyst: [Ru(*p*-cymene)(L-CH_3)Cl] (0.00001 mol%), bath temperature (100º C), time (30 min).

[b] Determined by GC-MS.

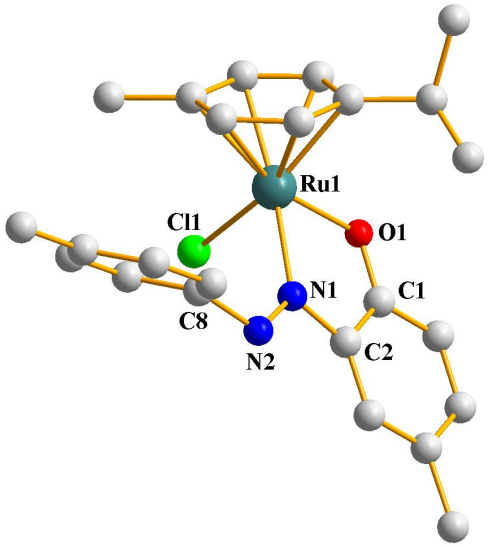


Fig. 1. Crystal structure of [Ru(*p*-cymene)(L-CH_3)Cl] (hydrogen atoms are omitted for clarity).

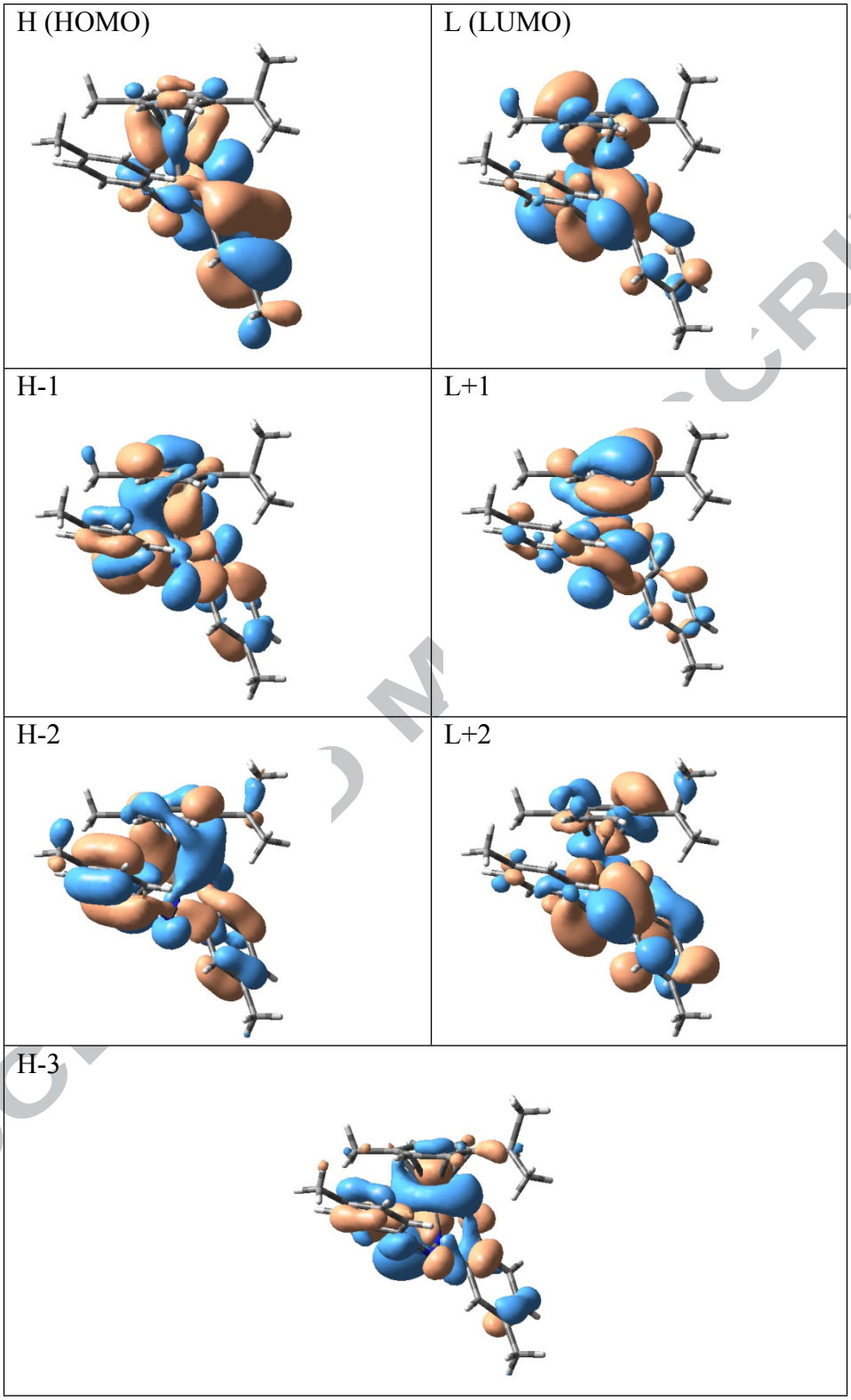
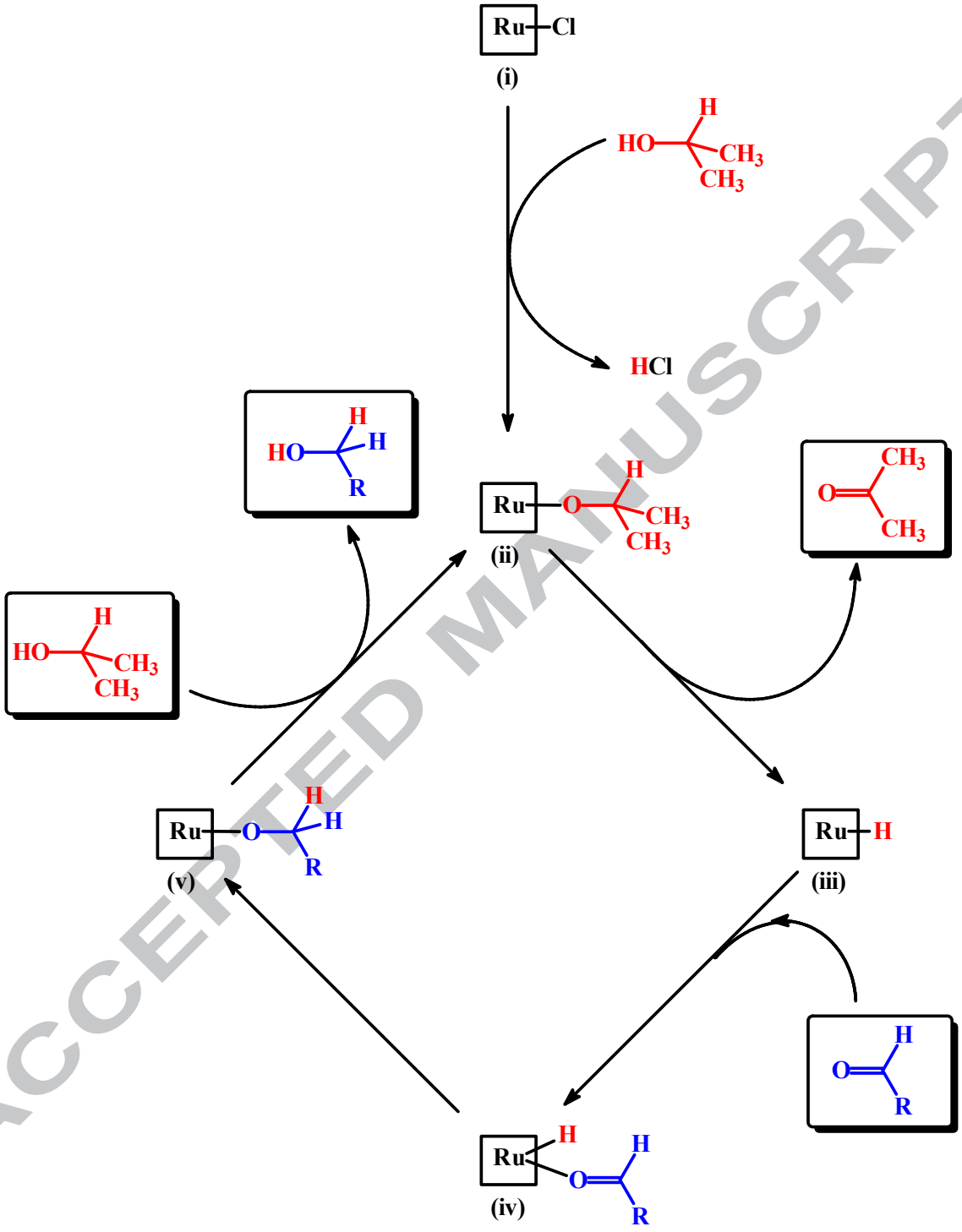


Fig. 2. Contour plots of molecular orbitals of [Ru(*p*-cymene)(L-CH_3)Cl], which are associated with the observed electronic spectral transitions.



Scheme 1. Probable mechanism for the observed transfer hydrogenation reaction. In the pre-catalyst (**i**), besides the Ru-Cl fragment no other coordinated ligand is shown.

Manuscript title: Arene-ruthenium complexes with 2-(arylazo)phenol as ancillary ligand: Synthesis, characterization, and utilization in catalytic transfer-hydrogenation

Authors: Jit Karmakar, Samaresh Bhattacharya*

Graphical Abstract

Synopsis

Reaction of 2-(arylazo)phenols (**HL-R**) with [{Ru(*p*-cymene)Cl_2}$_2$] in the presence of triethylamine afforded a group of complexes of type [Ru(*p*-cymene)(L-R)Cl], which are found to efficiently catalyze transfer-hydrogenation of aldehydes.

Manuscript title: Arene-ruthenium complexes with 2-(arylazo)phenol as ancillary ligand: Synthesis, characterization, and utilization in catalytic transfer-hydrogenation

Authors: Jit Karmakar, Samaresh Bhattacharya*

Graphical Abstract

Picture