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Synthesis, structural characterization and catalytic transfer hydrogenation of ruthenium(II) carbonyl complexes bearing N,N,O pincer type benzoylhydrazone ligands

Pandimuni Kalpaga Suganthy,^a Rupesh Narayana Prabhu,^b Venugopal Shanmugham Sridevi^{a,*}

^a Department of Chemistry, Periyar E.V.R. College, Tiruchirappalli 620 023, Tamil Nadu, India

^b School of Chemistry, University of Hyderabad, Hyderabad 500 046, Telangana, India

* Corresponding author. Tel.: +91–431–242–0079; fax: +91–431–2332010; e-mail: sridevi.evr@gmail.com (V.S. Sridevi)

Abstract

The convenient synthesis of four new octahedral ruthenium(II) carbonyl benzoylhydrazone complexes of the general molecular formula $[Ru(L)Cl(CO)(PPh_3)]$ (where HL = substituted 2–acetylpyridine benzoylhydrazones; the H represents the dissociable proton) has been described. The characterization of the complexes was accomplished by spectroscopic (FT-IR, ¹H NMR, UV-Vis) techniques as well as by elemental (C,H,N) analysis. A single crystal X-ray diffraction study of a representative complex, $[Ru(L1)Cl(CO)(PPh_3)]$ (1), confirms a pincer-like N,N,O coordination mode of the benzoylhydrazone ligand via the pyridine N, the azomethine N and the deprotonated amide O atoms, with the formation of two five-membered fused chelate rings, and indicates a distorted octahedral geometry around the ruthenium(II) centre. Further, the catalytic efficiency of complex **1** has been investigated for the transfer hydrogenation of substituted acetophenones to the corresponding secondary alcohols. The influence of base and catalyst loading in the transfer hydrogenation reaction was also evaluated. The complexes were found to be efficient catalysts in the presence of *iso*-propanol/KOH with conversions up to 99.2%.

Keywords: Benzoylhydrazone ligands, Pincer-type, Ru(II) carbonyl complexes, Crystal, Catalysis, Transfer hydrogenation of ketones

1. Introduction

The interest in ruthenium complexes bearing Schiff bases remains unwavering due to their multi-electron transfer properties, ability to have a wide range of oxidation states and potential catalytic activity [1-6]. Aroylhydrazones are Schiff bases that have synthetic flexibility, exhibit amide-imidol tautomerism, have a large number of potential donor atoms and hence display versatility in metal coordination. They coordinate to a metal ion through the imine nitrogen atom of the hydrazone moiety and the protonated/deprotonated amide oxygen atom [3,4,7]. The binding capacity of the Schiff base is further increased by having an additional donor atom (usually N or O) in a suitable position for chelation, normally resulting in tricoordination [3,7-11]. The mode of coordination depends on the nature of the central metal atom, the type of ligand as well as on the presence of other species capable of competing for coordination sites.

Transfer hydrogenation is a convenient and versatile method for the reduction of carbonyl compounds to their corresponding alcohols and is safe, highly selective, environmentally friendly and requires inexpensive reagents or mild conditions for the preparation of a broad scope of alcohols [12-14]. 2-Propanol is the most commonly used solvent and hydrogen source since it is easy to handle, inexpensive, relatively non-toxic and environmentally benign. Among the various metal complexes employed for transfer hydrogenation reactions, ruthenium complexes have a long pedigree as catalysts for homogeneous transfer hydrogenation reactions [15,16]. Ruthenium complexes containing cyclometallated and N-heterocyclic carbene ligands [17,18], pincer ligands [19,20], Schiff base ligands [3,21,22], tripodal ligands [23,24], arene ligands [25,26] and phosphine- or amine-based ligands [27,28] have been extensively investigated and well established as homogeneous catalysts for this transformation. Many reviews have appeared on the scope and versatility of ruthenium catalyzed hydrogen transfer reactions, giving emphasis to the design and nature of the coordinated ligands, reaction conditions (such as solvents, hydrogen donors, bases, additives, temperature), kinetic studies and mechanistic aspects [13-16,28-34]. Though a few Ru(II) complexes with tridentate N,N,O-donor aroylhydrazones have been structurally characterized [8-10], to the best of our knowledge there is no report on the structural characterization of a carbonyl Ru(II) complex containing a tridentate N,N,O-donor aroylhydrazone and its use as a catalyst for transfer hydrogenation reactions.

As a part of our ongoing research on the synthesis, characterization and catalytic applications of transition metal complexes [35,36], the present report accounts for the

synthesis and characterization of four new octahedral Ru(II) carbonyl complexes with pincerlike substituted 2-acetylpyridine benzoylhydrazones, with chloride and triphenylphosphine incorporated as ancillary ligands. The structure of a representative complex has been probed with the help of single crystal X-ray diffraction analysis and to the best of our knowledge this is the first example of a structurally characterized Ru(II) carbonyl complex incorporating a monoanionic tridentate N,N,O donor benzoylhydrazone ligand. Further, the catalytic efficiency of the complex has been investigated for the transfer hydrogenation of acetophenones containing different electronic effects to the corresponding secondary alcohols under optimized conditions of base and catalyst loading.

2. Experimental section

2.1 Materials

RuCl₃·3H₂O was purchased from Loba Chemie Pvt. Ltd and used as received. Triphenylphosphine, 2-acetylpyridine, benzoylhydrazide derivatives and the ketones used for the catalysis were obtained from Sigma-Aldrich and were used without further purification. The solvents were freshly distilled prior to use following standard procedures [37]. All other reagents used were purchased from commercially available sources and used as supplied. The 2-acetylpyridine benzoylhydrazones (HL1-HL4) were prepared by the condensation of 2acetylpyridine and 4-substituted benzoylhydrazide by following a procedure reported earlier [38]. The purity and identities of all the benzoylhydrazones were authenticated by FT-IR and ¹H NMR measurements. [RuHCl(CO)(PPh₃)₃] was prepared by the reported literature method [39].

2.2 Physical measurements and instrumentation

The microanalyses (C,H,N) were recorded by an analytic function testing Vario EL III CHN elemental analyzer. Infrared spectra were recorded in KBr pellets with a Perkin-Elmer 597 spectrophotometer in the range 4000-400 cm⁻¹. The ¹H NMR spectra were recorded with a Bruker 400 MHz spectrometer. Chemical shifts, given in ppm, are referenced to the deuterated solvents. Electronic spectra of the complexes in chloroform solution were recorded with a Cary 300 Bio UV-Vis Varian spectrophotometer in the range 800-230 nm using cuvettes of 1 cm pathlength. Organic compounds in the catalysis were identified by GC-MS using a Shimadzu Japan QP2010 S spectrometer using an RTX–5 MS detector

equipped with a capillary column (30 m x 0.25 mm x 0.25 μ m) and high purity helium as the carrier gas.

2.3 Synthesis of $[Ru(L1)Cl(CO)(PPh_3)]$ (1)

[RuHCl(CO)(PPh₃)₃] (95 mg, 0.1 mmol) and Et₃N (0.5 mL) were added to a benzene solution (20 mL) of HL1 (24 mg, 0.1 mmol). The reaction mixture was refluxed for 6 h under an atmosphere of nitrogen and the progress of the reaction was monitored using TLC. At the end of the reaction, the solution was concentrated to *ca*. 3 mL and *n*-hexane was added, whereby a solid separated out. This material was collected by filtration and transferred to a silica gel column packed with *n*-hexane. The first moving yellow band eluted with ethyl acetate/*n*-hexane (1:9) was discarded. The following red band containing complex **1** was eluted using methanol/chloroform (1:4). The red solution thus obtained was evaporated to dryness and the complex was collected as a dark red solid (Scheme 1). Yield: 52 mg (78%). Anal. Calc. for $C_{33}H_{27}ClN_3O_2PRu$ (665.08 g mol⁻¹): C, 59.59; H, 4.09; N, 6.32. Found: C, 59.65; H, 4.12; N, 6.37 %. Selected IR bands (KBr, cm⁻¹): 1595 s v_(C=N-N=C), 1241 m v_(C-O), 1946 s v_(C=O). ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 8.2-7.2 (m, 24H, aromatic), 2.7 (s, 3H, CH₃). UV-Vis (CHCl₃, λ_{max}/nm ; ε/dm^3 mol⁻¹ cm⁻¹): 420 (4,070), 315 (8,180), 243 (15,010).

Insert Scheme 1 here

2.4 Synthesis of $[Ru(L2)Cl(CO)(PPh_3)]$ (2)

This complex was synthesized by following the same procedure as described above for **1**, but using HL2 instead of HL1. Colour: Red. Yield: 51 mg (73%). Anal. Calc. for $C_{33}H_{26}Cl_2N_3O_2PRu$ (699.53 g mol⁻¹): C, 56.66; H, 3.75; N, 6.01. Found: C, 56.75; H, 3.80; N, 5.95 %. Selected IR bands (KBr, cm⁻¹): 1591 s $v_{(C=N-N=C)}$, 1259 s $v_{(C=O)}$, 1942 s $v_{(C=O)}$. ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 8.2-7.2 (m, 23H, aromatic), 2.7 (s, 3H, CH₃). UV-Vis (CHCl₃, λ_{max}/nm ; ϵ/dm^3 mol⁻¹ cm⁻¹): 424 (4,010), 310 (10,230), 247 (14,890).

2.5 Synthesis of $[Ru(L3)Cl(CO)(PPh_3)]$ (3)

The procedure used for the synthesis of **3** was identical to that described for **1**, except for the use of HL3 instead of HL1. Colour: Red. Yield: 54 mg (71%). Anal. Calc. for $C_{33}H_{26}BrClN_3O_2PRu$ (743.98 g mol⁻¹): C, 53.27; H, 3.52; N, 5.65. Found: C, 54.75; H, 3.80; N, 5.95 %. Selected IR bands (KBr, cm⁻¹): 1591 s $v_{(C=N-N=C)}$, 1259 s $v_{(C-O)}$, 1942 s $v_{(C=O)}$. ¹H

NMR (400 MHz, DMSO-d₆, δ ppm): 8.3-7.2 (m, 23H, aromatic), 2.8 (s, 3H, CH₃). UV-Vis (CHCl₃, λ_{max} /nm; ϵ /dm³ mol⁻¹ cm⁻¹): 429 (4,080), 319 (10,260), 242 (14,820).

2.6 Synthesis of $[Ru(L4)Cl(CO)(PPh_3)]$ (4)

Complex **4** was synthesized in 70% yield by following the same procedure as described above for **1**, but using HL4 instead of HL1. Colour: Red. Anal. Calc. for $C_{34}H_{29}CIN_3O_3PRu$ (695.11 g mol⁻¹): C, 58.75; H, 4.21; N, 6.05. Found: C, 58.68; H, 4.15; N, 5.93 %. Selected IR bands (KBr, cm⁻¹): 1594 s $v_{(C=N-N=C)}$, 1245 s $v_{(C-O)}$, 1944 s $v_{(C=O)}$. ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 8.2-7.1 (m, 23H, aromatic), 3.8 (s, 3H, OCH₃), 2.8 (s, 3H, CH₃). UV-Vis (CHCl₃, λ_{max}/nm ; ϵ/dm^3 mol⁻¹ cm⁻¹): 421 (4,110), 314 (9,290), 240 (14,680).

2.7 X-ray crystallography

Single crystals of $[Ru(L1)Cl(CO)(PPh_3)]\cdot H_2O$ (1·H₂O) suitable for X-ray diffraction analysis were obtained by slow evaporation of an ethanol solution of the complex at room temperature. The data collection was carried out using a Bruker AXS Kappa APEX II single crystal X-ray diffractometer using monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å). The absorption corrections were performed by the multi-scan method using SADABS software [40]. Corrections were made for Lorentz and polarization effects. The structure was solved by SIR92 [41] and refined by full-matrix least squares on F² using SHELXL 97 [42]. All nonhydrogen atoms were refined anisotropically and the hydrogen atoms in these structures were located from the difference Fourier map and constrained to ideal positions in the refinement procedure. The unit cell parameters were determined by the method of difference vectors using reflections scanned from three different zones of the reciprocal lattice. The intensity data were measured using ω and φ scans with a frame width of 0.5°. Frame integration and data reduction were performed using the Bruker SAINT-Plus (Version 7.06a) software [43]. The crystal and structure refinement data of complex **1** are given in Table 1.

Insert Table 1 here

2.8 Typical procedure for transfer hydrogenation of ketones

The ketone (2.5 mmol), catalyst (5 μ mol), base (20 μ mol) and *i*-PrOH (5 mL) were placed in an oven-dried round bottom flask at room temperature. The reaction mixture was

heated under reflux for the required reaction time under an atmosphere of nitrogen. The reaction was then cooled to room temperature and the catalyst precipitated from the reaction mixture by the addition of diethyl ether. The organic layer was neutralized with 1 N HCl, washed with water and dried over anhydrous Na₂SO₄. The combined organic layer was passed through a short path of silica gel and then subjected to GC–MS analysis. The conversions obtained are related to the residual unreacted ketone and are averages of two runs in the case of all catalytic reactions.

3. Results and Discussion

3.1 Synthesis and some properties

[RuHCl(CO)(PPh₃)₃] was allowed to react with the substituted 2-acetylpyridine benzoylhydrazones (HL) in an equimolar ratio in the presence of triethylamine as a base, resulting in the formation of new neutral complexes of the general formula [Ru(L)Cl(CO)(PPh₃)] in reasonably good yields (Scheme 1). Structural studies of the complexes showed that the ligands behave as mono anionic tridentate donors, replacing one hydride and two PPh₃ ligands from the ruthenium(II) precursor. Further, the oxidation state of ruthenium remains unchanged during the formation of the complex. The analytical data of all the ruthenium(II) complexes are in good agreement with the stoichiometries concluded from their elemental analysis data. All the complexes are red in colour, found to be non-hygroscopic and air stable in solution and in the solid state at room temperature. They are highly soluble in solvents such as benzene, toluene, chloroform, dichloromethane, acetonitrile, methanol, dimethylformamide, dimethyl sulfoxide etc., producing intense red coloured solutions.

3.2 Spectroscopic characteristics

3.2.1 IR spectroscopy

The selected infrared absorption bands for all the complexes are given in the experimental section. The IR spectra of the free Schiff bases (HL1-HL4) showed a medium to strong band in the regions 3176-3195 cm⁻¹ which is characteristic of the N–H functional group. The free ligands also display $v_{C=N}$ and $v_{C=O}$ absorptions in the region 1632-1650 cm⁻¹. The IR spectra of the complexes did not display any bands due to v_{N-H} and $v_{C=O}$ stretching vibrations, suggesting that the Schiff bases undergo tautomerization and subsequent coordination of the imidolate oxygen to the ruthenium(II) ion. This is further supported by

the appearance of new stretching frequencies in the regions 1241-1259 and 1591-1599 cm⁻¹ in the complexes, which may be attributed to the C–O and C=N–N=C fragments respectively of the coordinated ligand [3,4,8-10,44]. The typical strong band for the terminally coordinated carbonyl group in **1-4** is observed in the range 1940-1948 cm⁻¹ [3-5]. In addition, three strong bands displayed by all the complexes at ~520, ~695 and ~745 cm⁻¹ are attributed to the metal coordinated PPh₃ ligand [3,6,8-11,24,44].

3.2.2 NMR spectroscopy

Further, to confirm the coordination of the benzoylhydrazone ligands to the Ru(II) ion, the ¹H NMR spectra of the complexes were compared to the spectra of the free Schiff bases. A sharp singlet that appeared for the –NH proton of free HL (δ 12.0-11.7 ppm) is absent in all the complexes, supporting enolisation and coordination of the imidolate oxygen atom to the ruthenium(II) ion [3,4]. The signal due to the azomethine methyl group appears as a sharp singlet in the complexes (δ 2.9-2.8 ppm) and is slightly downfield in comparison with those of free HL (δ 2.4-2.3 ppm), suggesting deshielding of these methyl protons due to the coordination of the azomethine nitrogen atom to the metal centre. In addition, for complex **4**, the methoxy signal of the benzoylhydrazone ring resonates as a singlet at δ 3.8 ppm [3,4,8]. The remaining aromatic protons of the coordinated benzoylhydrazone ligand and PPh₃ appear as multiplets in the region δ 8.3-7.1 ppm.

3.2.3 Absorption spectroscopy

The absorption spectra of 1-4 were recorded in chloroform solution in the range 230-800 nm at room temperature. The spectral profiles of the complexes are comparable, except for some small shifts in the band positions. They display three intense absorptions in the wavelength range 240-429 nm. The high intensity bands in the region 240-319 nm region were assignable to ligand-centered (LC) transitions and have been designated as π - π * and n- π * transitions. In the visible region, the major feature displayed by these complexes is a band ~425 nm which was attributed to metal-to-ligand-charge-transfer (MLCT) transitions. Based on the pattern of the electronic spectra of all the complexes, an octahedral environment around the ruthenium(II) ion has been proposed, similar to that for other octahedral ruthenium(II) complexes [3-5,8,9].

3.3. X-ray molecular structure of 1

Attempts to grow single crystals of all the complexes (1-4) were made to confirm the coordination modes of the benzoylhydrazone ligands towards ruthenium(II) and the overall coordination geometry in these complexes by X-ray crystallography. However, only X-ray quality single crystals of complex 1 as a solvate $(1 \cdot H_2O)$ could be obtained. The ORTEP view of $1 \cdot H_2O$ is shown in Fig.1. The selected bond parameters involving the metal centre are listed in Table 2. As seen from the ORTEP diagram, the benzoylhydrazone ligand coordinates meridionally to the Ru(II) ion in a tridentate manner via the pyridine N, azomethine N and deprotonated amide O atoms in the benzoylhydrazone fragment, forming two five membered fused chelate rings. The carbonyl C atom occupies the fourth equatorial coordination site and forms a CN₂O square plane (basal plane). One chloride ion and the phosphine atom of a PPh₃ ligand occupy the two axial sites. The ruthenium ion is therefore sitting in a CN₂OCIP coordination environment and has a distorted octahedral geometry, as reflected from the bond parameters around the Ru(II) ion. The N-N, N-C and C-O bond lengths in the $=N-N=C(O^{-})-$ fragment of the coordinated ligand are consistent with the enolate form of the amide functionality [3,4,9,10]. The phenyl ring of the coordinated ligand is twisted from the basal plane, resulting in a dihedral angle of 21.25°. Around the Ru(II) ion, the chelate bite angle in the five membered ring formed by the azomethine N and deprotonated amide O atoms (76.19°) is slightly smaller than that in the five membered ring formed by the azomethine N and the pyridine N atoms (78.77°), indicating better chelation in the former ring [9,10]. The Ru–N(pyridine) bond length of 2.068(3) Å is slightly longer than the Ru–N(azomethine) bond length (2.023(3) Å). Most likely this difference could be due to the rigidity of the tridentate ligand and due to better π -back-bonding in the Ru-N(azomethine) bond compared to that in the Ru–N(pyridine) bond [9,10]. The other bond angles (°) around the Ru(II) ion are N3–Ru–O1 = 154.90(12), N1–Ru–C19 = 175.28(13) and P-Ru-Cl = 173.35(3), whereas the bond lengths (Å) are 1.882(4) for Ru-C19, 2.105(2) for Ru–O1, 2.4528(10) for Ru–Cl and 2.3046(10) for Ru–P. The bond lengths and bond angles are in good agreement with reported data on other octahedral Ru(II) benzoylhydrazone complexes [3,4,8,9]. Since the spectral properties of all the four complexes are similar, analogous molecular structures are assumed for the other three complexes.

Insert Fig. 1 here

Insert Table 2 here

3.4 Catalytic transfer hydrogenation reaction

In a transfer hydrogenation reaction hydrogen is transferred from one organic molecule to another, and it is of great importance as it has become an efficient tool in organic synthesis. A wide range of ruthenium complexes have used as effective homogeneous catalysts for transfer hydrogenation reactions and this encouraged us to carry out this type of reaction with the new ruthenium(II) benzoylhydrazone complexes.

3.4.1 Effect of bases

One of the complexes, **1**, was taken as a model catalyst and the conversion of acetophenone (as the substrate) to 1-phenylethanol using *iso*-PrOH as the solvent in the presence of different bases was initially screened (Table 3). The conversion was found to be strongly dependent on the base employed. In presence of a strong base like KOH, the conversion was high after 4 h. When weak bases such as Na₂CO₃, CH₃COONa or Et₃N were used, the conversion of the product was reduced drastically, even with longer timescales. Also, controlled experiments indicated that no conversion was observed in the absence of the base or catalyst even after longer reaction times. In addition, when RuCl₃·H₂O, the Ru(II) precursor or benzoylhydrazone ligands alone or as a mixture were used, no conversion was observed, ascertaining the necessity of the Ru(II) benzoylhydrazone complex for this reaction. From the above results it is observed that a reasonably good conversion can be achieved in the transfer hydrogenation of acetophenone by using *i*-PrOH/KOH at 82 °C.

Insert Table 3 here

3.4.2 Effect of catalyst loading

To ascertain the catalytic efficiency of the complex, different catalyst:substrate (C:S) ratios were tested in the transfer hydrogenation reaction of acetophenone using complex **1** as a model catalyst with *i*-PrOH/KOH and the results are summarized in Table 4. It is observed that the formation of 1-phenylethanol is excellent when a C:S ratio of 1:250 is used. Also, the reaction still proceeds smoothly but is accompanied by a drop in the conversion upon changing the C:S ratio to 1:500, 1:750 or 1:1000. Since the conversions are good with

appreciable turnover numbers (TON) when the C:S ratio is 1:500, it was concluded that this C:S ratio is the most suitable for the catalytic transfer hydrogenation reaction.

Insert Table 4 here

3.4.3 Transfer hydrogenation of ketones

In light of the results obtained, the transfer hydrogenation reactions of a series of substituted acetophenones were carried out with complex **1** as the model catalyst, using *i*-PrOH/KOH, and the results are summarized in Table 5. For a comparison of the results, all the reactions were carried out under identical conditions. The complex catalyzes the transfer hydrogenation of various acetophenones to their corresponding alcohols with good to excellent conversions in all cases. It was observed that the conversion is dependent on the substituent present on the acetophenone ring. The presence of an electron-withdrawing substituent (nitro, cyano or chloro) on the aryl ring gave higher conversions (entries 1-3) when compared to that of acetophenone (entry 4), whereas presence of an electron-donating substituent (methyl, methoxy or hydroxy) on the ring (entries 5-7) decreased the conversion. In terms of the TON/TOF, the catalytic efficiency of the new ruthenium(II) complexes is higher than that of other ruthenium(II) complexes [23,24,26,27,45].

Insert Table 5 here

4. Conclusions

The reactions of substituted 2-acetylpyridine benzoylhydrazone ligands with $[RuHCl(CO)(PPh_3)_3]$ resulted in the formation of new octahedral ruthenium(II) carbonyl benzoylhydrazone complexes of the general formula $[Ru(L)Cl(CO)(PPh_3)]$ (where HL = the substituted 2-acetylpyridine benzoylhydrazone ligand). The characterization of the complexes was accomplished by analytical and spectral (FT-IR, ¹H NMR, UV-Vis) methods. The coordination of the benzoylhydrazone ligand *via* the pyridine N, the azomethine N and the imidolate O atoms and the distorted octahedral geometry around the Ru(II) ion were confirmed by single crystal X-ray diffraction studies of complex **1**. In addition, complex **1** acts as an excellent catalyst for the transfer hydrogenation of a series of acetophenones to the corresponding secondary alcohols using *iso*-propanol/KOH under optimized conditions, with

conversions of up to 99.2%. The turnover number and turnover frequency are up to 496 and 124 h^{-1} respectively.

Appendix A. Supplementary data

CCDC 891960 contains the supplementary crystallographic data for complex **1**. 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.

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Scheme and Figure Captions

Scheme 1. Synthesis of the ruthenium(II) benzoylhydrazone complexes

Fig. 1. The ORTEP diagram of the complex 1 with 30% probability elipsoids. The solvent molecule is omitted for the sake of clarity.







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| Empirical formula | C ₃₃ H ₂₉ ClN ₃ O ₃ PRu |
|--|---|
| Formula weight | 683.08 |
| Colour | Red |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | P-1 |
| a (Å) | 8.9848(5) |
| b (Å) | 10.7226(6) |
| c (Å) | 17.4085(10) |
| α (°) | 96.253(5) |
| β (°) | 104.113(5) |
| γ (°) | 108.399(5) |
| Volume ($Å^3$) | 1511.56(15) |
| Z | 2 |
| Calculated density (Mg m^{-3}) | 1.501 |
| Absorption coefficient (mm ⁻¹) | 0.699 |
| F(000) | 696 |
| Crystal size (mm) | 0.29 x 0.25 x 0.22 |
| Theta range (°) | 3.36 to 29.13 |
| Limiting indices | $-9 \le h \le 12,$ |
| | $-13 \le k \le 13,$ |
| | $-19 \le 1 \le 23$ |
| Reflections collected/unique | 6917/5053 |
| Refinement method | Full–matrix least–squares on F^2 |
| Data/restraints/parameters | 6917/0/387 |
| Goodness–of–fit on F^2 | 1.042 |
| Final R indices $[I > 2\sigma(I)]$ | $R_1 = 0.0506, wR_2 = 0.0991$ |
| <i>R</i> indices (all data) | $R_1 = 0.0799, wR_2 = 0.1158$ |
| Largest diff. peak and hole (e $Å^{-3}$) | 0.059 and 0.002 |
| | |

Table 1. Crystal data and structure refinement for the complex $1 \cdot H_2O$

| | Bon | d Length (Å) | Bond Ar | ngle (°) |
|---|--------|--------------|-----------|------------|
| | Ru–P | 2.3046(10) | N3-Ru-O1 | 154.90(12) |
| | Ru–O1 | 2.105(2) | N1-Ru-C19 | 175.28(13) |
| | Ru–N1 | 2.023(3) | P-Ru-Cl | 173.35(3) |
| | Ru–N3 | 2.068(3) | N1-Ru-N3 | 78.77(13) |
| | Ru–C19 | 1.882(4) | O1-Ru-C19 | 105.51(12) |
| | Ru–Cl | 2.4528(10) | N3-Ru-C19 | 99.32(14) |
| | O2–C19 | 1.146(4) | N1–Ru–O1 | 76.19(10) |
| | N1-C25 | 1.300(4) | N3–Ru–Cl | 87.88(9) |
| | N2-N1 | 1.382(4) | N3–Ru–P | 98.76(9) |
| | N2-C27 | 1.340(4) | N1–Ru–Cl | 86.01(9) |
| | O1–C27 | 1.297(4) | N1–Ru–P | 94.93(8) |
| | PC1 | 1.842(3) | O1–Ru–Cl | 88.71(7) |
| | PC7 | 1.827(3) | O1–Ru–P | 85.13(7) |
| | PC13 | 1.832(4) | C19-Ru-Cl | 89.61(11) |
| | | | C19–Ru–P | 89.62(11) |
| | | | O1-C27-N2 | 125.9(3) |
| | | | C27–N2–N1 | 108.3(3) |
| | | | N2-N1-C25 | 121.9(3) |
| | | | | |
| P | | | | |

Table 2. Selected bond lengths (Å) and bond angles (°) for the complex $1 \cdot H_2O$

| ι | | | yurugenation or a | leetophenone | |
|---|-------|---------------------------------|--|-----------------------------|---|
| | | | Complex 1, Base <i>i</i> -PrOH, 82 °C | OH OH | 8 |
| | Entry | Base | Time (h) | Conversion ^b (%) | |
| | 1 | КОН | 4 | 98.4 | |
| | 2 | Na ₂ CO ₃ | 6 | 25 | |
| | 3 | CH ₃ COON | a 12 | 18 | |
| _ | 4 | Et ₃ N | 18 | Trace | |

Table 3. Effect of base in the transfer hydrogenation of acetophenone^a

^a Reaction conditions: acetophenone (2.5 mmol), 1 (10 μ mol), catalyst:base = 1:4 in *i*-PrOH (5 mL) at 82 °C.

^b The conversion was determined by GC-MS analysis and is the average of two runs.

| LUDIC II LITCOL OI CULLITUILI | Table 4. | Effect of | catalyst | loading ^a |
|--------------------------------------|----------|-----------|----------|----------------------|
|--------------------------------------|----------|-----------|----------|----------------------|

| t of catalys | st loaunig | | | | |
|--------------|------------------------|--------|-----------------------|------------------|-----|
| | O Com <i>i</i> -PrO | H, KOH | OF | H | PIP |
| Entry | C:S ratio | Conver | sion ^b (%) | TON ^c | |
| 1 | 1:250 | 98.4 | | 246 | |
| 2 | 1:500 | 92.8 | | 464 | |
| 3 | 1:750 | 70.0 | | 525 | |
| 4 | 1:1000 | 48.1 | | 481 | |
| | | | | | |

^a Reaction conditions: acetophenone (2.5 mmol), 1 (10-2.5 μ mol), catalyst:KOH = 1:4 in *i*-PrOH (5 mL) at 82 °C for 4 h. ^b The conversion was determined by GC-MS analysis and is the average of two runs. ^c TON = Turnover number = ratio of moles of product formed to moles of catalyst used.



^a Reaction conditions: ketone (2.5 mmol), **1** (5 µmol), KOH (20 µmol) in *i*-PrOH (5 mL) at 82 °C for 4 h.

^b The conversion was determined by GC–MS analysis and is the average of two runs.

^c TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

^d TOF = Turnover frequency = TON h^{-1} .

Graphical abstract – Pictogram



Graphical abstract - Synopsis

A simple route for the synthesis of four new Ru(II) carbonyl benzoylhydrazone complexes is described. The molecular structure was confirmed by a single crystal X-ray diffraction study. Further, the catalytic efficiency of the complexes has been evaluated for the transfer hydrogenation of substituted acetophenones to their corresponding secondary alcohols under optimized conditions.