Inorganica Chimica Acta 368 (2011) 124–131

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Synthesis and characterization of ruthenium(II) complexes based on diphenyl-2-pyridylphosphine and their applications in transfer hydrogenation of ketones

Prashant Kumar [a], Ashish Kumar Singh [a], Mahendra Yadav [a], Pei-zhou Li [b], Sanjay Kumar Singh [b], Qiang Xu [b], Daya Shankar Pandey [a,*]

[a] Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221 005, UP, India
[b] National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

ARTICLE INFO

Article history:
Received 24 May 2010
Received in revised form 18 December 2010
Accepted 21 December 2010
Available online 30 December 2010

Keywords:
Ruthenium
Diphenyl-2-pyridylphosphine
Diamine
Diimine
Acetophenone

ABSTRACT

Synthesis and characterization of the ruthenium complexes [RuH(CO)Cl(κ^1-*P*-PPh$_2$Py)$_2$(PPh$_3$)] (**1**) and [Ru(CO)Cl$_2$(κ^1-*P*-PPh$_2$Py)(κ^2-*P*–*N*-PPh$_2$Py)] (**2**) containing diphenyl-2-pyridylphosphine (PPh$_2$Py) are described. Spectral and structural data suggested linkage of the PPh$_2$Py in κ^1-P bonding mode in **1** and both the κ^1-P and κ^2-P–N bonding modes in **2**. The complex **1** reacted with *N*,*N*-donor bases viz., ethylenediamine (en), *N*,*N*′-dimethyl-(ethylenediamine) (dimen), 1,3-diaminopropane (diap), 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen) and di-2-pyridylaminomethylbenzene (dpa) to afford cationic complexes of formulation [RuH(CO)(κ^1-*P*-PPh$_2$Py)$_2$(N-N)]$^+$ (**3**–**8**) [N-N = en, **3**; dimen, **4**; diap, **5**; bipy, **6**; phen, **7**; and dpa, **8**], which have been isolated as their tetrafluoroborate salts. The complexes under investigation have been characterized by elemental analyses, spectroscopic and electrochemical studies. Molecular structures of **2**, **3**, **6**, and **8** have been determined by single crystal X-ray diffraction analyses. Further, the complexes **1**–**8** act as effective precursor catalyst in transfer hydrogenation of acetophenone/ketones in basic 2-propanol.

1. Introduction

The phosphines are indispensable ligands in transition metal catalyzed reactions. Their electronic and steric effects have a pronounced influence on organic transformations that take place at the transition metal centers [1–3]. In this context, hetero bifunctional phosphines containing "soft" phosphorus and "hard" nitrogen/oxygen donor atoms have drawn special attention [4–11]. These phosphines display interesting properties such as selective binding to various types of metal ions (hard and soft), dynamic behavior *via* reversible dissociation of the weaker metal–ligand bonds and stereo-electronic control about the metal centers [11]. It has been demonstrated that complexes containing "Ru–(P–N)" (P–N = pyridylphosphine) moieties serve as efficient catalysts in homogeneous catalytic hydrogenation reactions. Therefore a large number of ruthenium complexes containing hetero-bifunctional phosphines have been synthesized and their properties studied by spectroscopic and electrochemical techniques [12–19]. Furthermore, a number of homogeneous hydrogenation catalysts based on ruthenium complexes have been reported in the literature [9–11]. Highly active catalyst precursors of the type [*trans*-RuCl$_2$(diphosphine)(1,2-diamine)] for selective hydrogenation of ketones have been developed by Noyori et al. They have established that when diphosphine is chiral and diamine (H$_2$N–NH$_2$) is achiral, it can generate alcohol as the product with high *ee* values [20–22]. It has been proposed that such reactions follow metal–ligand bifunctional catalysis or so called ionic hydrogenation wherein substrate is not directly bonded to the metal center rather it involves an outer sphere H-bonding interaction between the "RuH–NH" unit and ketone, with added H$_2$ derived from metal hydride and an amine proton [23–25]. Notably, hydrogenation of substrates *via* a mechanism excluding direct bonding of substrate at the metal center has been demonstrated in late 1960's [26,27].

Hydrogen transfer (HT) catalysis is an attractive protocol in the reduction of ketones to alcohol. Ru(II) complexes are generally employed as the most useful catalysts for such reactions [3,28–33]. To develop and explore hydrogen transfer catalysts in the present study, we choose PPh$_2$Py as a versatile ligand which may bind the metal center in a monodentate, chelating or bridging mode depending upon requirements at the reaction center [34–39]. In its chelating coordination mode it forms four membered rings which are strained, relatively unstable and plays a vital role in catalysis [40–44]. In this paper we reported the syntheses, characterization and reactivity of hydrido carbonyl ruthenium(II)

* Corresponding author. Tel.: +91 542 6702480; fax: +91 542 2368174.
E-mail address: dspbhu@bhu.ac.in (D.S. Pandey).

0020-1693/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2010.12.057

complexes containing PPh_2Py and various bidentate *N,N*-donor bases. Also, we describe herein crystal structures of **2**, **3**, **6** and **8** and application of **1–8** as catalyst precursors for hydrogen-transfer activity in the reduction of ketones to alcohol in basic 2-propanol. In search of new procedures for bleaching pulp some of the substrates were chosen as a model for chromophore units present in lignin, the aim of hydrogenation being to reduce the degree of conjugation in lignin [45].

2. Results and discussion

2.1. Synthesis and characterization

The ruthenium complex $RuH(CO)Cl(PPh_3)_3$ reacted with heterobifunctional phosphine PPh_2Py in benzene under refluxing conditions to afford P-coordinated neutral complex $[RuH(CO)Cl(\kappa^1\text{-}P\text{-}PPh_2Py)_2(PPh_3)]$. In presence of an excess of NH_4Cl in methanol the complex **1** yielded $[Ru(CO)Cl_2(\kappa^1\text{-}P\text{-}PPh_2Py)(\kappa^2\text{-}P\text{–}N\text{-}PPh_2Py)]$ (**2**), containing both the κ^1-P and κ^2-P–N bonded PPh_2Py (Scheme 1). On the other hand, reactions of **1** with *N,N*-donor bases viz., ethylenediamine (en), *N,N′*-dimethyl-(ethylenediamine) (dimen), 1,3-diaminopropane (diap), 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), and di-2-pyridylaminomethylbenzene (dpa) gave cationic complexes of the formulations $[RuH(CO)(\kappa^1\text{-}P\text{-}PPh_2Py)_2(N\text{–}N)]^+$ (**3–8**) [N–N = en, **3**; dimen, **4**; diap, **5**; bipy, **6**; phen, **7**; and dpa, **8**], which were isolated as their tetrafluoroborate salts.

The complexes **1–8** are air-stable, non-hygroscopic crystalline solids, soluble in halogenated solvents viz., chloroform, dichloromethane, and insoluble in benzene, hexane, n-pentane, diethyl ether and petroleum ether. Characterization of the complexes under study has been achieved by means of standard spectroscopic techniques (FAB-MS, IR, ^1H and $^{31}P\{^1H\}$NMR, electronic absorption and electrochemical studies) as well as elemental analyses. FAB mass spectral data supported formation of the respective complexes. Resulting data along with their assignments are summarized in Section 3 and representative spectra for **1–3**, **6** and **7** are depicted in *Figs.* S1–S5 (supporting information). The position and overall fragmentation pattern of respective complexes conformed well to their formulations.

IR spectra of **1–8** displayed vibrations associated with ν(C=N) and ν(C=C) along with the bands corresponding to coordinated ν(CO) and ν(Ru–H) (Section 3). Interestingly, the position of ν(C≡O) and ν(Ru–H) displayed shift towards higher and lower frequency, respectively. It indicated a decrease in the metal to carbonyl carbon interaction and an increase in Ru–H bond order. In the precursor complex $RuH(CO)Cl(PPh_3)_3$, band associated with ν(C≡O) stretches at 1918 cm^{-1} while in complex **1** it vibrated at 1938 cm^{-1}. It shows that the PPh_2Py in **1** is relatively poor electron donor in comparison to PPh_3 in precursor complex $RuH(CO)Cl(PPh_3)_3$ [46].

2.2. X-ray crystallography

Molecular structures of **2**, **3**, **6**, and **8** have been determined crystallographically. ORTEP views at 30% thermal ellipsoid probability with atom numbering scheme is shown in Figs. 1–4. Details about the data collection, solution and refinement are given in the Section 3 and important geometrical parameters are summarized below the Figs. 1–4. *It should be noted that the ligand di-2-pyridylaminomethylbenzene in **8** is disordered however overall data strongly supported the proposed formulation.* Further, the ligand di-2-pyridyl-aminomethylbenzene coordinated to metal center ruthenium in complex **8** in bidentate manner.

Crystal structure of **2** exhibited that the ligand PPh_2Py is coordinated to ruthenium in a P,N-chelating mode forming a four membered chelate ring with a bite angle of 68.10(12)°. Distorted octahedral coordination geometry about the metal center in this complex is evidenced by the angles P1–Ru–P2, P1–Ru–N1, Cl1–Ru–Cl and C36–Ru1–Cl1 which are 104.16(5)°, 68.10(12)°, 89.73(4)° and 175.39(16)°, respectively. Ru1–P1 and Ru1–N1 bond distances in this complex are 2.320(12) and 2.143(4) Å, respectively which lies within the reported range [47,48]. The complexes **3**, **5**, and **8** (Figs. 2–4) displayed analogous structural features. In its crystal structure, these exhibited distorted octahedral geometry about the ruthenium center completed by nitrogen from bidentate diamine/diimine ligands, PPh_2Py phosphorus, hydride and carbonyl carbon. The angles N1–Ru–N2 in **3** and **6** are 77.3(3)° and

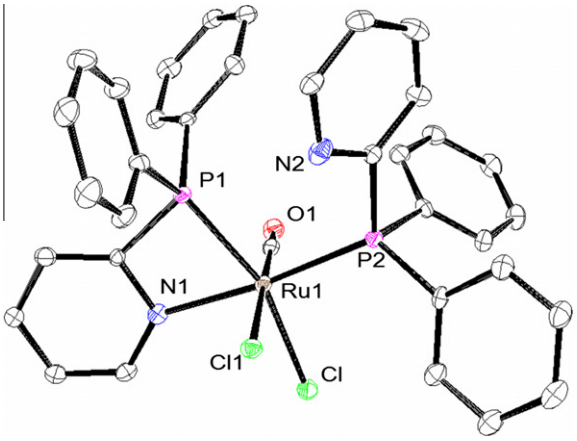
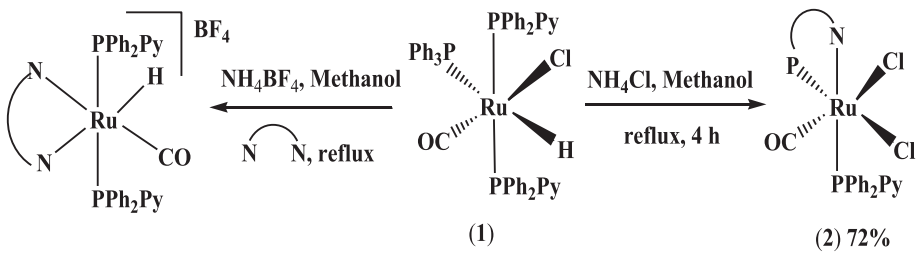


Fig. 1. Molecular structure of **2** and selected bond lengths (Å) and angles (°): Ru1–Cl 2.4393(13), Ru1–Cl1 2.4315(13), Ru1–C36$_{C\equiv O}$ 1.843(5), Ru1–P1 2.3207(12), Ru1–P2 2.3224(13), N1–Ru1–P1 68.10(12), N1–Ru1–P2 171.86(12), P1–Ru1–P2 104.16(5), P1–Ru1–Cl1 93.77(4), P2–Ru1–Cl1 90.30(5), Cl1–Ru1–Cl 89.73(4), N1–Ru1–Cl 91.31(12), N1–Ru1–Cl1 87.77(11), N1–Ru1–C36$_{C\equiv O}$ 90.52(19), P1–Ru1–C36$_{C\equiv O}$ 89.55(15), P2–Ru1–C36 91.99(16), O1–Ru1–C36$_{C\equiv O}$ 175.7(5), Cl–Ru1–C36$_{C\equiv O}$ 86.03(15), Cl1–Ru1–C36$_{C\equiv O}$ 175.39(16).



[N N = en (**3**) 94%, dimen (**4**) 90%, diap (**5**) 95%, bipy (**6**) 95%, phen (**7**) 94%, dpa (**8**) 86%]

Scheme 1. Preparation of **1–8**.

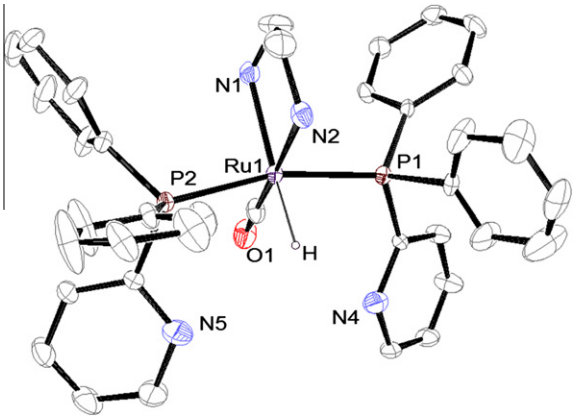


Fig. 2. Molecular structure of **3** and selected bond lengths (Å) and angles (°): Ru1–P1 2.3446(18), Ru1–P2 2.3482(19), Ru1–H1 1.60(11), Ru1–N1 2.213(7), Ru1–N2 2.175(7), Ru1–C24$_{C\equiv O}$ 1.761(9), N1–Ru1–N2 77.3(3), P1–Ru1–P2 165.78(6), N1–Ru1–P1 98.35(19), N1–Ru1–P2 95.70(19), N2–Ru1–P1 92.05(18), N2–Ru1–P2 93.15(18), N1–Ru1–H1 169(4), N2–Ru1–H1 93(3), P1–Ru1–H1 88(4), P2–Ru1–H1 79(4), C24$_{C\equiv O}$–Ru1–N1 97.6(4), C24$_{C\equiv O}$–Ru1–N2 174.3(4), C24$_{C\equiv O}$–Ru1–P1 86.2(3), C24$_{C\equiv O}$–Ru1–P2 89.9(3), C24$_{C\equiv O}$–Ru1–H1 92(3), O1–Ru1–C24$_{C\equiv O}$ 179.0(8).

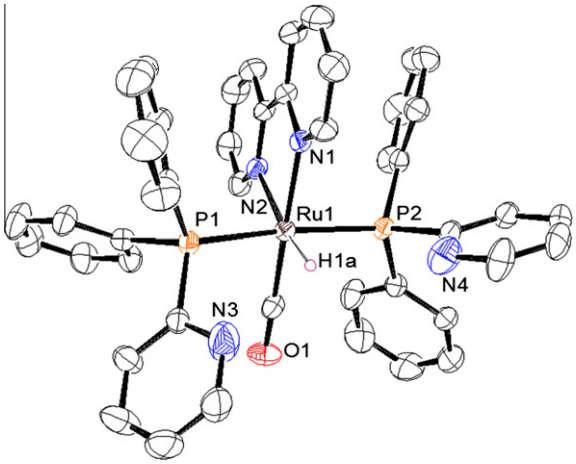


Fig. 3. Molecular structure of **6** and selected bond length (Å) and angles (°): Ru1–P1 2.3421(13), Ru1–P2 2.3693(13), Ru1–H1 1.49(4), Ru1–N1 2.134(4), Ru1–N2 2.188(4), Ru1–C45$_{C\equiv O}$ 1.847(6), N1–Ru1–N2 75.62(15), P1–Ru1–P2 171.54(4), N1–Ru1–P1 92.73(11), N1–Ru1–P2 89.11(11), N2–Ru1–P1 98.30(10), N2–Ru1–P2 90.15(10), N1–Ru1–H1 94.1(18), N2–Ru1–H1 169.5(17), P1–Ru1–H1 84.1(16), P2–Ru1–H1 87.6(16), C45$_{C\equiv O}$–Ru1–N1 176.9(2), C24$_{C\equiv O}$–Ru1–N2 107.4(2), C45$_{C\equiv O}$–Ru1–P1 86.29(17), C45$_{C\equiv O}$–Ru1–P2 91.44(17), C24$_{C\equiv O}$–Ru1–H1 82.9(18), O1–Ru1–C45$_{C\equiv O}$ 176.0(5).

75.62(15)°, respectively, while N1–Ru–N3 in **8** is 83.8(4)°. It suggested inward bending of the diamine/diimine moiety towards metal center. Further, its lower value in comparison to ideal angle of 90° is probably the source of observed distortion from octahedral geometry. Ru(1)–P(1) and Ru(1)–P(2) bond distances are 2.345(2) and 2.348(2) Å in **3**, 2.342(1) and 2.369(1) Å in **6** and 2.374(3) and 2.374(3) Å in **8**. These are essentially equivalent and comparable to those in other related complexes [49–52]. The PPh_2Py ligands are *trans*-disposed as indicated by P1–Ru1–P2 angles of 167.76(6)°, 171.54(4)° and 167.90(13)° in **3**, **6**, and **8**, respectively. Carbonyl carbon bond distances are normal [Ru1–C24, 1.768(9) Å, **3**; Ru1–C45, 1.847(6) Å, **6**; and Ru1–C33, 1.842(1) Å, **8**] [53]. Ru(1)–H(1) bond distances in **3**, **6** and **8** are 1.60(11), 1.49(4) and 1.38(8) Å, respectively. These are shorter in comparison to those reported in other complexes [54,55]. Ru–N

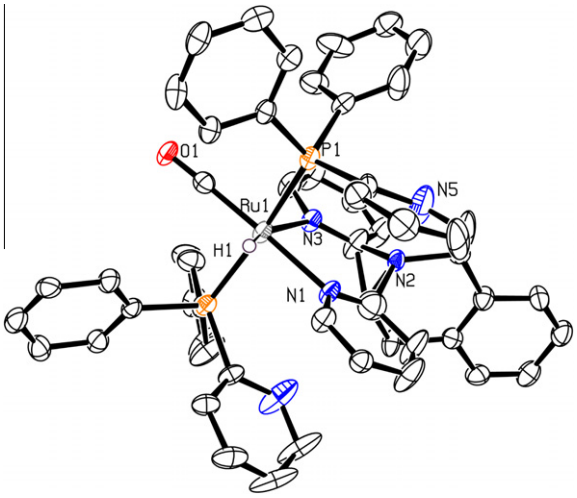


Fig. 4. Molecular structure of **8** and selected bond lengths (Å) and angles (°): Ru1–P1 2.373(3), Ru1–H1 1.00(2), Ru1–N1 2.177(9), Ru1–N3 2.234(9), Ru1–C33$_{C\equiv O}$ 1.847(14), N1–Ru1–N3 83.7(4), P1–Ru1–P1 167.76(11), N1–Ru1–P1 90.65(6), N3–Ru1–P1 96.12(5), N1–Ru1–H1 79(4), N3–Ru1–H1 162(4), P1–Ru1–H1 84.16(13), C33$_{C\equiv O}$–Ru1–N1 176.0(5), C33$_{C\equiv O}$–Ru1–N3 100.3(4), C33$_{C\equiv O}$–Ru1–P1 88.93(7), C33$_{C\equiv O}$–Ru1–H1 97(4), O1–Ru1–C33$_{C\equiv O}$ 177.0(11). The unlabeled part is generated by symmetry. Symmetry code = x, $-y+1/2$, z.

bond lengths are comparable to the bond distances in other closely related Ru(II) amine complexes [56].

Crystal structures of **2**, **3**, **6**, and **8** revealed the presence of extensive intermolecular C–H···X (X = N, Cl and F) and C–H···π interactions. These interactions play significant role in the building of huge supramolecular moieties [57]. Some interesting motifs resulting from weak bonding interactions (intermolecular C–H···π (2.74 Å) in **8** are shown in Figs. 5 and 6.

2.3. NMR spectral studies

The ^{1}H and ^{31}P NMR spectral data of the complexes is summarized in Section 3. Shifts in the position of resonances associated with various protons of the ligand and ^{31}P nuclei in comparison to the precursor complex $RuH(CO)Cl(PPh_3)$ have been taken as an evidence for coordination of PPh_2Py to the metal center ruthenium. Metal bound hydride in **1** and **3**–**8**, resonated in high field side at δ −7.62 (dt, 12 Hz), −10.34 (t, 21 Hz), −10.68 (t, 16 Hz), −10.86 (t, 18 Hz), −11.34 (t, 17 Hz), −11.68 (t, 18 Hz), and −11.78 (t, 23 Hz) ppm, respectively. The presence of a triplet associated with metal bound hydride in ^{1}H NMR spectra of respective complexes suggested coupling of the hydride with two ^{31}P nuclei [58,59]. The ^{31}P{^{1}H}NMR spectra of respective complexes like ^{1}H NMR revealed

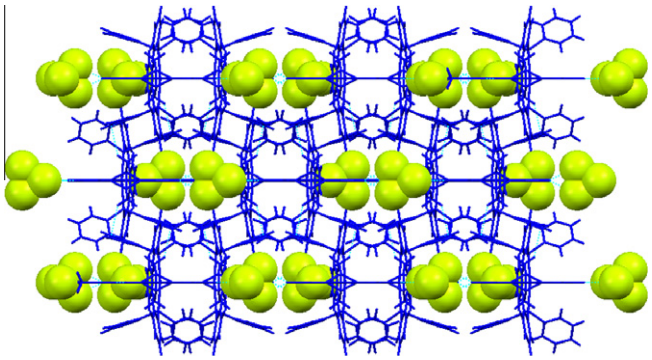


Fig. 5. Counter anion (BF_4^-) encapsulated in self-assembled cavity of complex **8**.

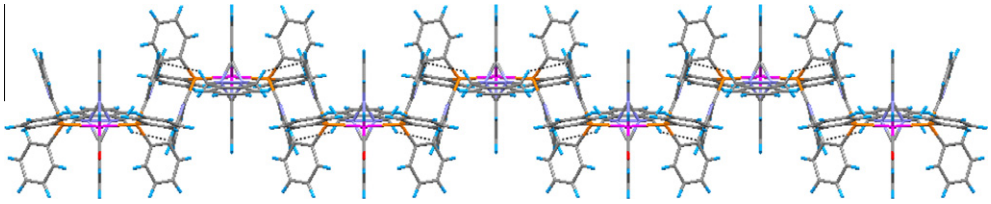


Fig. 6. C–H···π interactions in **8** generating zig-zag motif [C(19)–H19B···Cg {C(7)–C(8)–C(9)–C(10)–C(11)–N(5)} = 3.341 Å (range 2.754–4.287 Å)].

the presence of a single species. $^{31}P\{^{1}H\}$NMR spectrum of **1** exhibited doublets at δ 49.54 ppm and a triplet at 46.35 ppm assignable to the ^{31}P nuclei of coordinated PPh_2Py and PPh_3. On the other hand, **2** displayed a singlet at δ −11.10 ppm and doublet at δ 30.80 ppm associated with the chelated and unchelated PPh_2Py. It is interesting to note that in complex **2**, the ^{31}P nuclei of PPh_2Py exhibited an up-field shift in comparison to the uncoordinated ligand (δ −3.9 ppm). It may be attributed to involvement of the phosphorus nuclei in the formation of a strained four membered ring about the metal center. In an analogous manner, $^{31}P\{^{1}H\}$NMR spectra of **3–8** displayed singlets in the region δ 40.40–8.02 ppm, consistent with the octahedral structure containing a C_2 axis, essentially that of the solid state structure with minor distortions.

2.4. Electronic absorption spectral studies

The electronic absorption spectra of **1–8** were acquired in acetonitrile (10^{-4} M) at room temperature. Resulting data is summarized in the Section 3 and spectra of **3** and **5–8** are depicted in Fig. 7. Ruthenium(II) hydrido complexes usually exhibit intense peaks in the UV region corresponding to ligand based π–π* transitions with overlapping metal-to-ligand charge transfer (MLCT) transitions in the visible region [60,61]. An analogous general pattern has been observed in the electronic absorption spectra of complexes under study. The complexes **1–8** displayed intense transitions in the UV–Vis region. On the basis of its intensity and position, the lowest energy transitions in the visible region at ~488–411 and 393–335 nm have been tentatively assigned to $M_{d\pi} \rightarrow L_{\pi*}$ metal to ligand charge transfer transitions (MLCT). Bands in the high-energy side at ~243–288 nm have been assigned to intra-ligand $\pi \rightarrow \pi^*/n \rightarrow \pi^*$ transitions [60]. Absorption bands at ~251, 257 and 249 nm in the spectra of **6**, **7**, and **8**, respectively have been assigned to $\pi \rightarrow \pi^*$ transitions associated with aromatic imine ligands [61].

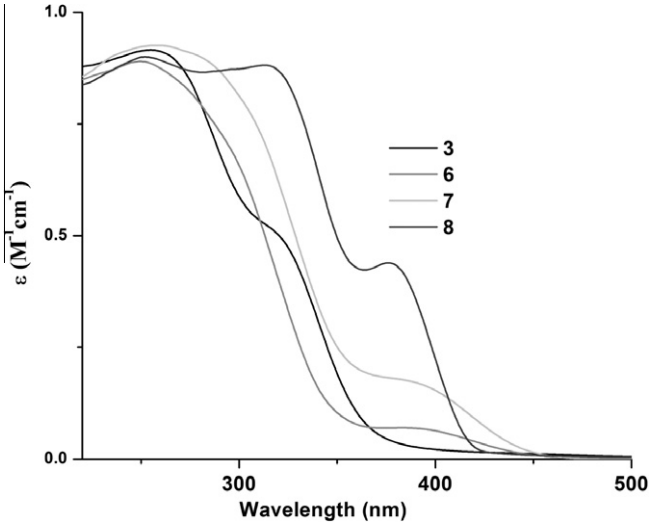


Fig. 7. UV–Vis spectra of **3** and **6–8**.

2.5. Electrochemistry

Electrochemical properties of **3**, **6**, and **7** have been studied by cyclic voltammetry using 0.1 M tertabutylammonium perchlorate (TBAP) as supporting electrolyte. Potential of the Fc/Fc^+ couple under experimental conditions was 0.10 V (80 mV) versus Ag/Ag^+. Resulting data is summarized in Table 1 and selected voltammograms are depicted in Fig. S6 (supporting information). In the anodic potential window, **3** displayed an irreversible peak at 0.83 V, which has been assigned to $Ru^{II/III}$ oxidation. On the other hand, three irreversible peaks at −0.48, −0.96 and −1.31 V in cathodic potential window have been assigned to stepwise reduction of the *N,N*-donor ligands 'en'. The complexes **6** and **7** in its cyclic voltammogram exhibited oxidative responses at 0.78 (63) and 0.72 (75) V, respectively assignable to $Ru^{II/III}$ oxidations. The oxidations in **6** and **7** are reversible and characterized by a peak-to-peak separation (δEp) of ~100 mV and the anodic peak current (i_{pa}) is almost equal to cathodic peak current (i_{pc}), which is expected for a reversible one electron-transfer process. The higher potential required for oxidation of the metal center in **6** as compared to that in **7**, may be attributed to coordination of a π-acceptor ligand. As phen is better π-acceptor in comparison to bipy, the oxidation in **7** takes place at lower potential in comparison to **6**. In the cathodic potential window, **6** and **7** displayed three irreversible peaks at −1.32, −1.41, −1.92 V (**6**) and −1.22, −1.33, −1.87 V (**7**), which may be assigned to the stepwise reduction of diimine ligands.

2.6. Transfer hydrogenation of ketones

Ruthenium complexes with the formulations $[RuCl_2(P–P)(N–N)]$ have been utilized as hydrogenation precursor catalysts using 2-propanol as the source of hydrogen [20,23–25,62–65]. To examine applicability of the complexes under study as catalysts, these were tested for hydrogenation of acetophenone in basic 2-propanol solution at 80 °C, (Eq. (1), Table 2), using the complex (0.01 mmol), added KOH (0.2 mmol), and ketone (1.2 g, 10.0 mmol) at a catalyst/base/substrate (Cat/Base/S) ratio of 1:20:1000. Resulting data indicated that **1–8** are reasonably good hydrogen-transfer catalysts in an inert atmosphere.

$$PhCOCH_3 + (CH_3)_2CH(OH) \xrightarrow[80^\circ C]{\text{catalyst,KOH}} PhCH(OH)CH_3 + (CH_3)_2CO \quad (1)$$

A "blank" experiment was performed in the absence of ruthenium complexes (using 0.02 M KOH and 1.0 M acetophenone in

Table 1
Cyclic voltammetric data of the complexes.

Complex	$E_{1/2}$ (V) Ru II/III	$E_{1/2}$ (V) Ligand centered
3	0.83*	−0.48, −0.96, −1.31
6	0.78(63)	−1.32, −1.41, −1.92
7	0.72(75)	−1.22, −1.33, −1.87

* Irreversible peak.

Table 2
Catalyzed hydrogen-transfer hydrogenation of acetophenone.[a]

Precursor catalysts	Conversion (%)
[Ru(CO)ClH(κ^1-*P*-PPh_2Py)$_2$(PPh_3)] (**1**)	86
[Ru(CO)Cl$_2$(κ^2-*P*-*N*-PPh_2Py)(κ^1-*P*- PPh_2Py)] (**2**)	81
[Ru(CO)H(κ^1-*P*-PPh_2Py)$_2$(en)]BF_4 (**3**)	94
[Ru(CO)H(κ^1-*P*-PPh_2Py)$_2$(dimen)]BF_4 (**4**)	88
[Ru(CO)H(κ^1-*P*-PPh_2Py)$_2$(diap)]BF_4 (**5**)	84
[Ru(CO)H(κ^1-*P*-PPh_2Py)$_2$(bipy)]BF_4 (**6**)	80
[Ru(CO)H(κ^1-*P*-PPh_2Py)$_2$(phen)]BF_4.(**7**)	92
[Ru(CO)H(κ^1-*P*-PPh_2Py)$_2$(dpa)]BF_4 (**8**)	90
[RuCl(*p*-cymene)]$_2$(μ-Cl)$_2$	42

[a] Experimental conditions (see Section 3): Reactions were carried out at 80 °C for 24 h, catalyst:base:substrate being 1:20:1000.

2-propanol, S/base = 50). It showed ~15% conversion of acetophenone after 24 h, however higher concentration of KOH (0.66 M KOH, S/base = 1.5), exhibited 86% conversion. Such metal free base catalysed conversions are well documented in literature [66,67]. Complexes **1–8** gave ~65% conversion after 5 h and relative activity sequence was en ~phen > dpa > bipy ~ dimen (up to ~12 h). Conversion versus time plots for PPh_2Py containing precursor catalysts **3**, and **5–8** is depicted in Fig. 8. Activities of the imine containing complexes were found to be comparable to those of amine based complexes. It suggested that active hydrogen on nitrogen are not essential for hydrogenation and mechanisms other than ionic such as more classical "hydride" or "unsaturated" mechanisms may be operative [20,23–25,63,68–70]. Such findings for "NH-free" active Ru(II) systems are not novel and have been described in literature [32]. Hydrogenation catalysed by **3** followed bifunctional mechanism in which "RuH–NH" unit plays a significant role. For example in first 3 h at 80 °C, conversion achieved using **3** was almost twice in comparison to that observed in presence of **4**, a factor consistent with the fact that **3** statistically has twice as many H atoms available compared to **4** for forming the required H-bonded reaction intermediates.

Data for the reduction of respective ketones to alcohol is illustrated in Table 2. Reduction of C=C bond in styrene was not observed when lignin model compound 3,4-dimethoxystyrene was tested as the substrate under analogous hydrogen-transfer conditions, further demonstrating general selectivity of [RuH(CO)Cl((κ^1-*P*-PPh_2Py)$_2$(N–N)]$^+$ systems in the reduction of polar C=O bond [8,23–25,65–67]. Among the complexes under study, **3** and **7** exhibited highest activity towards hydrogen-transfer

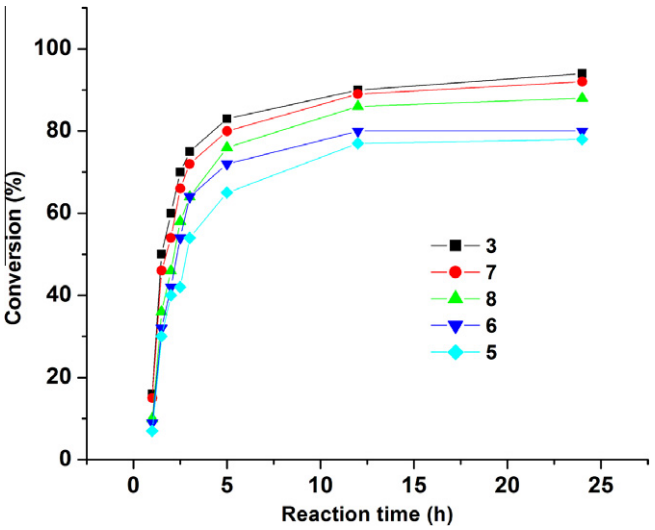
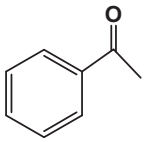
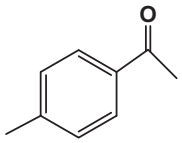
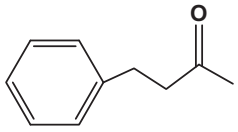
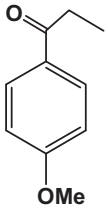
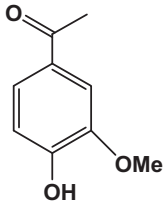


Fig. 8. Conversion of acetophenone vs. reaction time plots for **3** and **5–8**.

Table 3
Transfer-hydrogenation of substrates catalyzed by **3**.

Substrate	Structure	Conversion[a] (%)
Acetophenone		94
4-Methylacetophenone		96
4-Phenyl-2-butanone		86
4-Methoxypropiophenone		76
Acetovanillone		16

[a] Isolated yield after column chromatography.

hydrogenation of acetophenone (Table 3). This catalyst system was tested for several alkyl-aryl ketones selected as model substrate for carbonyl components of the lignin (see Table 3). It was observed that the substituents like *p*-Me and *p*-OMe on aryl moiety do not seriously inhibit hydrogenation process however, introduction of a *p*-OH group influences the course of reaction, as evidenced by ineffective reduction of acetovanillone. The phenyl substituted dialkyl ketone 4-phenyl-2-butanone gets readily reduced. Reetz and Li have recently reported the use of *p*-cymene containing precursor [{(η^6-$C_{10}H_{14}$)RuCl (μ-Cl)}$_2$] in presence of BINOL-derived diphosphonites for extremely effective asymmetric hydrogen-transfer hydrogenation (from 2-propanol) of ketones, it is notable that these systems do not require ancillary diamine ligands [71]. In addition, Deng's and Noyori's group have earlier used the same precursor in presence of a chiral diamine for hydrogenation of ketones in either aqueous media using sodium formate or basic 2-propanol [72,73].

3. Experimental

3.1. Reagents

The solvents were purified by standard procedures prior to its use [74]. Hydrated ruthenium(III) chloride, diphenyl-2-pyridylphosphine, triphenylphosphine, ethylenediamine, *N*,*N*′-dimethyl (ethylenediamine), 1,3-diaminopropane, 2,2′-bipyridine, 1,10-phenanthroline, dipyridylbenzylamine, ammonium tetrafluoroborate, acetophenone, 4-methylacetophenone, 4-phenyl-2-butanone,

4-methoxypropiophenone and acetovanillone, (all Sigma–Aldrich) were used as received without further purifications. The ligand di-2-pyridylbenzylamine and precursor complex RuH(CO)Cl(PPh_3)$_3$ were synthesized and purified following the literature procedures [75,76].

3.2. General considerations

Elemental analyses for C, H and N were performed on an Exeter Analytical Inc. Model CE-440 Elemental analyser. IR and electronic absorption spectra were acquired on a Varian 3300 FT-IR and Shimadzu UV-1700 series spectrometers, respectively. ^{1}H and ^{31}P NMR spectra were obtained on a JEOL AL 300 FT-NMR spectrometer at room temperature in $CDCl_3$. Residual protonated species in the deuterated solvents were used as internal references, all the ^{1}H shifts (s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad) are reported relative to external TMS, while ^{31}P{^{1}H} NMR shifts relative to external aqueous H_3PO_4 (85%) and *J* values are given in Hz. FAB mass spectra were obtained on a JEOL SX 102/Da-600 Mass Spectrometer. Cyclic voltammetric measurements were performed on a CHI 620c Electrochemical Analyzer. A platinum working electrode, platinum wire auxiliary electrode and Ag/Ag$^+$ reference electrode were used in a standard three-electrode configuration. Tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte and solution concentration was ca. 10^{-3}. The potential of Fc/Fc$^+$ couple under experimental conditions was 0.10 V (80 mV) versus Ag/Ag$^+$.

3.3. Synthesis of [RuH(CO)Cl(κ^1-*P*-PPh_2Py)$_2$(PPh_3)] **1**

To a suspension of RuH(CO)Cl(PPh_3)$_3$ (95 mg, 0.1 mmol) in benzene (25 ml), PPh_2Py (52 mg, 0.2 mmol) was added and contents of the flask were refluxed for 6 h whereupon it turned orange. After cooling to room temperature, benzene was removed under reduced pressure and diethyl ether (5 mL) added to it. The orange product thus obtained was filtered, washed twice with diethyl ether and dried under vacuum. Yield: 89 mg (94%). Microanalytical data $C_{53}H_{44}N_2OP_3RuCl$ requires: C, 66.70; H, 4.65; N, 2.94. Found: C, 66.64; H, 4.62; N, 2.90%. FAB-MS [*m*/*z*, obs. (calcd.) assignments]: 954.3 (954) [RuH(CO)Cl(κ^1-*P*-PPh_2Py)$_2$(PPh_3)]; 692.1 (692) [RuH(CO)Cl(κ^1-*P*-PPh_2Py)$_2$]; 428.9 (429) [RuH(CO)Cl(κ^1-*P*-PPh_2Py)]. ^{1}H NMR (δ ppm): 8.26 [d, 1H, H6 py (PPh_2Py)], 7.99 [m, 1H, H3 py (PPh_2Py)], 7.92–7.85 [m, 4H, H2 Ph (PPh_2Py)], 7.10 [m, 1H, H5 py (PPh_2Py)], 6.68–7.55 [m, 25H, Ph (PPh_2Py) and (PPh_3)], −7.62 (t, Ru–H, 12 Hz, 1H). ^{31}P{^{1}H} NMR (δ ppm): 49.54 (d, PPh_2Py) and 46.35 (t, PPh_3). IR (KBr pellets, cm^{-1}): 2008 ν(Ru–H), 1938 ν(CO), 1625, 1593, 1475, 1434, 1394, 1087, 1055, 950, 746, 696. UV–Vis, λ_{max}, nm (ε): 468 (2680), 371 (6360), 246 (39 300).

3.4. Synthesis of [Ru(CO)Cl$_2$(κ^2-*P*-*N*-PPh_2Py)(κ^1-*P*-PPh_2Py)] **2**

To a suspension of **1** (95 mg, 0.1 mmol) in methanol (25 mL) an excess of NH_4Cl was added and contents of the flask were refluxed for 4 h. Slowly it dissolved and gave a yellow solution which was filtered to remove any solid residue, concentrated to ~10 mL under reduced pressure and kept in a refrigerator for slow crystallization. After 24 h, microcrystalline product separated, which was filtered washed with diethyl ether and dried under *vacuo*. Yield: 0.30 g (72%). Microanalytical data $C_{35}H_{28}Cl_2N_2OP_2Ru$ requires: C, 57.86; H, 3.88; N, 3.86. Found: C, 57.88; H, 3.84; N, 3.88%. FAB-MS [*m*/*z*, obs. (calcd.) assignments]: 726.5 (726) [Ru(CO)Cl$_2$(κ^1-*P*-PPh_2Py)(κ^2-*P*-*N*-PPh_2Py)]; 463.3 (463) [Ru(CO)Cl$_2$(κ^2-*P*-*N*-PPh_2Py)]; 427.8 (428) [Ru(CO)Cl(κ^2-*P*-*N*-PPh_2Py)]$^+$. ^{1}H NMR (δ ppm): 8.45 [d, 1H, H6 py (PPh_2Py)], 8.01 [m, 1H, H3 py (PPh_2Py)], 7.94–7.88 [m, 4H, H2 Ph (PPh_2Py)], 7.22 (m, 1H, H5 py (PPh_2Py)], 6.72–7.58 [m, 25H, Ph (PPh_2Py) and (PPh_3)]. ^{31}P{^{1}H} NMR (δ, ppm): −10.65 (s), 30.80 (d, *J* = 16.1 Hz, κ^1-*P*-*N*-PPh_2Py). IR (KBr pellets, cm^{-1}): 1938 ν(CO), 1618, 1584, 1483, 1432, 1354, 1088, 1026, 948, 736, 698. UV–Vis, λ_{max}, nm (ε): 482 (6850), 380 (27 070), 288 (26 270).

3.5. Synthesis of [Ru(CO)H(κ^1-*P*-PPh_2Py)$_2$(en)]BF_4 **3**

To a suspension of **1** (87 mg, 0.091 mmol) in methanol (25 mL) ethylenediamine (en) (0.1 mmol) was added and refluxed for 8 h, whereupon orange suspension turned yellowish-green. After cooling to room temperature it was concentrated under reduced pressure to about 5 mL and a saturated solution of ammonium tetrafluoroborate dissolved in methanol was added to it. It gave a yellow product which was filtered, washed twice with diethyl ether (2 × 5 mL) and dried under vacuum. Yield: 74 mg (94%). Microanalytical data $C_{37}H_{37}BN_4OF_4P_2Ru$ requires: C, 55.31; H, 4.64; N, 6.97. Found: C, 55.34; H, 4.62; N, 6.87%. FAB-MS [*m*/*z*, obs. (calcd.) assignments]: 716.7 (716) [RuH(CO)(κ^1-*P*-PPh_2Py)$_2$(en)]$^+$; 453.5 (453) [RuH(CO)(κ^1-*P*-PPh_2Py)(en)]$^+$. ^{1}H NMR (δ ppm): 1.55 (br s, 4H, NH_2), 2.70 (br s, 4H, CH_2), 8.42 [d, 1H, H6 py (PPh_2Py)], 7.90 [m, 1H, H3 py(PPh_2Py)], 7.80–7.66 [m, 4H, H2 Ph (PPh_2Py)], 7.24 (m, 1H, H5 py (PPh_2Py), 6.68–7.55 [m, 20H, Ph (PPh_2Py)], −10.34 (t, Ru–H, 21 Hz). ^{31}P{^{1}H} NMR (δ ppm): 40.40 (s, PPh_2Py). IR (KBr pellets, cm^{-1}): 3329, 3252, 3055, 2938, 2005 ν(Ru–H), 1933 ν(CO), 1562, 1482, 1434, 1161, 1094, 1028, 750, 694. UV–Vis, λ_{max}, nm (ε): 453 (110), 362 (5242), 259 (9160).

The complexes **4**–**8** were synthesized following exactly the same procedure as described for **3** using respective bases. Characterization data of these complexes are summarized below.

3.6. Characterization data of [RuH(CO)(κ^1-*P*-PPh_2Py)$_2$(dimen)]BF_4 **4**

Yield: 75 mg (86%). Microanalytical data $C_{39}H_{39}BN_4OF_4P_2Ru$ requires: C, 56.46; H, 4.74; N, 6.75. Found: C, 56.42; H, 4.68; N, 6.77%. ^{1}H NMR (δ ppm): 1.58 (br s, 2H, N*H*), 2.01 (d, 6H, CH_3), 2.92 (br, s, 4H, CH_2), 8.38 [d, 1H, H6 py (PPh_2Py)], 7.94 [m, 1H, H3 py (PPh_2Py)], 7.88–7.82 [m, 4H, H2 Ph (PPh_2Py)], 7.18 [m, 1H, H5 py (PPh_2Py)], 6.72–7.58 (m, 20H, Ph (PPh_2Py)], −10.68 (t, Ru–H, 16 Hz). ^{31}P{^{1}H} NMR (δ ppm): 48.06 (s, PPh_2Py). IR (KBr pellets, cm^{-1}): 3292, 3269, 3058, 2919, 2018 ν(Ru–H), 1936 ν(CO), 1625, 1593, 1482, 1434, 1397, 1183, 1180, 1054 ν(BF_4^-), 1038, 937, 820, 696. UV–Vis, λ_{max}, nm (ε): 435 (370), 355 (5420), 243 (5500).

3.7. Characterization data of [RuH(CO)(κ^1-*P*-PPh_2Py)$_2$(diap)]BF_4 **5**

Yield: 74 mg (85%). Microanalytical data $C_{38}H_{39}BN_4OF_4P_2Ru$ requires: C, 55.83; H, 4.81; N, 6.85. Found: C, 55.84; H, 4.78; N, 6.88%. ^{1}H NMR (δ ppm): 1.59 (s, 4H, NH_2), 2.82 (s, 6H, CH_2), 9.28 (d, 1H, H6 py (PPh_2Py)], 8.64 (m, 1H, H3 py (PPh_2Py)], 7.98–7.82 [m, 4H, H2 Ph (PPh_2Py)], 7.28 [m, 1H, H5 py (PPh_2Py)], 6.82–7.48 (m, 20H, Ph (PPh2Py), −10.68 (t, Ru–H, 16 Hz). ^{31}P{^{1}H} NMR (δ ppm): 46.36 (s, PPh_2Py). IR (KBr pellets, cm^{-1}): 3329, 3313, 3243, 3054, 2927, 2014 ν(Ru–H), 1938 ν(CO), 1638, 1560, 1482, 1434, 1092,1046 ν(BF_4^-), 1038, 958, 750, 695. UV–Vis., λ_{max}, nm (ε): 411 (315), 335 (5260), 253 (8745).

3.8. Characterization data of [Ru(CO)H(κ^1-*P*-PPh_2Py)$_2$(bipy)]BF_4·H_2O **6**

Yield: 83 mg (95%). Microanalytical data $C_{45}H_{39}BF_4N_4O_2P_2Ru$ requires: C, 58.90; H, 4.28; N, 6.11. Found: C, 58.88; H, 4.30; N, 6.09%. FAB-MS [*m*/*z*, obs. (calcd.) assignments]: 812.8 (812) [RuH(CO)(κ^1-*P*-PPh_2Py)$_2$(bipy)]$^+$; 784.7 (784) [RuH(κ^1-*P*-PPh_2Py)$_2$(bipy)]$^+$; 521.5 (521) [RuH(κ^1-*P*-PPh_2Py)(bipy)]$^+$. ^{1}H NMR (δ ppm): 6.80–8.50 (m, 36H, Ph), −11.34 (t, Ru–H, 17 Hz). ^{31}P{^{1}H}NMR (δ

ppm): 44.20 (s, PPh_2Py). IR (KBr pellets, cm^{-1}): 3099, 3076, 3050, 2010 ν(Ru–H), 1948 ν(CO), 1482, 1443, 1432, 1164, 1091, 1056 $\nu(BF_4^-)$, 1039, 751, 696. UV–Vis, λ_{max}, nm (ε): 447 (700), 393 (6160), 251 (8890).

3.9. Characterization data of $[Ru(CO)H(\kappa^1\text{-}P\text{-}PPh_2Py)_2(phen)]BF_4$ **7**

Yield: 84 mg (96%). Microanalytical data $C_{47}H_{37}BN_4OF_4P_2Ru$ requires: C, 61.12; H, 4.04; N, 6.07. Found: C, 61.10; H, 4.08; N, 6.03%. FAB-MS [*m*/*z*, obs. (calcd.) assignments]: 923.6 (923) $[RuH(CO)(\kappa^1\text{-}P\text{-}PPh_2Py)_2(phen)]BF_4$; 836.8 (836) $[RuH(CO)(\kappa^1\text{-}P\text{-}PPh_2Py)_2(phen)]^+$; 573.6 (573) $[RuH(CO)(\kappa^1\text{-}P\text{-}PPh_2Py)(phen)]^+$; 545.5 (546) $[RuH(\kappa^1\text{-}P\text{-}PPh_2Py)(phen)]^+$. ^{1}HNMR ($\delta$ ppm): 6.70–8.30 (m, 36H, Ph), −11.68 (t, Ru–H, 18 Hz). $^{31}P\{^1H\}$ NMR (δ ppm): 46.80 (s, PPh_2Py). IR (KBr pellets, cm^{-1}): 3099, 3046, 3017, ν(Ru–H) 2001, ν(CO) 1953, 1585, 1482, 1431, 1152, 1091, $\nu(BF_4^-)$ 1055, 1038, 846, 694. UV–Vis, λ_{max}, nm (ε): 433 (338), 387 (1730), 257 (9240).

3.10. Characterization data of $[Ru(CO)H(\kappa^1\text{-}P\text{-}PPh_2Py)_2(dpa)]BF_4$ **8**

Yield: 76 mg (86%). Microanalytical data $C_{56}H_{48}BF_4N_6OP_2Ru$ requires: C, 62.73; H, 4.52; N, 7.84. Found: 62.70; H, 4.53; N, 7.82%. ^{1}H NMR (δ ppm): 8.77 (d, 6H, PPh_2Py), 8.36 (2H, d, py), 7.54 (2H, t, py), 7.38 (2H, d, py), 7.27 (2H, d, Ph), 7.20 (1H, t, Ph), 7.18 (2H, d, Ph), 6.92 (2H, t, py), 5.58 (2H, s, CH_2), −11.78 (t, Ru–H, 23 Hz). $^{31}P\{^1H\}$ NMR (δ ppm): 36.48 (s, PPh_2Py). IR (KBr pellet, cm^{-1}): 2023 ν(Ru–H), 1950 ν(CO), 1599, 1477, 1434, 1185, 1093, 1053 $\nu(BF_4^-)$, 846, 694. UV–Vis, λ_{max}, nm (ε): 417 (500), 377 (4420), 249 (8930).

3.11. X-ray structure determinations

Suitable crystals of **2**, **3**, **5** and **8** for single X-ray diffraction analyses were obtained from CH_2Cl_2/petroleum ether (40–60 °C) at room temperature by slow diffusion method. Preliminary data on the space group and unit cell dimensions as well as intensity data were collected on an R-AXIS RAPID II diffractometer using graphite-monochromatized Mo Kα radiation. Structures were solved by direct methods (SHELXS 97) and refined with full-matrix least squares on F^2 (SHELX 97) [77–79]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model. The computer program PLATON was used for analyzing the interactions and stacking distances [77–79].

Complex ***2***: Formula = $C_{35}H_{28}Cl_2N_2OP_2Ru$, Mr = 726.54, monoclinic, P 21/n, a = 11.5092(11), b = 10.8017(10), c = 25.399(2), β = 93.662, V = 3151.2(5), Z = 6, D_{calc} = 2.294, μ = 1.200, T(K) = 293(2), λ = 0.71073, R(all) = 0.0850, $R(I > 2\sigma(I))$ = 0.0589, wR_2 = 0.2356, wR_2 [$I > 2\sigma(I)$] = 0.1600, GOF = 1.072.

Complex 3: Formula = $C_{37}H_{37}BF_4N_4OP_2Ru$, Mr = 803.55, orthorhombic, P 21 21 21, a = 12.594(3), b = 15.155(3), c = 19.534(4), $\alpha = \beta = \gamma$ = 90.00, V = 3728.1(13), Z = 4, D_{calc} = 1.542, μ = 0.574, T(K) = 293(2), λ = 0.71073, R(all) = 0.0910, $R(I > 2\sigma(I))$ = 0.0726, wR_2 = 0.1515, wR_2 [$I > 2\sigma(I)$] = 0.1260, GOF = 1.002.

Complex 6: Formula = $C_{45}H_{39}BF_4N_4O_2P_2Ru$, Mr = 917.62, monoclinic, P 21/c, a = 11.198(2), b = 22.121(4), c = 19.365(6), α = 90.00, β = 116.682, γ = 90.00, V = 4286.2(17), Z = 4, D_{calc} = 1.422, μ = 0.500, T(K) = 293(2), λ = 0.71073, R(all) = 0.1171, $R(I > 2\sigma(I))$ = 0.0538, wR_2 = 0.1545, wR_2 [$I > 2\sigma(I)$] = 0.1169, GOF = 1.035.

Complex 8: Formula = $C_{56}H_{48}BF_4N_6OP_2Ru$, Mr = 1070.86, orthorhombic, *P n m a*, a = 19.375(4), b = 16.930(3), c = 15.385(3), $\alpha = \beta = \gamma$ = 90.00, V = 5046.6(17), Z = 1, D_{calc} = 0.331, μ = 0.108, T(K) = 293(2), λ = 0.71073, R(all) = 0.1827, R($I > 2\sigma(I)$) = 0.1091, wR_2 = 0.3301, wR_2 [$I > 2\sigma(I)$] = 0.2946, GOF = 1.059.

3.12. General procedure for the catalytic studies

Standard literature procedures were followed for hydrogen-transfer catalysis experiments [23–25,65]. All the catalytic reactions were carried out under inert atmosphere (N_2) using 10^{-5} M catalyst in 2-propanol (10 ml) and the catalyst/KOH/substrate in a molar ratio of 1:20:1000. The reaction mixture was magnetically stirred and heated at 80 °C for 24 h. The reactions were quenched at 0 °C and samples were collected and diluted with 1 mL of ethyl acetate and acetone (4:1 v/v). The products were isolated and identified by ^{1}H NMR in $CDCl_3$ and the yield of respective processes was calculated considering relative integrals of the ketones and alcohol.

4. Conclusions

In summary, through this work we have developed a range of new cationic hydrido-carbonyl Ru(II) complexes incorporating hetero-difunctional P,N-phosphine, diphenyl-2-pyridylphosphine and diamine (en, dimen and diap) or diimine (bipy, phen and dpa) ligands. From spectral and structural studies it has been established that the coordinated PPh_2Py acts both as monodentate and chelating ligand. Furthermore, it has been shown that **1–8** act as precursor catalysts for transfer hydrogenation of acetophenone and some other related ketones under inert atmosphere.

Acknowledgements

We gratefully acknowledge financial support from the Department of Science and Technology, Ministry of Science and Technology, New Delhi, India (Grant No. SR/SI/IC-15/2007). We are also thankful to the Head, Department of Chemistry, Banaras Hindu University, Varanasi (UP) India and National Institute of Advanced Industrial Science and Technology (AIST), Osaka, Japan for extending facilities.

Appendix A. Supplementary material

CCDC 755241, 755242, 755243 and 755244 contain the supplementary crystallographic data for **2**, **3**, **6** and **8**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. FAB spectra (S1–S5), cyclic voltammograms of **1**, **6** and **7** (S6), figures of weak interactions of **2**, **6**, and **8** (S7-S11), respectively. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.12.057.

References

[1] C.A. Tolman, Chem. Rev. 77 (1977) 313.
[2] P.W.N.M. van Leeuwen, P.C.J. Kamer, J.N.H. Reek, P. Dierkes, Chem. Rev. 100 (2000) 2741.
[3] M.T. Reetz, X.-G. Li, J. Am. Chem. Soc. 128 (2006) 1044.
[4] C.S. Slone, D.A. Weinberger, C.A. Mirkin, Prog. Inorg. Chem. 48 (1999) 233.
[5] A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27.
[6] G.R. Newkome, Chem. Rev. 93 (1993) 2067.
[7] P. Espinet, K. Soulantica, Coord. Chem. Rev. 193–195 (1999) 499.
[8] P. Braunstein, F. Naud, Angew. Chem., Int. Ed. 40 (2001) 680.
[9] Evans, J.A. Osborn, F.H. Jardine, G. Wilkinson, Nature 208 (1965) 1203.
[10] J. Halpern, J.F. Harrod, B.R. James, J. Am. Chem. Soc. 88 (1966) 5150.
[11] G. Francio, R. Scopelliti, C. Grazia Arena, G. Bruno, D. Drommi, F. Faraone, Organometallics 17 (1998) 338.
[12] S.L. Queiroz, A.A. Batista, G. Oliva, M.T.P. Gambardella, R.H.A. Santos, K.S. MacFarlane, S.J. Rettig, B.R. James, Inorg. Chim. Acta 267 (1998) 209.
[13] S.L. Queiroz, A.A. Batista, M.P. de Araujo, R.C. Bianchini, J. Ellena, B.R. James, Can. J. Chem. 81 (2003) 1263.
[14] A.A. Batista, E.A. Polato, S.L. Queiroz, O.L. Nascimento, B.R. James, S.J. Rettig, Inorg. Chim. Acta 230 (1995) 111.
[15] M.P. de Araujo, E.M. Valle, J. Ellena, E.E. Castellano, E.N. dos Santos, A.A. Batista, Polyhedron 23 (2004) 3163.
[16] S.E. Clapham, A. Hadyovic, R.H. Morris, Coord. Chem. Rev. 248 (2004) 2201.
[17] R. Noyori, T. Ohkuma, Angew. Chem., Int. Ed. 40 (2001) 40.

[18] K. Abdur-Rashid, A.J. Lough, R.H. Morris, Organometallics 20 (2001) 1047.
[19] K. Abdur-Rashid, S.E. Clapham, A. Hadzovic, J.N. Harvey, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 124 (2002) 15104.
[20] H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A.F. England, T. Ikariya, R. Noyori, Angew. Chem., Int. Ed. 37 (1998) 1703.
[21] T. Ohkuma, M. Koizumi, H. Doucet, T. Pham, M. Kozawa, K. Murata, E. Katayama, T. Yokozawa, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 120 (1998) 13529.
[22] K. Mikami, T. Korenaga, M. Terada, T. Ohkuma, T. Pham, R. Noyori, Angew. Chem., Int. Ed. 38 (1999) 495.
[23] M.P. Magee, J.R. Norton, J. Am. Chem. Soc. 123 (2001) 1778.
[24] R.M. Bullock, Chem. Eur. J. 10 (2004) 2366.
[25] T. Ikariya, K. Murata, R. Noyori, Org. Biomol. Chem. 4 (2006) 393.
[26] J. Halpern, L.-Y. Wong, J. Am. Chem. Soc. 90 (1968) 6665.
[27] B.R. James, Chem. Eng. News 11 (2002) 8.
[28] T. Ikariya, A.J. Blacker, Acc. Chem. Res. 40 (2007) 1300.
[29] X. Wu, J.L. Xiao, Chem. Commun. (2007) 2449.
[30] S. Gladiali, E. Alberico, Chem. Soc. Rev. 35 (2006) 226.
[31] J.S.M. Samec, J.-E. Bajckvall, P.G. Andersson, P. Brandt, Chem. Soc. Rev. 35 (2006) 237.
[32] M.J. Palmer, M. Wills, Tetrahedron: Asymmetry 10 (1999) 2045.
[33] R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97.
[34] K. Wajda, F. Pruchnik, T. Lis, Inorg. Chim. Acta 40 (1980) 207.
[35] K. Wajda-Hermanowicz, F.P. Pruchnik, Transition Met. Chem. 13 (1988) 101.
[36] V.K. Jain, V.S. Jakkal, R. Ohra, J. Organomet. Chem. 389 (1990) 417.
[37] C.G. Arena, E. Rotondo, F. Araone, Organometallics 10 (1991) 3877.
[38] P. Braunstein, D.G. Kelly, A. Tiripicchio, F. Ugozzoli, Bull. Soc. Chim. Fr. 132 (1995) 1083.
[39] P. Kumar, A.K. Singh, D.S. Pandey, J. Organomet. Chem. 694 (2009) 3643.
[40] K. Nishide, S. Ito, M. Yoshifuji, J. Organomet. Chem. 682 (2003) 79.
[41] P. Govindaswamy, Y.A. Mozharivskyj, M. Kollipara, Polyhedron 23 (2004) 3115.
[42] I. Moldes, E. De la Encarnacion, J. Ros, A. Alvarez-Larena, J.F. Piniella, J. Organomet. Chem. 566 (1998) 165.
[43] E. Drent, P. Arnoldy, P.H.M. Budzelaar, J. Organomet. Chem. 455 (1993) 247.
[44] C.S. Consorti, G. Ebeling, J. Dupont, Tetrahedron Lett. 43 (2002) 753.
[45] T.Q. Hu, B.R. James, in: T.Q. Hu (Ed.), Chemical Modification, Properties and Usage of Lignin, Kluwer Publishers, Dordrecht, The Netherlands, 2002, p. 247.
[46] G.A. Olalere, L. Ling-Kang, Inorg. Chim. Acta 360 (2007) 2464.
[47] T. Hayashida, H. Nagashima, Organometallics 21 (2002) 3884.
[48] H. Aneetha, P.S. Zacharias, B. Srinivas, G.H. Lee, Y. Wang, Polyhedron 18 (1999) 299.
[49] J.C. McConway, A.C. Skapski, L. Phillips, R.J. Young, G. Wilkinson, J. Chem. Soc., Chem. Commun. (1974) 327.
[50] I. de Los Rios, M.J. Tenorio, M.A.J. Tenorio, M.C. Puerta, P. Valerga, J. Organomet. Chem. 57 (1996) 525.
[51] P. Ghosh, A. Chakravorty, Inorg. Chem. 36 (1997) 64.
[52] O.S. Sisodia, A.N. Sahay, D.S. Pandey, U.C. Agrawala, N.K. Jha, P. Sharma, A. Toscano, A. Cabrera, J. Organomet. Chem. 560 (1998) 35.
[53] M. Chandra, A.N. Sahay, D.S. Pandey, M.C. Puerta, P. Valerga, J. Organomet. Chem. 648 (2002) 39.
[54] K. Osakada, T. Yamamoto, A. Yamamoto, A. Takenaka, Y. Sasada, Inorg. Chim. Acta 9 (1979) 105.
[55] M.R. Churchill, K.M. Keil, F.V. Bright, S. Pandey, G.A. Baker, J.B. Keister, Inorg. Chem. 39 (2000) 5807.
[56] B.K. Panda, S. Chattopadhyaya, K. Ghosh, A. Chakravorty, Organometallics 21 (2002) 2773.
[57] A. Singh, A.K. Singh, M. Trivedi, D.S. Pandey, J. Organomet. Chem. 690 (2005) 4243.
[58] D.K. Gupta, O.S. Sisodia, A.N. Sahay, D.S. Pandey, Synth. React. Inorg. Metal – Org. Chem. 28 (1998) 355.
[59] M. Trivedi, M. Chandra, D.S. Pandey, M.C. Puerta, P. Valerga, J. Organomet. Chem. 689 (2004) 879.
[60] S. Kar, T.A. Millar, S. Chakraborty, B. Sarkar, B. Pradhan, R.K. Singh, T. Kunda, M.D. Ward, G.K. Lahiri, Dalton Trans. (2003) 2591.
[61] H.A.S. Silva, R.M. Carlos, A.J. Camargo, C.M.C. Picchi, R.H. de Almeida Santos, B.R. McGarvey, D.W. Franco, Inorg. Chim. Acta 357 (2004) 3147.
[62] J.-X. Gao, T. Ikariya, R. Noyori, Organometallics 15 (1996) 1087.
[63] O.M. Akotsi, K. Metera, R.D. Reid, R. McDonald, S.H. Bergens, Chirality 12 (2000) 514.
[64] E. Lindner, H.A. Mayer, I. Warad, K. Eichele, J. Organomet. Chem. 665 (2003) 176.
[65] E. Lindner, I. Warad, K. Eichele, H.A. Mayer, Inorg. Chim. Acta 350 (2003) 49.
[66] M.D. Le Page, B.R. James, Chem. Commun. (2000) 1647.
[67] C. Thoumazet, M. Melaimi, L. Ricard, F. Mathey, P.L. Floch, Organometallics 22 (2003) 1580.
[68] C. Standfest-Hauser, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao, W. Weissensteiner, J. Chem. Soc., Dalton Trans. (2001) 2989.
[69] B.R. James, Adv. Organomet. Chem. 17 (1979) 319.
[70] R.A.W. Johnstone, A.H. Wilby, I.D. Entwistle, Chem. Rev. 85 (1985) 129.
[71] M.P. de Araujo, A.T. de Figueiredo, A.L. Bogado, G.V. Poelhsitz, J. Ellena, E.E. Castellano, C.L. Donnici, J.V. Comasseto, A.A. Batista, Organometallics 24 (2005) 6159.
[72] Y. Ma, H. Liu, L. Chen, X. Cui, J. Zhu, Deng, J. Org. Lett. 5 (2003) 2103.
[73] M. Yamakawa, I. Yamada, R. Noyori, Angew. Chem., Int. Ed. 40 (2001) 2818.
[74] D.D. Perrin, W.L.F. Armango, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, Oxford, UK, 1986.
[75] N. Ahmad, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 45.
[76] B. Antonioli, J.B. David, K.C. Jack, G. Kerstin, G. Karsten, K. Olga, F.L. Leonard, C.M. John, J.S. Peter, J.S. Christopher, W. Marco, Dalton Trans. (2006) 4783.
[77] S. Mackay, W. Dong, C. Edwards, A. Henderson, C. Gilmox, N. Stewart, K. Shankland, A. Donald, University of Glasgow, Scotland, 1999.
[78] G.M. Sheldrick, SHELXS-97-A Program for Automatic Solution of Crystal Structures, University of Goettingen, Germany, 1997. Release 97-2; G.M. Sheldrick, Acta Cryst. A46 (1990) 467.
[79] PLATON A.L. Spek, Acta Crystallogr., Sect. A 46 (1990) C31.