Received: 6 May 2019 | Revised: 19 June 2019 | Accepted: 21 June 2019

DOI: 10.1002/aoc.5111

FULL PAPER

WILEY Applied Organometallic Chemistry

Half-sandwich Ru (II) complexes containing (N, O) Schiff base ligands: Catalysts for base-free transfer hydrogenation of ketones

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Funding information
Council for Scientific and Industrial Research, New Delhi, India, Grant/Award Number: 01(2701)/12/EMR-II

Two new half-sandwich Ru (II)(*p*-cymene) complexes (**1** and **2**) containing dopamine-based (N, O) Schiff base ligands ($\mathbf{L^1H}$ and $\mathbf{L^2H}$) were synthesized and characterized by FT-IR, UV–Visible and ^{1}H & ^{13}C NMR spectral techniques, and elemental analyses. The spectroscopic and analytical data revealed monobasic bidentate coordination of the ligands with Ru ion. The molecular structures of $\mathbf{L^1H}$, $\mathbf{L^2H}$ and **2** were further confirmed by single crystal X-ray diffraction study. Complexes **1** and **2** have been employed as catalysts in the transfer hydrogenation of ketones using 2-propanol as a hydrogen source at 85 °C under base-free condition. Good to the excellent yield of secondary alcohols, gram scale synthesis, and high TON and TOF made this catalytic system interesting.

KEYWORDS
base free, NO ligands, ruthenium, Schiff base, transfer hydrogenation

1 | INTRODUCTION

Catalytic hydrogenation is a key step in many organic transformations. The significance of hydrogenation is due to the potential applications of hydrogenated products in vast areas. The most common reducing agents like $LiAlH_4$, $NaBH_4$, N_2H_4, and H_2 gas in presence of metals or metal complexes of phosphine-based ligands are efficient, but most of them are highly specific, expensive, toxic, non-recyclable, air and moisture sensitive, hence not efficient at industrial level applications. Because of these practical, environmental and societal demerits, the development of highly efficient, cost-effective, eco-friendly, sustainable and phosphine-free metal complexes as hydrogenation catalysts has been one of the upfront challenges of catalysis research.[1] Transfer hydrogenation (TH) reactions catalyzed by transition metal complexes are one of the environmentally benign procedures to replace conventional hydrogenation reactions. Transition metal complexes, particularly of noble metals have been explored,[2] among which Ru complexes[3] are efficient TH catalysts and more economical than Pd, Pt, Rh, and Ir catalysts. Mainly, Ru (II)-arene complexes are known to be a well-versed platform for catalysing TH reactions as well as bioinorganic applications due to their inherent properties. These types of

catalysts have been explored quite well for the reduction of various organic functional groups such as carbonyl, nitrile, nitro, alkene, and an alkyne. The inert arene moiety stabilizes the oxidation state of Ru in the catalytic cycle. Ligand(s) also have a major role in the transition metal catalyzed TH reactions especially in tuning the reactivity and selectivity. In the recent past, Schiff base ligands have grown into a special class of ligands due to the few simple and green synthesis using inexpensive and readily available substrates and exhibit excellent coordination chemistry.[4,5] Schiff bases prepared from *o*-hydroxy aldehydes/ketones are stabilized by intramolecular hydrogen bonding and many of them are crystalline solids, which favour monobasic bidentate (N, O) coordination mode to form stable complexes with most of the transition metals.[6] Combination of Schiff base ligands (LH) and Ru (II)(*p*-cymene) precursors led to the formation of half-sandwich, piano-stool complexes of the type [Ru (II)(*p*-cymene)(L)Cl]. These special features of [Ru (II)(η6-*p*-cymene)(L)Cl] complexes made them excel as catalysts in TH reactions.[6,7]

Most of the Ru (II)-arene catalysts used for TH reactions were active only in the basic medium.[8] But the limitations in using base along with the catalyst are a) corrosion of reaction vessels in the industries, b) base sensitive ketones cannot be used and c) stereoselectivity is also affected. Only very few reports are available on base-free transition metal catalyzed TH of ketones.[3c, 9] To overcome the limitations caused by a base, the current interest lies in designing a catalyst for TH under base-free conditions. Inspired by the potential applications of Schiff base ligands and their Ru complexes in catalysis, we report new Ru (II)(p-cymene) complexes (**1** and **2**) of two simple (N, O) Schiff base ligands (**L^{1-2}H**) as excellent catalysts for TH of various ketones. The ligands were derived from 2-(3,4-dimethoxyphenyl)ethanamine, a dimethyl derivative of dopamine (DA).

2 | RESULTS AND DISCUSSION

2.1 | Synthesis of ligands (L^{1-2}H) and their complexes (1 and 2)

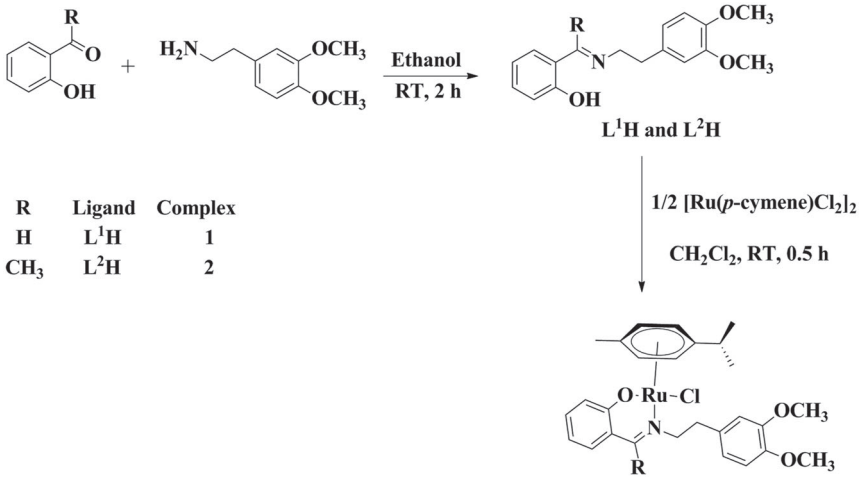
The Schiff base ligands, **L^1H** and **L^2H** were synthesized in high yields (95%) as per the reported method.[10]The new Ru (II) complexes (**1** and **2**) were obtained from direct reaction of the ligands with $[Ru(p\text{-cymene})Cl_2]_2$ in a 2:1 molar ratio in CH_2Cl_2 at room temperature. On completion of the reaction, the solvent was removed and orange-red solids of the desired complexes (**1** and **2**) were obtained in high yields (80–85%) (Scheme 1).

2.2 | Characterization

Composition of the Ru (II) complexes (**1** and **2**) determined by elemental analysis (C, H, and N) was in agreement with their expected molecular formulae [Ru(*p*-cymene)Cl(**L^{1-2}**)]. Structure of **1** and **2** was confirmed by various methods such as UV–Visible, FT-IR, ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy and mass spectrometry. The molecular structures of **L^1H**, **L^2H** and **2** were further confirmed by single crystal X-ray diffraction.

2.3 | UV–visible spectroscopy

The electronic spectra of complexes **1** and **2** have been recorded in CH_3OH at 2×10^{-5} M concentration. In the electronic spectra of complexes **1** and **2**, the intense high-energy absorption bands observed around λ_{max}, 204 and 230 nm were attributed to intra-ligand $\pi \rightarrow \pi^*$ transitions which were blue shifted of about 40 nm when compared to the free ligands.[10] The bands observed around λ_{max}, 286 nm were also due to intra-ligand $n \rightarrow \pi^*$ transitions. The bands obtained around λ_{max},



R	Ligand	Complex
H	L^1H	1
CH_3	L^2H	2

SCHEME 1 Synthesis of the ligands (L1H and L2H) and their Ru (II) complexes (1 and 2)

390 nm were due to the ligand to metal charge transfer (LMCT) transitions.[11] A band at λ_{max}, 487 nm due to metal to ligand charge transfer (MLCT) transition has appeared only when the spectra were recorded at higher concentration (10^{-3} M).

2.4 | FT-IR spectroscopy

A strong band observed for O-H stretching at 3418 ($\mathbf{L^1H}$) and 3392 ($\mathbf{L^2H}$) cm^{-1} in the spectra of ligands[10] disappeared in the spectra of complexes **1** and **2**. Similarly, the C=N stretching frequency of the ligands (1634/1607 cm^{-1}) decreased (1610/1595 cm^{-1}) on complexation. The phenolic C-O stretching frequency of the ligands was shifted to a lower wave number upon coordination.[10] These changes indicated the monobasic bidentate coordination of the ligands through (N, O) donors with ruthenium. The bands for C=C, C-N, etc. were observed in the characteristic region of the IR spectra of **1** and **2**.

2.5 | NMR spectroscopy

In the proton NMR spectra of the complexes, the methyl protons of isopropyl (^{i}Pr) group of *p*-cymene appeared as two independent doublets in the range δ, 1.03–1.26 ppm. The *p*-cymene protons in both **1** and **2** were appeared as four doublets in the range 5.172–5.767 ppm, indicating the presence of *p*-cymene ligand in the complexes.[12] The signal for phenolic OH proton observed in the spectra of ligands disappeared in the spectra of complexes **1** and **2**. The imine (CH=N) proton in the complexes appeared at 7.77 ppm which was shielded by about 0.5 ppm when compared to the corresponding proton in the ligands. The NCH_2 protons were appeared as two signals due to their diastereotopic nature in the range 4.47–4.62 and 4.126–4.261 ppm; these protons showed a down-field shift of about 0.5–0.7 ppm when compared to these signals in the respective ligands. But there was no significant change in the chemical shift of $ArCH_2$ protons in both the complexes compared to the free ligands. The methoxy protons in the ligands appeared as two singlets at 3.79 and 3.74 ppm as reported earlier,[13] which were slightly shielded on complex formation. These observations indicated that the ligands $\mathbf{L^1H}$ and $\mathbf{L^2H}$ coordinated to the Ru center in **1** and **2** respectively in deprotonated ($\mathbf{L^1}$ and $\mathbf{L^2}$) monoanionic bidentate (N, O) fashion.

In the carbon NMR spectra, the PhC-O^- carbons appeared at 164.33 and 165.01 ppm in complexes **1** and **2** respectively. These carbons showed the down-field shift of about 4–5 ppm whereas the signals for C=N carbons observed at 168.68 and 171.33 ppm respectively in **1** and **2** but these carbons showed up-field shift only of about 1–2 ppm when compared to those carbons in the ligands.[10] The NCH_2 carbon peak appeared at 71 and 65 ppm in the spectra of complexes **1** and **2** respectively, which showed a downfield shift of 10–11 ppm as these carbons appeared at 60 and 55 ppm respectively in the spectra of ligands $\mathbf{L^1H}$ and $\mathbf{L^2H}$. The peaks for *p*-cymene carbons in **1** and **2** appeared in the range 81–85 ppm, indicating that the arene ligand coordinated to the Ru ion. The other aliphatic and aromatic carbons showed chemical shifts at characteristic δ values. The observations from the IR and proton NMR spectra indicated that the ligands coordinate with Ru by monobasic (NO) donors.

2.6 | Single crystal X-ray diffraction

The single crystals of $\mathbf{L^1H}$, $\mathbf{L^2H}$ and **2** were obtained by recrystallization of the respective compounds in a suitable solvent system and their structures were determined by single crystal X-ray diffraction. A suitable crystal of each compound was selected, then mounted on X-ray diffractometer using MoKα radiation (λ = 0.71073) and collected the data. The crystal data and structure refinement parameters of $\mathbf{L^1H}$, $\mathbf{L^2H}$ and **2** are given in Table S1. The ligands $\mathbf{L^1H}$ and $\mathbf{L^2H}$ crystallized in monoclinic ($P2_1/c$) and orthorhombic ($P2_12_12_1$) crystal systems respectively. The molecular structures of ligands $\mathbf{L^1H}$ and $\mathbf{L^2H}$ are shown in Figures 1 and 2 respectively. The C=N (1.2756(16) and 1.294 (3) Å), C-N (1.4603(15) and 1.466 (2) Å) and ArC-OH (1.3521(15) and 1.349 (2) Å) bond lengths in ligands $\mathbf{L^1H}$ and $\mathbf{L^2H}$ respectively were found in agreement with those reported for similar Schiff bases.[14] The selected bond lengths and bond angles are given in Table S2. There exist O-H···N intramolecular hydrogen bonding in $\mathbf{L^1H}$ (1.843 Å) and $\mathbf{L^2H}$ (1.768 Å) as observed generally for Schiff bases derived from 2-hydroxy aldehydes or ketones.[12,14] There exist strong CH···O secondary interactions in the solids of ligands $\mathbf{L^1H}$ (2.55, 2.56 and 2.59 Å) and $\mathbf{L^2H}$ (2.59 and 2.47 Å) (Figure S10 and Figure S11).

Ru complex **2** crystallized in the orthorhombic crystal system with the space group $Pca2_1$. The molecular structure of **2** is given in Figure 3. Both C(9)-N (1) (1.559(17) Å) and O(1)-C (1) (1.508(19) Å) bonds in **2** were found lengthened when compared to these bonds in ligand $\mathbf{L^2H}$. The Ru-O, Ru-N and Ru-Cl bond lengths were 2.019 (12), 2.103 (13) and 2.441 (4) Å respectively. These Ru-atom (ligand) bond lengths were in agreement with the values reported in the literature for similar Ru-Schiff base complexes.[7b] The complex **2** has pseudo-octahedral geometry and attained piano stool also known as "half-sandwich" structure. The complex contained CH···O

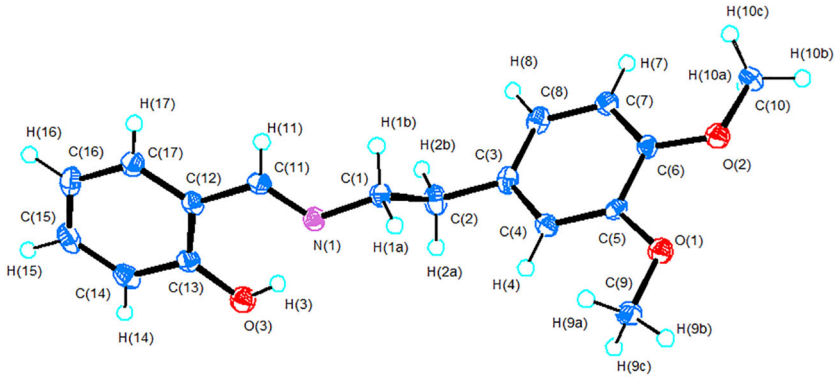


FIGURE 1 ORTEP diagram of L1H with 50% probability ellipsoids

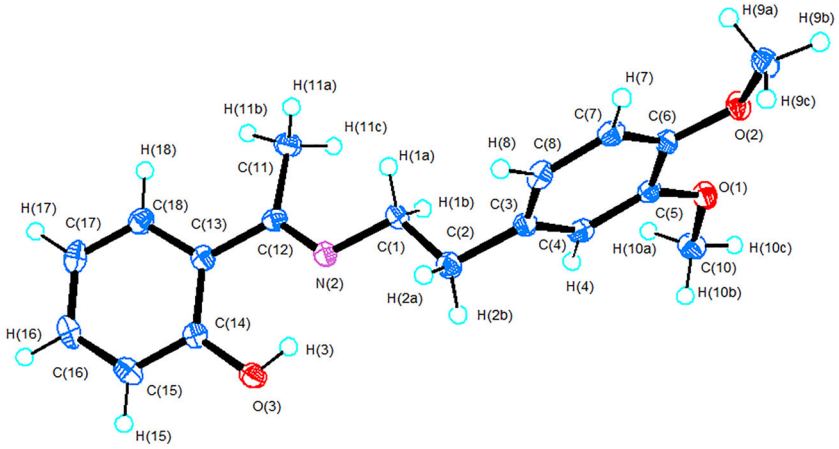


FIGURE 2 ORTEP diagram of L2H with 50% probability ellipsoids

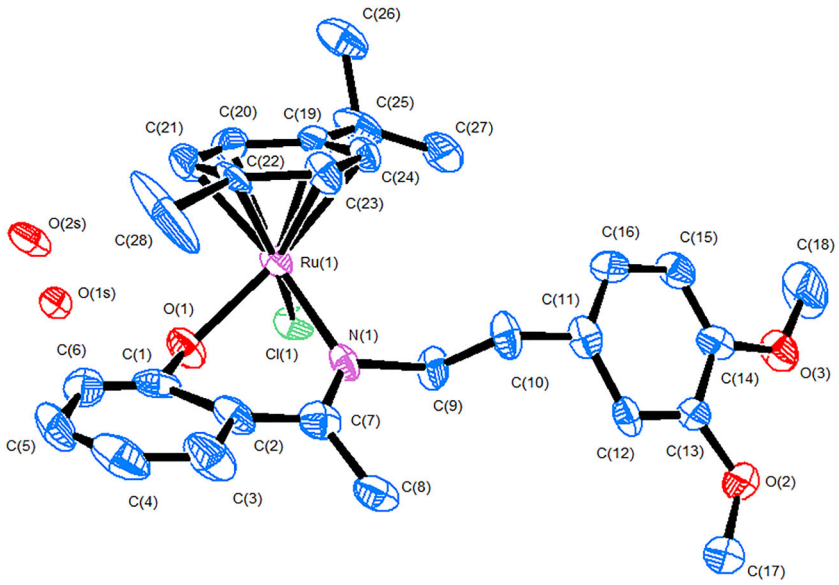


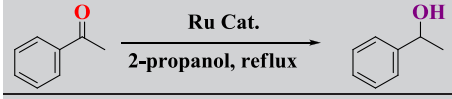
FIGURE 3 ORTEP diagram of [Ru(p-cymene)(L2)Cl].2H2O (2) with 30% probability ellipsoids (H atoms areomitted for clarity).

[2.663 (2) Å] secondary interactions resulting in the supramolecular structure as shown in Figure S12.

2.7 | Base-free TH of ketones

The *p*-cymene based half-sandwich Ru (II) complexes (**1** and **2**) of (N, O) Schiff base ligands were assessed for their catalytic efficiency towards the TH of ketones into secondary alcohols. The results of optimization studies are tabulated in Table S4. Acetophenone was employed as a substrate for the optimization studies. Interestingly, with this catalytic system, the TH reaction was successful even in the absence of a base, which was a rare scenario in TH catalysis. Various hydrogen sources such as methanol, ethylene glycol, glycerol, formic acid, 2-propanol (IPA), and a

TABLE 1 Base-free TH of ketones[a]



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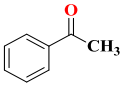
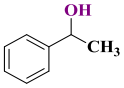
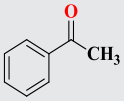
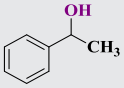
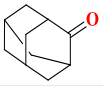
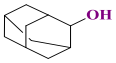
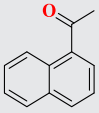
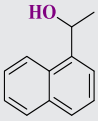
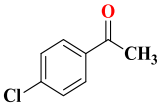
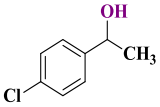
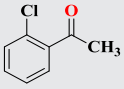
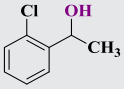
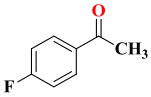
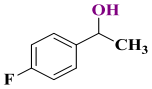
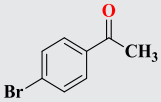
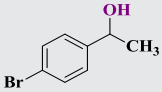
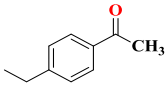
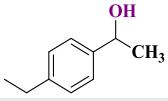
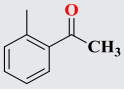
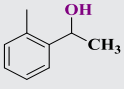
1			7.0	99	990	141
2[b]			2.0	99	198	99
3			5.0	99	990	198
4			6.0	99	990	165
5			6.0	99	990	165
6[b]			3.0	99	198	66
7[b]			3.0	99	198	66
8[b]			3.0	99	198	66
9[b]			3.0	97	194	64
10[b]			3.0	99	198	66
11[b]			5.0	99	198	40
12[b]			2.0	99	198	99
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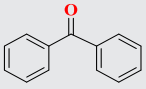
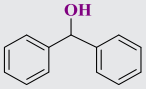
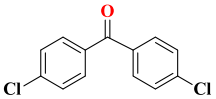
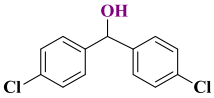
14[b]			6.0	96	192	32
15[b]			3.0	99	198	66

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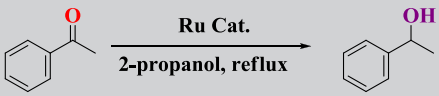
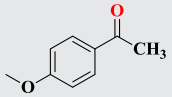
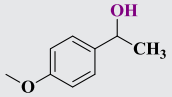
TABLE 1 (Continued)



Entry	Substrate	Product	Time (h)	Yield (%)[c]	TON[d]	TOF[e] (h^{-1})
16[b]			8.0	77	154	19.25

[a]Reaction conditions: Substrate (1 mmol), catalyst **1** (0.1 mol%), 2-propanol (2 ml) and T = 85 °C.

[b]Catalyst **1** (0.5 mol%).

[c]Yield (%) was analyzed by GC–MS.

[d]Turn over number (TON) = No. of moles of product formed per mole of catalyst.

[e]Turn over frequency (TOF) = TON/Time (h).

mixture of triethylamine and formic acid were tried but IPA was found to be compatible and effective hydrogen source (Table S4: entries 1–5 & 18). One mL of IPA was sufficient for the base-free TH of 1 mmol of ketone but two mL of IPA was used in some cases due to the solubility issues (Table S4: entries 6–9). The temperature of the reaction was optimized as 85 °C, below that there was a significant decrease in the conversion of acetophenone (Table S4: entries 11–15). The optimization reactions were carried out under aerobic condition. The presence of 0.1 mol% of the catalyst was sufficient for the complete conversion of acetophenone to 1-phenylethanol in 7 hr under base-free condition but when the catalyst amount was increased to 0.5 mol%, the same conversion was achieved within 2 hr. This shows the influence of catalyst amount over the reaction time (Table S4: entries 15–18). Both catalysts **1** and **2** were efficient for base-free TH but catalyst **1** was comparatively more efficient than catalyst **2**. This slight difference in the catalytic activity was expected due to the +I effect of methyl group attached to the imine carbon of catalyst **2**, which reduces the electron deficiency of the metal that leads to lesser reactivity to some extent, and steric factors might also decrease the activity of **2**, which were absent in catalyst **1**. Hence catalyst **1** was used for the extension of substrate scope (Table S4: entries 18–19). Even when NaOH was used as a base in the presence of 0.1 mol % of the catalyst, it took the same time (7h) to yield 97% of 1-phenylethanol (Table S4: entry 10).

Scope of catalyst **1** has been extended for the TH of various substituted ketones into their corresponding secondary alcohols. The experimental conditions, yields of the products, TON and TOF are given in Table 1. The reactions were carried out under the optimized conditions until the ketone was completely reduced. The reaction was monitored at regular intervals by collecting an aliquot of the reaction mixture, passing it through the short pad of silica bed to remove any inorganic impurities and then analyzed by GC/GC–MS. TON and TOF were higher when 0.1 mol% of catalyst was used compared to 0.5 mol% of catalyst (Table 1: entries 1 and 2). **Entries 3–5** (Table 1) showed more time due to the low catalyst loading. From the literature, it was observed that the halo-substituted ketones had poor yield due to the lability of halogens in basic medium.[2a] Since this catalytic system was base-free, halogens were not labile and hence 100% selectivity was achieved in halo substituted ketones (Table 1: entries 7–10 and 15). Generally, *o*-substituted ketones produce significantly lower yield than the *p*-substituted ketones due to the steric effect. But in this system, no significant difference was observed (Table 1: entries 7 and 8). The trend followed in terms of electronic effect was that the ketones substituted with electron donating groups were readily reduced compared to the those with electron withdrawing groups (Table 1: entries 11 and 16). Interestingly, 4-chromanone was successfully reduced to its corresponding alcohol with an excellent yield in less time (Table 1: entry 13). This confirmed that the catalyst was effective even for heterocyclic ketones. These results revealed the catalytic potential of ruthenium complexes in TH of ketones under base-free condition. The high catalytic activity of the complexes may be due to the long side chain amine moiety used for the formation of the ligands, which provided room for the easy attack of substrate ketone on the metal center and facilitated the reduction. Few Ru (II) complexes of (N, O) Schiff base ligands have been reported in the literature as catalysts for TH of ketones, but these catalysts possess limitations that include use of a base or salts of organic acids along with suitable hydrogen source and higher yields of product alcohols resulted only at higher temperatures and longer reaction times.[8d, 15]

Gram scale synthesis of 2-adamantanol, an important intermediate for several commercial drugs,[16] from 2-adamantanone was achieved with 97% of isolated yield (Figure 4). This established that the catalyst was compatible with the bulk scale synthesis under base-free

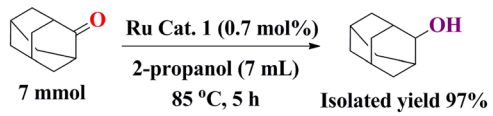


FIGURE 4 Gram scale synthesis of 2-adamantanol from 2-adamantanone

condition, which paved the way for the industrial application of the catalyst.

Sommer *et al.* [3a] reported azocarboxamide based Ru (II) (*p*-cymene) complexes as catalysts for base-free TH. The yield of 1-phenylethanol from acetophenone was 75% in 6 hr at 100 °C with 0.5 mol% of the catalyst under base-free condition using IPA as a hydrogen source. Farrar-Tobar *et al.*[3b] reported commercially available phosphine based Ru-MACHOTM-BH catalyst for selective base-free TH of α,β-unsaturated carbonyl compounds. This catalytic system was efficient even with 0.1 mol% of the catalyst. The carbonyl compounds were converted into their corresponding alcohols within 2–30 min. Carmen Carrión *et al.*[3c] described Ru (II)(p-cymene) complexes containing bis (pyrazol-1-yl)methane ligands as catalysts for base-free TH of carbonyl compounds. This system required 0.2 mol% of the catalyst and IPA as hydrogen source but the time taken for the complete conversion was 24 hr. Andrew Ruff *et al.*[3d] reported [Cp*Ir (pyridinesulfonamide)Cl] pre-catalyst for base-free TH of ketones. But 1 mol% of Ir pre-catalyst was used and time taken for 88% conversion of acetophenone to 1-phenylethanol was 3 h when refluxed in IPA. Pooja Dubey *et al.*[3e] reported η5-Cp*Ir (III) complexes containing Schiff base ligands for base-free TH of carbonyl compounds with IPA. This system needed 0.5 mol% of the Ir catalyst and achieved a 93% conversion of acetophenone to 1-phenylethanol in 4 hr (Figure 5). When compared to the previously reported base-free TH catalysts, the current catalytic system is cost-effective,

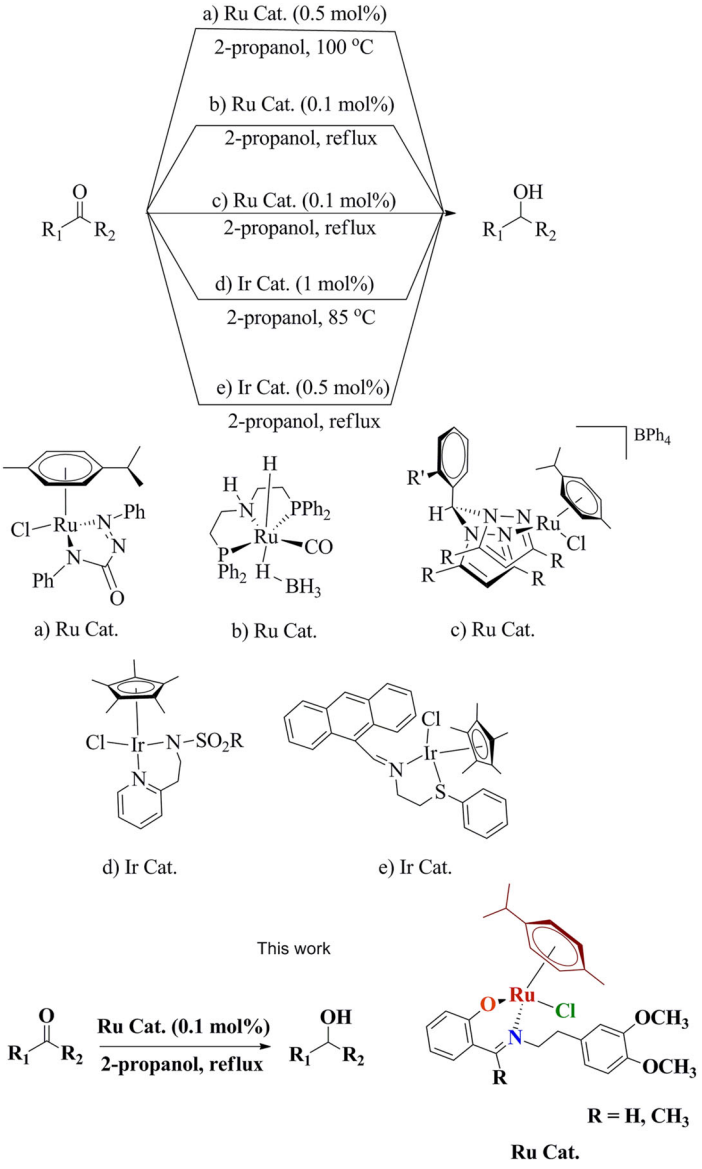


FIGURE 5 Reported TH catalysts for the reduction of ketones to alcohols under base-free conditions

efficient, phosphine-free, air stable, tolerant to gram scale synthesis, and simple and easy methodology in terms of catalyst preparation and catalysis.

3 | CONCLUSIONS

The new Ru (II)(p-cymene) complexes of simple (N, O) Schiff base ligands were synthesized and characterized by spectral and analytical techniques. The molecular structures of $\mathbf{L^1H}$, $\mathbf{L^2H}$ and **2** were confirmed by single crystal X-ray diffraction studies. There exist an intramolecular OH⋯⋯ N ($\mathbf{L^1H}$ and $\mathbf{L^2H}$) and intermolecular CH⋯⋯O (**2**) secondary bonding interactions. Complex **2** has a pseudo-octahedral piano stool structure. Both the Ru complexes were explored as catalysts in TH of ketones. These new complexes **1** and **2** served as excellent catalysts in aerobic, mild and base-free conditions for the TH of various types of ketones; achieved excellent TON, TOF and selectivity. The complexes were synthesized by simple methodology using easily available starting materials and hence the catalysts are cost effective, air-stable, and phosphine-free. The catalysts were compatible even for gram scale synthesis. Hence, these complexes would be very promising than the previously reported base-free TH catalysts and can be extended for industrial applications.

4 | EXPERIMENTAL

4.1 | Materials

2-(3,4-Dimethoxyphenyl)ethanamine (97%) and $RuCl_3.xH_2O$ were purchased from Sigma Aldrich, Bangalore, India. 2-Hydroxybenzaldehyde (99.5%) and 2′-hydroxy acetophenone (99%) were purchased from Merck Specialties India Pvt. Ltd. $[Ru(p\text{-cymene})Cl_2]_2$ was prepared according to the reported literature procedure.[17] Solvents such as C_2H_5OH, CH_3OH, 2-propanol, petroleum ether, hexane, $CHCl_3$, and CH_2Cl_2 were of reagent grade, purchased from Merck India Pvt. Ltd. and used without further purification. The organic substrates were purchased from Sigma Aldrich or Alfa Aesar.

4.2 | Analytical methods

Elemental analyses (C, H, and N) were performed on a LECO–CHSNO–9320 elemental analyzer. ^1H and $^{13}C\{^1H\}$ NMR spectra of Ru (II) complexes (**1** and **2**) were recorded on a Bruker 500 MHz and 126 MHz spectrometers respectively using TMS as an internal standard. The FT-IR spectra of **1** and **2** were recorded by scan method in the wave number range of 4000–500 cm^{-1} with an Agilent FT-IR spectrometer. UV–Visible spectra were recorded on a Shimadzu UV-2600 spectrophotometer using CH_3OH as a solvent. Melting points were determined with a Gallenkamp melting point apparatus in capillary tubes closed at one end and are uncorrected. Single crystal X-ray diffraction data of $\mathbf{L^1H}$, $\mathbf{L^2H}$ and **2** were collected on a Bruker SMART APEX CCD-based X-ray diffractometer with Mo Kα radiation (λ = 0.71073 Å, T = 193 K). The molecular structures of $\mathbf{L^1H}$, $\mathbf{L^2H}$ and **2** were solved by direct methods and refinement was carried out with SHELXL-97[18] package and empirical absorption correction has been applied by SADABS. The refinement was made by full-matrix least-squares on F2 with anisotropic refinement in calculated positions. The reactions involving the synthesis of complexes were monitored by thin layer chromatography (TLC) using pre-coated silica gel aluminum plates. The catalytic TH reactions were monitored by gas chromatography (GC) and purity of the products obtained in TH reactions was confirmed by gas chromatography–mass spectrometry (GC–MS).

4.3 | General procedure for the synthesis of Ru complexes (1-2)

$[Ru(p\text{-cymene})Cl_2]_2$ (100 mg, 0.163 mmol) was dissolved in 20 ml of CH_2Cl_2 and the resulting solution was stirred for 10 min. A solution of ligand $\mathbf{L^1H}$/$\mathbf{L^2H}$ (93/98 mg, 0.326 mmol) made in 20 ml of CH_2Cl_2 was added slowly to the above solution with vigorous stirring. The stirring was continued further for 30 min. The progress of the reaction was monitored on TLC. After completion of the reaction, the red color solution was concentrated. The resulted orange-red solid was washed with n-hexane (15 mL × 2) followed by diethyl ether (15 mL × 2) and then recrystallized in 1:1 mixture of CH_2Cl_2 and n-hexane.

$[Ru(p\text{-cymene})Cl(\mathbf{L^1})]$ (**1**): Yield: 150 mg (82.9%). M.P.: 188–189 °C. Element. Anal. Calcd. (Found) for $C_{27}H_{32}ClNRuO_3$: C, 58.42 (58.40); H, 5.81 (5.80); N, 2.52 (2.51). FT-IR (ν, cm^{-1}): 2962, 2931, 2873, 2833, 2336, 1737, 1610, 1535, 1506, 1463, 1448, 1409, 1330, 1265, 1232, 1201, 1148, 1118, 1030, 1015, 933, 910, 887, 865, 760, 734, 500, 435; UV–Visible (Methanol), λ_{max} in nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$): 204 (44650), 227 (28350), 286 (8700) and 393 (2450); ^1H NMR (500 MHz, DMSO-d_6) δ 7.77 (s, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.04 (s, 1H), 6.97–6.90 (m, 3H), 6.72 (d, J = 8.4 Hz, 1H), 6.36 (t, J = 7.2 Hz, 1H), 5.76 (d, J = 5.6 Hz, 1H), 5.63 (d, J = 6.0 Hz, 1H), 5.58 (d, J = 6.1 Hz, 1H), 5.32 (d, J = 5.6 Hz, 1H), 4.62–4.51 (m, 1H), 4.26 (dt, J = 12.1, 8.0 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 2.75–2.64 (m, 1H), 2.18 (s, 3H), 1.24 (dd, J = 11.3, 7.1 Hz, 5H), 1.13 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz,

DMSO-d_6) δ 165.01, 164.33, 149.02, 147.77, 135.00, 134.37, 132.08, 121.58, 121.28, 119.62, 113.63, 113.29, 112.41, 100.34, 97.43, 86.95, 83.15, 82.18, 81.04, 71.00, 56.01, 55.85, 46.00, 36.63, 30.56, 22.86, 21.87, 18.61, 9.14; HR-MS: m/z found: 520.15 [(M–Cl) = 520.14)] and calcd for $C_{27}H_{32}ClNRuO_3$ is 555.07.

[Ru(p-cymene)Cl($\mathbf{L^2}$)].2H_2O (**2**): Yield: 149 mg (80%). M.P.: 190–192 °C. Element. Anal. Calcd. (Found) for $C_{28}H_{34}ClNRuO_3$: C, 59.09 (59.02); H, 6.02 (5.99); N, 2.46 (2.42). FT-IR (ν, cm^{-1}): 3574, 3375, 3275, 2958, 2933, 2904, 2872, 2837, 1595, 1512, 1466, 1439, 1315, 1255, 1230, 1153, 1140, 1022, 850, 764, 744, 624,528. UV–Visible (Methanol), λ_{max} in nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$): 204 (42350), 233 (23250), 285 (7550) and 382 (2400); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.38 (dd, J = 8.0, 1.6 Hz, 1H), 7.10–7.05 (m, 1H), 6.94 (d, J = 1.6 Hz, 1H), 6.87–6.84 (m, 2H), 6.75 (d, J = 8.2 Hz, 1H), 6.46–6.41 (m, 1H), 5.43 (d, J = 5.8 Hz, 1H), 5.36 (d, J = 5.9 Hz, 1H), 5.33 (d, J = 5.8 Hz, 1H), 5.17 (d, J = 5.8 Hz, 1H), 4.47 (td, J = 12.4, 5.5 Hz, 1H), 4.12 (td, J = 12.4, 4.9 Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.15 (ddd, J = 12.4, 8.7, 3.8 Hz, 1H), 2.89 (td, J = 12.6, 5.6 Hz, 1H), 2.60–2.53 (m, 1H), 2.48 (s, 3H), 2.05 (s, 1H), 1.77 (s, 3H), 1.06 (d, J = 6.9 Hz, 3H), 1.03 (d, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.33, 168.68, 149.20, 147.92, 132.41, 132.15, 130.74, 128.75, 123.17, 121.10, 114.42, 113.14, 112.47, 103.04, 95.36, 83.52, 82.15, 81.20, 80.01, 65.34, 56.06, 55.96, 34.70, 31.24, 30.69, 22.82, 21.82, 19.13, 18.35; HR-MS: m/z found: 534.16 [(M-Cl) = 534.16] calcd for $C_{28}H_{34}ClNRuO_3$ is 569.09.

4.4 | General procedure for TH of ketones

A mixture of ketone (1.0 mmol), Ru catalyst (0.1 mol% of **1** or **2**) and hydrogen source (2 mL) was refluxed at 85 °C in an aerobic atmosphere. After every half an hour, a small amount of the reaction mixture was filtered through a short pad of silica bed, eluted with 20 ml of 50% n-hexane-ethyl acetate mixture to remove the catalyst and analyzed by GC till the completion of the reaction. Most of the alcohol products were isolated by this simple filtration method. The purity and yields of the products were determined by GC/GCMS. Some of the products were isolated and confirmed by ^{1}H NMR spectroscopy.

ACKNOWLEDGEMENTS

P. R. K. thanks CSIR, New Delhi, India for funding this project [01(2701)/12/EMR-II]. We sincerely thank Prof. T. N. Guru Row, Solid State, and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India for XRD data collection ($\mathbf{L^1H}$ and $\mathbf{L^2H}$).

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How to cite this article: Satheesh CE, Sathish Kumar PN, Kumara PR, Karvembu R, Hosamani A, Nethaji M. Half-sandwich Ru (II) complexes containing (N, O) Schiff base ligands: Catalysts for base-free transfer hydrogenation of ketones. *Appl Organometal Chem*. 2019;e5111;e5111. https://doi.org/10.1002/aoc.5111