Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 99 (2012) 174–180

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Ruthenium(II) complexes containing quinone based ligands: Synthesis, characterization, catalytic applications and DNA interaction

P. Anitha [a], R. Manikandan [a], A. Endo [b], T. Hashimoto [b], P. Viswanathamurthi [a,*]

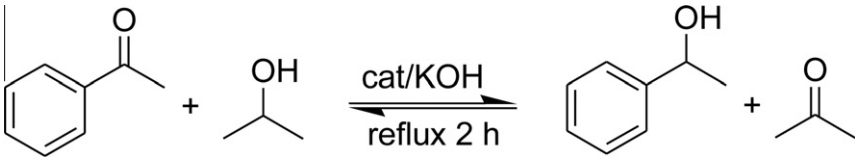
[a] Department of Chemistry, Periyar University, Salem 636 011, India
[b] Department of Materials and Life Sciences, Sophia University, Tokyo 102-8554, Japan

HIGHLIGHTS

- A new series of ruthenium(II) complexes were synthesized.
- Analytical and spectral data confirm the structure of the complexes.
- The complexes used as catalysts in the oxidation and transfer hydrogenation reaction.
- The obtained complexes are potent DNA cleaving agents.

GRAPHICAL ABSTRACT

Ruthenium(II) complexes containing 1,2-naphthaquinone semicarbazone/isonicotinylhydrazone/thiosemicarbazone were synthesized and characterized. They have been assigned an octahedral structure. The new complexes were found to be efficient catalyst for oxidation and transfer hydrogenation reactions. The complexes also successfully cleaved the DNA.



ARTICLE INFO

Article history:
Received 6 August 2012
Accepted 9 September 2012
Available online 16 September 2012

Keywords:
Quinone based ligands
Ruthenium(II) complexes
Catalytic oxidation
Catalytic transfer hydrogenation
DNA cleavage

ABSTRACT

1,2-Naphthaquinone reacts with amines such as semicarbazide, isonicotinylhydrazide and thiosemicarbazide in high yield procedure with the formation of tridentate ligands HL_n ($n = 1–3$). By reaction of ruthenium(II) starting complexes and quinone based ligands HL_n ($n = 1–3$), a series of ruthenium complexes were synthesized and characterized by elemental and spectroscopic methods (FT-IR, electronic, ^1H, ^{13}C, ^{31}P NMR and ESI-MS). The ligands were coordinated to ruthenium through quinone oxygen, imine nitrogen and enolate oxygen/thiolato sulfur. On the basis of spectral studies an octahedral geometry may be assigned for all the complexes. Further, the catalytic oxidation of primary, secondary alcohol and transfer hydrogenation of ketone was carried out. The DNA cleavage efficiency of new complexes has also been tested.

Introduction

Thiosemicarbazones usually react as chelating ligands with transition metal ions by bonding through the sulfur and the azomethine nitrogen atoms and in some cases they behave as tridentate ligands and bond through the sulfur and two nitrogen atoms [1]. Particularly, thiosemicarbazones have emerged as an important class of sulfur donor ligands for transition metal ions because of their mixed hard–soft donor character and versatile coordination behavior [2]. Thiosemicarbazones and semicarbazones of aromatic aldehydes or ketones are known to act as tridentate ligands can yield cyclometallated complexes having two fused five-membered chelate rings at the metal center [3]. The structural peculiarities of coordination compounds of 1,2-benzoquinone ligands have been studied by several workers [4–7] and comprehensively reviewed by Pierpont and coworkers [8]. Surprisingly analogous 1,2-naphthaquinone ligands have remained marginally investigated. Some of these like beta-lapachone, exhibit remarkable antiproliferative activities against a variety of tumor cell lines [9]. Recently the structural and biological properties of 1,2-naphthaquinone ligands appended with thiosemicarbazone/semicarbazone along with their transition metal complexes have been studied [10–15]. However the catalytic activity of these complexes has been omitted.

Among the different metal catalyzed hydrogenation reactions, ruthenium-based catalytic systems are found to be effective in the transfer hydrogenation of ketones [16] and imines [17]. The

* Corresponding author. Fax: +91 427 2345124.
E-mail address: viswanathamurthi@rediffmail.com (P. Viswanathamurthi).

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http://dx.doi.org/10.1016/j.saa.2012.09.019

ability of ruthenium complexes to dehydrogenate alcohols and deliver the hydrides to a ketone [18] or an α,β-unsaturated ketone has made them useful as transfer hydrogenation catalysts [19]. Also Ru-based oxidation catalysis is a powerful and extremely versatile synthetic tool to afford selectively oxygenated products both in homogeneous and in heterogeneous conversions [20,21]. DNA is the primary target for most anticancer and antiviral therapies according to cell biology. Investigation of the interaction of DNA with small molecules is a basic study in the design of new type of pharmaceutical molecules. When some kinds of metal complexes [22] interact with DNA, they could induce the breakage of DNA strands by appropriate ways. Thus, to cancer genes, after DNA strand are cleaved by metal complexes and other cleaving agents, the DNA double strand break. Based on the above facts, syntheses of quinone based ligands and study of their coordination behavior with ruthenium metal, catalytic and DNA interaction properties gained importance. Hence, in this article, we describe the synthesis and characterization of ruthenium(II) complexes bearing 1,2-naphthaquinone binded with semicarbazone/isonicotinylhydrazone/thiosemicarbazone. Furthermore the catalytic properties and DNA cleavage of the synthesized complexes have been investigated.

Experimental

Materials and methods

All the reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures [23]. $RuCl_3{\cdot}H_2O$ was purchased from Loba Chemie Pvt. Ltd. Microanalysis of carbon, hydrogen and nitrogen was carried out using Vario EL III Elemental analyzer at SAIF – Cochin India. The IR spectra of the ligand and their complexes were recorded as KBr pellets on a Nicolet Avatar model spectrophotometer in 4000–400 cm^{-1} range. Electronic spectra of the ligand and their complexes have been recorded in dichloromethane using a Shimadzu UV – 1650 PC spectrophotometer in 800–200 nm range. ^1H, ^{13}C and ^{31}P NMR spectra were recorded in Jeol GSX – 400 instrument using DMSO as the solvent. ^1H NMR and ^{13}C NMR spectra were obtained at room temperature using TMS as the internal standard. ^{31}P NMR spectra of the complexes were obtained at room temperature using ortho phosphoric acid as a reference. The ESI-MS spectra were recorded by using LC–MS Q–ToF Micro Analyzer (Shimadzu) in the SAIF, Panjab University, Chandigarh. Melting points were recorded on a Technico micro heating table and are uncorrected. The catalytic yields were determined using ACME 6000 series GC–FID with DP-5 column of 30 m length, 0.53 mm diameter and 5.00 μm film thickness. DNA cleavage studies were carried out at Biogenics, Hubli. The starting complexes $[RuHCl(CO)(PPh_3)_3]$ [24], $[RuHCl(CO)(Py)(PPh_3)_2]$ [25], $[RuHCl(CO)(AsPh_3)_3]$ [26], $[RuH_2(CO)(PPh_3)_3]$ [24] and ligands HL_1, HL_3 [15] were prepared according to literature procedures.

Preparation of naphthaquinone isonicotinylhydrazone (HL_2)

Isonicotinyl hydrazide (0.14 g, 1.0 mmol) dissolved in hot distilled water (3.0 cm^3) was added to a hot ethanolic suspension (50 cm^3) of 1,2-naphthaquinone (0.16 g, 1.0 mmol) resulting in a clear brown solution which was refluxed on a water bath for 3 h. The precipitate formed upon cooling the reaction mixture to room temperature was filtered off, washed several times with cold ethanol and dried in *vacuo*. Yield 76%, Brown solid, m.p. 170 °C, Anal. Found: C 69.66, H 3.58, N 15.01. Calcd for $C_{16}H_{11}N_3O_2$: C 69.31, H 4.00, N 15.15. IR (KBr, cm^{-1}): 3165 (N^k—H), 1676 (C^l=O), 1651 (C^i=O), 1599 (C^h=N). UV λ_{max}: 305, 291, 248. ^1H NMR (DMSO-d_6, δ, ppm): 10.68 (s, 1H^k, NH), 8.36 (d, 2H^{o,p}, J = 6.6 Hz, CH), 8.10 (d, 2H^{n,q}, J = 6.6 Hz, CH), 7.54 (d, 1H^a, J = 7.2 Hz, CH), 7.58 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.90 (d, 1H^d, J = 7.2 Hz, CH), 7.02 (d, 1H^f, J = 7.2 Hz, CH), 6.86 (d, 1H^g, J = 7.2 Hz, CH). ^{13}C NMR (DMSO-d_6, δ, ppm): 176.48 (C^i, C=O), 161.20 (C^h, C=N), 164.72 (C^l, C=O), 150.25 ($C^{o,p}$, CH), 140.28 (C^m, tert), 124.32 ($C^{n,q}$, CH), 129.02 (C^a, CH), 128.60 (C^b, CH), 134.22 (C^c, CH), 125.30 (C^d, CH), 135.98 (C^e, tert), 136.85 (C^f, CH), 123.20 (C^g, CH), 134.20 (C^j, tert). The structures of the ligands used in this study are given in Fig. 1.

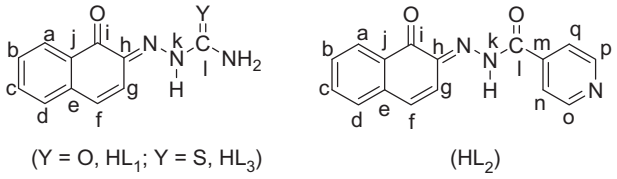


Fig. 1. Structure of ligands.

General procedure for synthesis of new ruthenium(II) complexes

All the new metal complexes were prepared according to the following general procedure. To a solution of $[RuHX(CO)(EPh_3)_2(B)]$ (X=H or Cl, E = P or As, B = PPh_3, $AsPh_3$ or Py) (0.1 g, 0.1 mmol) in benzene (20 cm^3), the appropriate ligand (0.023–0.029 g, 0.1 mmol) was added in 1:1 M ratio. The mixture was heated under reflux for 5 h on water bath. Then the resulting solution was concentrated to 3 cm^3 and the product precipitated by the addition of petroleum ether (60–80 °C) was recrystallised using CH_2Cl_2.The compounds were dried under vacuum and the purity of the complexes was checked by TLC.

[RuCl(CO)(PPh$_3$)(L$_1$)]

Yield 79%, Brown solid, m.p. 210 °C, Anal. Found: C 56.08, H 3.46, N 6.16. Calcd for $C_{30}H_{23}ClN_3O_3PRu$: C 56.21, H 3.62, N 6.56. IR (KBr, cm^{-1}): 1964 (C^r≡O), 1188 (C^l—O), 1620 (C^i=O), 1536 (C^h=N). UV λ_{max}: 620, 380, 262. ^1H NMR (DMSO-d_6, δ, ppm): 8.92 & 8.66 (s, 2H, NH_2), 7.20 (d, 1H^a, J = 7.2 Hz, CH), 7.28 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.48 (d, 1H^d, J = 7.2 Hz, CH), 6.94 (d, 1H^f, J = 7.2 Hz, CH), 6.80 (d, 1H^g, J = 7.2 Hz, CH), 7.92–7.56 (m, 15H, PPh_3). ^{13}C NMR (DMSO-d_6, δ, ppm): 204.82 (C^r, C≡O), 180.62 (C^i, C=O), 163.04 (C^h, C=N), 168.50 (C^l, C—O), 130.68 (C^a, CH), 129.76 (C^b, CH), 134.28 (C^c, CH), 124.96 (C^d, CH), 136.72 (C^e, tert), 135.88 (C^f, CH), 124.78 (C^g, CH), 134.66 (C^j, tert), 138.02, 136.28, 128.67, 126.78 (PPh_3). ^{31}P NMR ($CDCl_3$, δ, ppm): 28.87. MS (ESI), m/z = 641.10 [M^+].

[RuCl(CO)(PPh$_3$)(L$_2$)]

Yield 78%, Green solid, m.p. 210 °C, Anal. Found: C 59.38, H 3.32, N 5.36. Calcd for $C_{35}H_{25}ClN_3O_3PRu$: C 59.79, H 3.58, N 5.98. IR (KBr, cm^{-1}): 1950 (C^r≡O), 1182 (C^l—O), 1590 (C^i=O), 1550 (C^h=N). UV λ_{max}: 517, 327, 262, 244. ^1H NMR (DMSO-d_6, δ, ppm): 8.42 (d, 2H^{o,p}, J = 6.6 Hz, CH), 8.20 (d, 2H^{n,q}, J = 6.6 Hz, CH), 7.42 (d, 1H^a, J = 7.2 Hz, CH), 7.50 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.82 (d, 1H^d, J = 7.2 Hz, CH), 6.78 (d, 1H^f, J = 7.2 Hz, CH), 6.71 (d, 1H^g, J = 7.2 Hz, CH), 8.02–7.84 (m, 15H, PPh_3). ^{13}C NMR (DMSO-d_6, δ, ppm): 204.52 (C^r, C≡O), 183.80 (C^i, C=O), 162.24 (C^h, C=N), 171.72 (C^l, C—O), 152.40($C^{o,p}$, CH), 143.86(C^m, tert), 126.68 ($C^{n,q}$, CH), 129.44 (C^a, CH), 128.82 (C^b, CH), 134.48 (C^c, CH), 125.64 (C^d, CH), 136.66 (C^e, tert), 137.02 (C^f, CH), 123.42 (C^g, CH), 134.62 (C^j, tert), 138.21, 134.72, 130.05, 128.46 (PPh_3). ^{31}P NMR ($CDCl_3$, δ, ppm): 30.02.

[RuCl(CO)(PPh$_3$)(L$_3$)]

Yield 80%, Green solid, m.p. 203 °C, Anal. Found: C 54.45, H 3.19, N 6.11, S 4.62. Calcd for $C_{30}H_{23}ClN_3O_2PSRu$: C 54.84, H 3.53, N 6.39, S 4.88. IR (KBr, cm^{-1}): 1936 (C^r≡O), 760 (C^l—S), 1575 (C^i=O), 1531 (C^h=N). UV λ_{max}: 600, 454, 275. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.68 & 8.26 (s, 2H, NH$_2$), 7.32 (d, 1H^a, J = 7.2 Hz, CH), 7.48 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.70 (d, 1H^d, J = 7.2 Hz, CH), 6.78 (d, 1H^f, J = 7.2 Hz, CH), 6.90 (d, 1H^g, J = 7.2 Hz, CH), 8.18–7.76 (m, 15H, PPh$_3$). ^{13}C NMR (DMSO-d_6, δ, ppm): 204.28 (C^r, C≡O), 183.42 (C^i, C=O), 162.94 (C^h, C=N), 171.86 (C^l, C—S), 128.30 (C^a, CH), 127.96 (C^b, CH), 136.02 (C^c, CH), 125.88 (C^d, CH), 138.10 (C^e, tert), 136.74 (C^f, CH), 125.76 (C^g, CH), 135.06 (C^j, tert), 138.74, 135.03, 129.72, 128.20 (PPh$_3$). ^{31}P NMR (CDCl$_3$, δ, ppm): 29.02.

[RuCl(CO)(Py)(L$_1$)]

Yield 74%, Violet solid, m.p. 270 °C, Anal. Found: C 44.48, H 2.41, N 12.40. Calcd for $C_{17}H_{13}ClN_4O_3Ru$: C 44.60, H 2.86, N 12.24. IR (KBr, cm^{-1}): 1954 (C^r≡O), 1192 (C^l—O), 1609 (C^i=O), 1523 (C^h=N). UV λ_{max}: 461, 323, 275, 231. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.62 & 8.30 (s, 2H, NH$_2$), 7.24 (d, 1H^a, J = 7.2 Hz, CH), 7.60 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.72 (d, 1H^d, J = 7.2 Hz, CH), 6.93 (d, 1H^f, J = 7.2 Hz, CH), 6.80 (d, 1H^g, J = 7.2 Hz, CH), 8.26–7.78 (m, 5H, Py). ^{13}C NMR (DMSO-d_6, δ, ppm): 204.66 (C^r, C≡O), 180.82 (C^i, C=O), 163.04 (C^h, C=N), 169.01 (C^l, C—O), 129.27 (C^a, CH), 127.08 (C^b, CH), 135.03 (C^c, CH), 126.98 (C^d, CH), 134.98 (C^e, tert), 135.07 (C^f, CH), 124.40 (C^g, CH), 133.76 (C^j, tert), 137.90, 133.46, 129.26 (Py).

[RuCl(CO)(Py)(L$_2$)]

Yield 73%, Brown solid, m.p. 235 °C, Anal. Found: C 50.53, H 2.54, N 10.62. Calcd for $C_{22}H_{15}ClN_4O_3Ru$: C 50.82, H 2.91, N 10.78. IR (KBr, cm^{-1}): 1950 (C^r≡O), 1178 (C^l—O), 1600 (C^i=O), 1558 (C^h=N). UV λ_{max}: 680, 327, 259, 245. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.38 (d, 2H^{o,p}, J = 6.6 Hz, CH), 8.16 (d, 2H^{n,q}, J = 6.6 Hz, CH), 7.22 (d, 1H^a, J = 7.2 Hz, CH), 7.36 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.86 (d, 1H^d, J = 7.2 Hz, CH), 6.98 (d, 1H^f, J = 7.2 Hz, CH), 6.82 (d, 1H^g, J = 7.2 Hz, CH), 8.08–7.90 (m, 5H, Py). ^{13}C NMR (DMSO-d_6, δ, ppm): 202.78 (C^r, C≡O), 178.02 (C^i, C=O), 162.48 (C^h, C=N), 169.24 (C^l, C—O), 150.90 (C^{o,p}, CH), 141.28 (C^m, tert), 129.88 (C^{n,q}, CH), 128.42 (C^a, CH), 127.86 (C^b, CH), 133.22 (C^c, CH), 126.71 (C^d, CH), 135.24 (C^e, tert), 135.48 (C^f, CH), 124.32 (C^g, CH), 133.40 (C^j, tert), 136.48, 133.26, 130.63 (Py).

[RuCl(CO)(Py)(L$_3$)]

Yield 72%, Violet solid, m.p. 218 °C, Anal. Found: C 43.37, H 2.60, N 11.96, S 6.63. Calcd for $C_{17}H_{13}ClN_4O_2SRu$: C 43.09, H 2.76, N 11.82, S 6.77. IR (KBr, cm^{-1}): 1952 (C^r≡O), 782 (C^l—S), 1587 (C^i=O), 1535 (C^h=N). UV λ_{max}: 612, 528, 385, 254. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.64 & 8.41 (s, 2H, NH$_2$), 7.28 (d, 1H^a, J = 7.2 Hz, CH), 7.40 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.75 (d, 1H^d, J = 7.2 Hz, CH), 6.84 (d, 1H^f, J = 7.2 Hz, CH), 6.73 (d, 1H^g, J = 7.2 Hz, CH), 8.34–7.82 (m, 5H, Py). ^{13}C NMR (DMSO-d_6, δ, ppm): 205.32 (C^r, C≡O), 182.54 (C^i, C=O), 162.78 (C^h, C=N), 171.22 (C^l, C—S), 128.92 (C^a, CH), 127.41 (C^b, CH), 135.48 (C^c, CH), 126.86 (C^d, CH), 137.48 (C^e, tert), 136.22 (C^f, CH), 124.86 (C^g, CH), 134.40 (C^j, tert), 138.43, 133.22, 130.08 (Py).

[RuCl(CO)(AsPh$_3$)(L$_1$)]

Yield 77%, Brown solid, m.p. 242 °C, Anal. Found: C 52.97, H 2.96, N 5.89. Calcd for $C_{30}H_{23}ClN_3O_3AsRu$: C 52.61, H 3.38, N 6.13. IR (KBr, cm^{-1}): 1944 (C^r≡O), 1190 (C^l—O), 1616 (C^i=O), 1583 (C^h=N). UV λ_{max}: 440, 319, 271, 230. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.92 & 8.36 (s, 2H, NH$_2$), 7.40 (d, 1H^a, J = 7.2 Hz, CH), 7.42 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.70 (d, 1H^d, J = 7.2 Hz, CH), 6.76 (d, 1H^f, J = 7.2 Hz, CH), 6.48 (d, 1H^g, J = 7.2 Hz, CH), 7.90–7.62 (m, 15H, AsPh$_3$). ^{13}C NMR (DMSO-d_6, δ, ppm): 203.68 (C^r, C≡O), 183.98 (C^i, C=O), 163.09 (C^h, C=N), 169.96 (C^l, C—O), 128.74 (C^a, CH), 127.42 (C^b, CH), 135.84 (C^c, CH), 126.30 (C^d, CH), 136.08 (C^e, tert), 137.26 (C^f, CH), 124.96 (C^g, CH), 134.96 (C^j, tert), 137.63, 132.21, 128.43, 126.72 (AsPh$_3$).

[RuCl(CO)(AsPh$_3$)(L$_2$)]

Yield 77%, Green solid, m.p. 200 °C, Anal. Found: C 55.88, H 3.55, N 5.21. Calcd for $C_{35}H_{25}ClN_3O_3AsRu$: C 56.27, H 3.37, N 5.62. IR (KBr, cm^{-1}): 1955 (C^r≡O), 1186 (C^l—O), 1620 (C^i=O), 1500 (C^h=N). UV λ_{max}: 582, 436, 318, 242. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.31(d, 2H^{o,p}, J = 6.6 Hz, CH), 8.12 (d, 2H^{n,q}, J = 6.6 Hz, CH), 7.36 (d, 1H^a, J = 7.2 Hz, CH), 7.48 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.82 (d, 1H^d, J = 7.2 Hz, CH), 7.02 (d, 1H^f, J = 7.2 Hz, CH), 6.90 (d, 1H^g, J = 7.2 Hz, CH), 8.12–7.86 (m, 15H, AsPh$_3$). ^{13}C NMR (DMSO-d_6, δ, ppm): 204.06 (C^r, C≡O), 181.83 (C^i, C=O), 162.78 (C^h, C=N), 170.23 (C^l, C—O), 154.28 (C^{o,p}, CH), 143.60 (C^m, tert), 126.72 (C^{n,q}, CH), 129.35 (C^a, CH), 128.23 (C^b, CH), 136.18 (C^c, CH), 127.56 (C^d, CH), 138.01 (C^e, tert), 137.37 (C^f, CH), 126.78 (C^g, CH), 135.40 (C^j, tert), 138.24, 132.73, 129.46, 126.02 (AsPh$_3$).

[RuCl(CO)(AsPh$_3$)(L$_3$)]

Yield 78%, Green solid, m.p. 220 °C, Anal. Found: C 50.96, H 3.12, N 5.81, S 4.32. Calcd for $C_{30}H_{23}ClN_3O_2AsSRu$: C 51.40, H 3.31, N 5.99, S 4.57. IR (KBr, cm^{-1}): 1955 (C^r≡O), 768 (C^l—S), 1610 (C^i=O), 1538 (C^h=N). UV λ_{max}: 417, 270. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.16 & 8.62 (s, 2H, NH$_2$), 7.42 (d, 1H^a, J = 7.2 Hz, CH), 7.58 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.72 (d, 1H^d, J = 7.2 Hz, CH), 6.98 (d, 1H^f, J = 7.2 Hz, CH), 6.96 (d, 1H^g, J = 7.2 Hz, CH), 7.98–7.74 (m, 15H, AsPh$_3$). ^{13}C NMR (DMSO-d_6, δ, ppm): 203.94 (C^r, C≡O), 182.70 (C^i, C=O), 163.01 (C^h, C=N), 171.66 (C^l, C—S), 129.30 (C^a, CH), 128.60 (C^b, CH), 135.02 (C^c, CH), 126.20 (C^d, CH), 137.41 (C^e, tert), 135.90 (C^f, CH), 127.12 (C^g, CH), 135.51 (C^j, tert), 137.16, 132.24, 129.48, 128.30 (AsPh$_3$).

[RuH(CO)(PPh$_3$)(L$_1$)]

Yield 73%, Brown solid, m.p. 230 °C, Anal. Found: C 59.62, H 3.72, N 6.35. Calcd for $C_{30}H_{24}N_3O_3PRu$: C 59.40, H 3.99, N 6.93. IR (KBr, cm^{-1}): 1946 (C^r≡O), 1176 (C^l—O), 1610 (C^i=O), 1552 (C^h=N). UV λ_{max}: 401, 272, 244. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.94 & 8.18 (s, 2H, NH$_2$), 7.34 (d, 1H^a, J = 7.2 Hz, CH), 7.47 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.66 (d, 1H^d, J = 7.2 Hz, CH), 7.68 (d, 1H^f, J = 7.2 Hz, CH), 6.52 (d, 1H^g, J = 7.2 Hz, CH), 7.83–7.72 (m, 15H, PPh$_3$), −8.13 (s, 1H, Ru-H). ^{13}C NMR (DMSO-d_6, δ, ppm): 203.16 (C^r, C≡O), 181.78 (C^i, C=O), 162.98 (C^h, C=N), 168.76 (C^l, C—O), 131.20 (C^a, CH), 128.48 (C^b, CH), 134.76 (C^c, CH), 125.56 (C^d, CH), 136.11 (C^e, tert), 135.26 (C^f, CH), 125.16 (C^g, CH), 134.18 (C^j, tert), 139.22, 137.03, 128.40, 125.42 (PPh$_3$). ^{31}P NMR (CDCl$_3$, δ, ppm): 28.04.

[RuH(CO)(PPh$_3$)(L$_2$)]

Yield 74%, Brown solid, m.p. 248 °C, Anal. Found: C 62.36, H 3.32, N 5.81. Calcd for $C_{35}H_{26}N_3O_3PRu$: C 62.87, H 3.92, N 6.28. IR (KBr, cm^{-1}): 1944 (C^r≡O), 1174 (C^l—O), 1624 (C^i=O), 1553 (C^h=N). UV λ_{max}: 406, 217. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.56 (d, 2H^{o,p}, J = 6.6 Hz, CH), 8.26 (d, 2H^{n,q}, J = 6.6 Hz, CH), 7.46 (d, 1H^a, J = 7.2 Hz, CH), 7.60 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.7 (d, 1H^d, J = 7.2 Hz, CH), 7.26 (d, 1H^f, J = 7.2 Hz, CH), 6.98 (d, 1H^g, J = 7.2 Hz, CH), 7.80–7.66 (m, 15H, PPh$_3$), −8.30 (s, 1H, Ru-H). ^{13}C NMR (DMSO-d_6, δ, ppm): 204.26 (C^r, C≡O), 180.44 (C^i, C=O), 162.25 (C^h, C=N), 169.98 (C^l, C—O), 151.26 (C^{o,p}, CH), 142.48 (C^m, tert), 127.83 (C^{n,q}, CH), 129.40 (C^a, CH), 128.66 (C^b, CH), 136.72 (C^c, CH), 127.44 (C^d, CH), 138.46 (C^e, tert), 137.92 (C^f, CH), 126.08 (C^g, CH), 135.26 (C^j, tert), 136.22, 133.40, 131.02, 129.47 (PPh$_3$). ^{31}P NMR (CDCl$_3$, δ, ppm): 29.48.

[RuH(CO)(PPh$_3$)(L$_3$)]

Yield 77%, Violet solid, m.p. 245 °C, Anal. Found: C 57.62, H 3.72, N 6.95, S 4.88. Calcd for $C_{30}H_{24}N_3O_2PSRu$: C 57.87, H 3.89, N 6.75, S

5.15. IR (KBr, cm^{-1}): 1945 (C^r≡O), 776 (C^l—S), 1600 (C^i=O), 1540 (C^h=N). UV λ_{max}: 520, 354, 280, 224. ^1H NMR (DMSO-d_6, δ, ppm): 8.83 & 8.10 (s, 2H, NH_2), 7.26 (d, 1H^a, J = 7.2 Hz, CH), 7.46 (t, 2H^{b,c}, J = 7.3 Hz, CH), 7.82 (d, 1H^d, J = 7.2 Hz, CH), 6.83 (d, 1H^f, J = 7.2 Hz, CH), 6.60 (d, 1H^g, J = 7.2 Hz, CH), 7.98–7.84 (m, 15H, PPh_3), −8.35 (s, 1H, Ru-H). ^{13}C NMR (DMSO-d_6, δ, ppm): 204.98 (C^r, C≡O), 182.66 (C^i, C=O), 163.04 (C^h, C=N), 172.78 (C^l, C—S), 129.36 (C^a, CH), 128.48 (C^b, CH), 135.43 (C^c, CH), 126.98 (C^d, CH), 137.92 (C^e, tert), 136.88 (C^f, CH), 126.70 (C^g, CH), 135.02 (C^j, tert), 138.92, 133.66, 130.04, 128.62 (PPh_3). ^{31}P NMR ($CDCl_3$, δ, ppm): 28.64.

Catalytic oxidation

Catalytic oxidation of primary alcohols to corresponding aldehydes and secondary alcohols to ketones by ruthenium(II) complexes were studied in the presence of N-methyl morpholine N-oxide (NMO) as co-oxidant. In a typical reaction, ruthenium(II) complexes as a catalyst and primary or secondary alcohol, as substrates at 1:100 M ratios was described as follows. A solution of ruthenium complexes (0.01 mmol) in CH_2Cl_2 (20 cm^3) was added to the mixture containing substrate (1 mmol), NMO (3 mmol) and molecular sieves. The solution mixture was refluxed for 2 h and the solvent was then evaporated from the mother liquor under reduced pressure. The solid residue was extracted with petroleum ether (60–80 °C) (20 cm^3) concentrated to ~1 ml and was analyzed by GC. The oxidation products were identified by GC co-injection with authentic samples.

Catalytic transfer hydrogenation

The catalytic transfer hydrogenation reactions were also studied using ruthenium(II) complexes as a catalyst, ketone as substrate and KOH as base at 1:500:2.5 M ratios. The procedure was described as follows. A mixture containing ketone (5 mmol), the ruthenium complex (0.01 mmol) and KOH (0.025 mmol) was heated to reflux in 10 cm^3 of *i*-PrOH for 2 h. After completion of reaction the catalyst was removed from the reaction mixture by the addition of petroleum ether followed by filtration and subsequent neutralization with 1 M HCl. The ether layer was filtered through a short path of silica gel by column chromatography. The filtrate was subjected to GC analysis and the hydrogenated product was identified and determined with authentic samples.

DNA cleavage experiments

DNA cleavage experiments were carried out according to reported procedure [27]. For the gel electrophoresis experiment, supercoiled DNA of Escherichia coli was treated with the ruthenium(II) complexes in TAE buffer (10 mmol Tris acetate, 10 mmol EDTA, pH 8.0) and the solution was then incubated at 37 °C for 2 h. The samples were analyzed by electrophoresis for 30 min at 50 V on a 0.8% agarose gel in TAE (4.84 g Tris–acetate, 0.5 mol EDTA/1 l, pH 8.0). The gel was stained with 10 μg/ml ethidium bromide and observe the bands under UV illuminator.

Result and discussion

All the complexes are stable in air at room temperature, brown in color, non-hygroscopic in nature and highly soluble in common organic solvents such as dichloromethane, benzene, acetonitrile, chloroform and DMSO. The analytical data are in good agreement with the general molecular formula proposed for all the complexes. In addition, ESI-mass spectra was also used to check the composition of the complexes. For example the molecular ion peak observed for the complex [RuCl(CO)(PPh_3)(L_1)] at m/z = 641.10 (Calcd. 641.03) confirms the stoichiometry of the complex (Fig. 2).

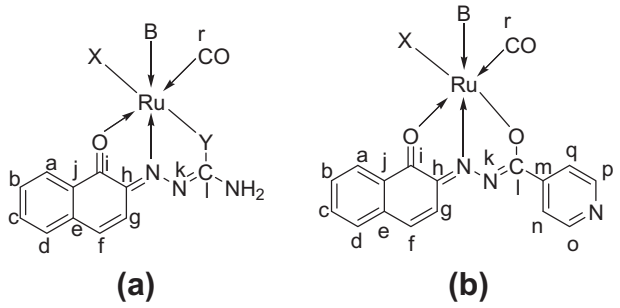


Fig. 2. Structure of complexes.

Infrared spectroscopic analysis

In IR spectra, the free ligands display υ(C=O)/υ(C=S) absorption at 1688–1676 cm^{-1}/863 cm^{-1}. The absence of υ(O—H)/υ(S—H) in the free ligand suggests that they are exist in the ketone/thione form. The new band appeared around 1192–1174 cm^{-1} which corresponds to υ(C—O) for semicarbazone and isonicotinylhydrazone complexes and the υ(C—S) appeared at 782–760 cm^{-1} in thiosemicarbazone complexes. The IR spectra of the complexes did not display υ(O—H)/υ(S—H) at 3419–3409 cm^{-1}/2585–2570 cm^{-1} suggesting the deprotonation of the enol/thiol proton prior to coordination [28–31]. The bands assigned to azomethine (C=N) and quinone carbonyl (C=O) appearing at 1600–1597 and 1672–1637 cm^{-1} respectively in the spectra of free ligands are shifted to lower wave numbers on complexation [32] indicates the other coordination through imine nitrogen and quinone oxygen. The IR spectrum of free ligands display two bands around 3450 and 3300 cm^{-1} due to υ_{as} and υ_{sym} of terminal NH_2 group [33]. These bands remain unaltered in the corresponding metal complexes indicating the non-involvement of this group on complexation. The existence of very strong band in the 1964–1936 cm^{-1} region for all the complexes revealed the presence of terminally coordinated carbon monoxide [34]. A medium intensity band is observed in the region 1094–1091 cm^{-1} characteristic of the coordinated pyridine [35]. Further the Ru-H absorption appeared around 2020–2010 cm^{-1} for complexes containing Ru-H coordination. The peak around 480 cm^{-1} has been assigned to Ru-Cl vibrations for complexes containing metal chloride bond [36]. In addition other characteristic bands due to triphenylphosphine and triphenylarsine are present around 1436–1432 cm^{-1}, in the spectra of all the complexes.

Electronic spectroscopic analysis

All the new ruthenium(II) complexes are diamagnetic indicating the presence of ruthenium in the +2 oxidation state. The ground state of ruthenium(II) is $^1A_{1g}$ arising from the t_2^6g configuration in an octahedral environment. The excited state corresponding to the $t_2^5g\ e_g^1$ configuration are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Hence, four bands corresponding to the transitions $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$, $^1A_{1g} \rightarrow {}^1T_{2g}$ are possible in the order of increasing energy.

The electronic spectra of ligands and the complexes in CH_2Cl_2 showed two to four bands in the region 680–217 nm. The bands around 680–600 nm range have been assigned to the spin allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. The other high intensity bands

around 582–318 nm have been assigned to charge transfer transitions arising from the metal t_{2g} level to the unfilled molecular orbitals derived from the π^* level of the ligands based on their extinction coefficient values. The bands below 300 nm were characterized by intra-ligand charge transfer. The electronic spectra are similar to those observed for other octahedral ruthenium(II) complexes [37].

^{1}H NMR spectroscopic analysis

The ^{1}H NMR spectra of the ligand and the corresponding ruthenium(II) complexes were recorded in DMSO to confirm the presence of coordinated ligand in the complexes. The singlet at 14.22–10.68 ppm are assigned to hydrazinic N—H proton indicates that in solution the ligands HL_n (n = 1–3) exist in ketonic/thionic forms [38,39]. These bands are not found in the spectra of complexes, which is consistent with deprotonation of these ligands upon metal complexation. Ligands and complexes showing two singlets in the region 9.16–8.10 ppm are assigned for terminal NH_2 protons. The singlet at −8.13 to −8.35 ppm are assigned for complexes containing Ru-H coordination [40]. The multiplets at 8.18–6.48 ppm are assigned to aromatic protons present in the ligands, triphenylphosphine/triphenylarsine/pyridine.

^{13}C NMR spectroscopic analysis

The ^{13}C NMR spectra of the complexes have showed a peak at 205.32–202.78 ppm region is due to terminal $C^r{\equiv}O$ carbon. The presence of a peak at 183.98–178.02 ppm region is assigned to quinone carbonyl ($C^i{=}O$) carbon. The azomethine ($C^h{=}N$) carbon exhibit its peak in the region of 163.09–162.46 ppm. In addition, the peak in the region 171.72–168.50 and 172.78–171.22 ppm is assigned to ($C^l{-}O$) and ($C^l{-}S$) respectively. The peaks observed at the 154.28–123.20 ppm range has been assigned to aromatic carbons.

^{31}P NMR spectroscopic analysis

^{31}P NMR spectra of some of the complexes were recorded to confirm the presence of triphenylphosphine group in the complexes. A sharp singlet was observed around 30.02–28.04 ppm due to presence of triphenylphosphine ligand in the complexes.

Catalytic oxidation

The catalytic oxidation of primary and secondary alcohols by the synthesized ruthenium(II) complexes in CH_2Cl_2–NMO system have been studied. All the complexes oxidize primary and secondary alcohols to corresponding aldehydes and ketones respectively. The aldehydes or ketones formed were determined by GC using the internal standard method. [RuCl(CO)(PPh_3)L_2] was selected as a model catalyst for optimization of the reaction conditions. In order to study the effect of time on the activity, the product analysis was done at regular intervals of time under similar reaction conditions (Fig. 3). It was found that the optimum reaction time was 2 h in CH_2Cl_2–NMO system.

The oxidation of other complexes was then examined using the optimized reaction conditions. All the synthesized ruthenium(II) complexes were found to catalyze the oxidation of alcohols to corresponding carbonyl compounds. [RuCl(CO)(PPh_3)L_2] showed better results than all the other complexes (Table 1). The results for the oxidation of benzyl alcohol to benzaldehyde resulted in 90–99% yield and cyclohexanol to cyclohexanone resulted in 76–87% yield. The relatively higher yield obtained for the oxidation of benzyl alcohol as compared to cyclohexanol is due to the fact that the α-CH unit of benzyl alcohol is more acidic than cyclohexanol [41].

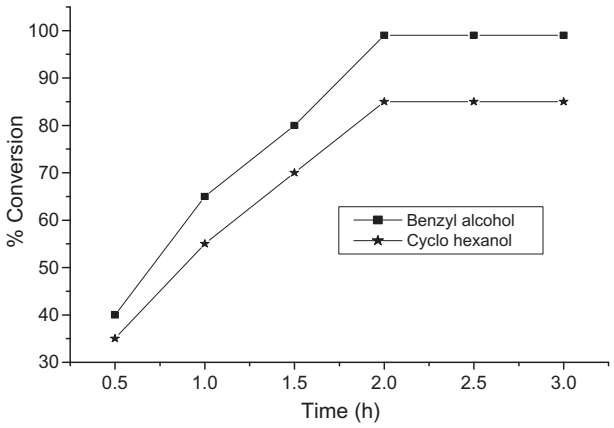


Fig. 3. Catalytic oxidation of benzylalcohol and cyclohexanol in different time intervals.

Table 1
Catalytic oxidation data of ruthenium(II) complexes.

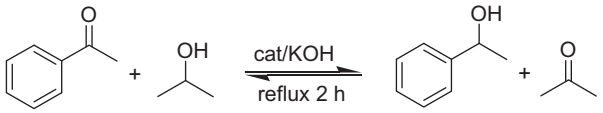
Complex	Substrate	Product	Conversion (%)[a]
[RuCl(CO)(PPh_3)(L_1)]	Benzyl alcohol	Benzaldehyde	94
	Cyclohexanol	Cyclohexanone	80
[RuCl(CO)(PPh_3)(L_2)]	Benzyl alcohol	Benzaldehyde	99
	Cyclohexanol	Cyclohexanone	87
[RuCl(CO)(PPh_3)(L_3)]	Benzyl alcohol	Benzaldehyde	96
	Cyclohexanol	Cyclohexanone	79
[RuCl(CO)(Py)(L_1)]	Benzyl alcohol	Benzaldehyde	90
	Cyclohexanol	Cyclohexanone	76
[RuCl(CO)(Py)(L_2)]	Benzyl alcohol	Benzaldehyde	92
	Cyclohexanol	Cyclohexanone	76
[RuCl(CO)($AsPh_3$)(L_1)]	Benzyl alcohol	Benzaldehyde	92
	Cyclohexanol	Cyclohexanone	78
[RuCl(CO)($AsPh_3$)(L_2)]	Benzyl alcohol	Benzaldehyde	94
	Cyclohexanol	Cyclohexanone	81
[RuCl(CO)($AsPh_3$)(L_3)]	Benzyl alcohol	Benzaldehyde	94
	Cyclohexanol	Cyclohexanone	79
[RuH(CO)(PPh_3)(L_1)]	Benzyl alcohol	Benzaldehyde	95
	Cyclohexanol	Cyclohexanone	83
[RuH(CO)(PPh_3)(L_2)]	Benzyl alcohol	Benzaldehyde	97
	Cyclohexanol	Cyclohexanone	84

[a] The conversion of product determined by GC and comparing with analyses of authentic samples.

Results of the present investigations suggest that the complexes are able to react efficiently with NMO to yield a high valent ruthenium-oxo species capable of oxygen atom transfer to alcohols. This was further supported by spectral changes that occur by addition of NMO to dichloromethane solution of the ruthenium(II) complexes. The appearance of a peak at 390 nm is attributed to the formation of RuIV = O species, which is in confirmed with other oxo ruthenium(IV) complexes [42,43]. Further support in favor of the formation of such species was identified from the IR spectrum of the solid mass (obtained by evaporation of the resultant solution to dryness), which showed a band at 860 cm^{-1}, characteristic of RuIV = O species [44].

Catalytic transfer hydrogenation

Transfer hydrogenation of ketone in the presence of ruthenium(II) complexes has been studied in isopropanol/KOH medium (Scheme 1). The reactions were conducted at a catalyst, substrate and base (C/S/base) in molar ratio 1:500:2.5 respectively. In order to optimize the reaction conditions, different catalyst:substrate (C/S) ratios were tested and the results are summarized in Table 2.



Scheme 1. Catalytic transfer hydrogenation of ketone.

Table 2
Catalytic transfer hydrogenation by $[RuCl(CO)(PPh_3)L_2]$/i-PrOH/KOH.[a]

Entry	C/S	Time (h)	Conversion (%)[b]
1	1:1500	2	73
2	1:1000	2	86
3	1:500	2	99

[a] Conditions: reactions were carried out at 80 °C using substrate (5–15 mmol), catalyst (0.01 mmol) in 10 ml of isopropanol, KOH (0.025 mmol).
[b] The conversion of product determined by GC and comparing with analyses of authentic samples.

For the initial experiments, cyclohexanone was selected as a test substrate and was allowed to react in 2-propanol with catalytic quantity of $[Ru(Cl)(CO)(PPh_3)L_2]$ in the presence of KOH. When increasing the C/S ratio to 1:1000, 1:1500 in 2-propanol, the reaction proceeds with lower conversions. Thus, it was concluded that catalyst:substrate ratio of 1:500 is the best compromise between optimum reaction rate and C/S ratio in 2-propanol.

The ruthenium(II) complexes reduces the aliphatic and aromatic ketones with good conversions over a period of 2 h (Table 3). The conversion of cyclohexanone to cyclohexanol was completed with 99% yield. 4-Methylpentane-2-one underwent transfer hydrogenation to afford the corresponding alcohol up to 70–78% yield. Similarly, acetophenone was converted to 1-phenylethanol up to 82–89% yield. In this reaction, the base facilitates the formation of ruthenium alkoxide by abstracting the proton of the alcohol and subsequent β-elimination of alkoxide generates ruthenium-hydride, which is an active species in this reactions. Although no mechanistic studies have been performed, the catalytic transformation of ketones most probably follows the classical pathway in which ketones coordinate to hydride ruthenium metal intermediate [45,46].

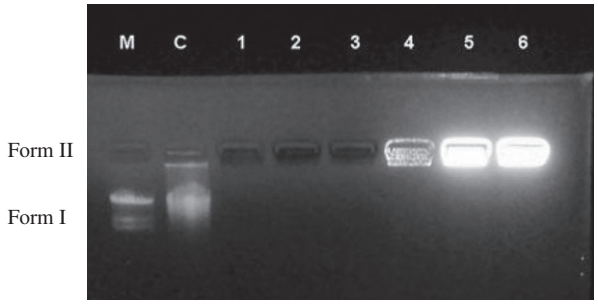


Fig. 4. Agarose gel electrophoresis diagram showing the cleavage DNA of Escherichia coli by ruthenium(II) complex in TAE Buffer (4.84 g Tris base, pH = 8, 0.5 M EDTA/1 l). Lane M, DNA alone, Lane C, Control DNA (untreated complex). Lane 1, 2 & 3 by $[RuCl(CO)(PPh_3)L_2]$ at 20, 40 & 60 μg/ml respectively, Lane 4, 5 & 6 by $[RuCl(CO)(PPh_3)L_3]$ at 20, 40 & 60 μg/ml respectively.

DNA cleavage studies

When circular plasmid DNA is subjected to electrophoresis, relatively fast migration will be observed for the intact supercoil form (Form I), if scission occurs on one strand (nicking), the supercoil will relax to generate a slower-moving open circular form (Form II) [47]. The gel electrophoresis separation of supercoiled DNA of Escherichia coli after incubation with the complexes $[RuCl(CO)(PPh_3)(L_2)]$, $[RuCl(CO)(PPh_3)(L_3)]$ and irradiated at UV is shown in Fig. 4. No obvious DNA cleavage was observed for controls in which complexes were absent. The complexes exhibited single-strand cleavage of supercoiled Form I to nicked Form II.

Table 3
Catalytic transfer hydrogenation of ketones by ruthenium(II) complexes.

Complex	Substrate	Product	Conversion (%)[a]
$[RuCl(CO)(PPh_3)(L_1)]$	Acetophenone	1-Phenylethanol	87
	4-Methylpentane-2-one	4-Methylpentane-2-ol	75
	Cyclohexanone	Cyclohexanol	97
$[RuCl(CO)(PPh_3)(L_2)]$	Acetophenone	1-Phenylethanol	89
	4-Methylpentane-2-one	4-Methylpentane-2-ol	78
	Cyclohexanone	Cyclohexanol	99
$[RuCl(CO)(PPh_3)(L_3)]$	Acetophenone	1-Phenylethanol	86
	4-Methylpentane-2-one	4-Methylpentane-2-ol	76
	Cyclohexanone	Cyclohexanol	97
$[RuCl(CO)(Py)(L_1)]$	Acetophenone	1-Phenylethanol	82
	4-Methylpentane-2-one	4-Methylpentane-2-ol	70
	Cyclohexanone	Cyclohexanol	93
$[RuCl(CO)(Py)(L_2)]$	Acetophenone	1-Phenylethanol	83
	4-Methylpentane-2-one	4-Methylpentane-2-ol	73
	Cyclohexanone	Cyclohexanol	95
$[RuCl(CO)(AsPh_3)(L_2)]$	Acetophenone	1-Phenylethanol	85
	4-Methylpentane-2-one	4-Methylpentane-2-ol	74
	Cyclohexanone	Cyclohexanol	95
$[RuCl(CO)(AsPh_3)(L_3)]$	Acetophenone	1-Phenylethanol	84
	4-Methylpentane-2-one	4-Methylpentane-2-ol	72
	Cyclohexanone	Cyclohexanol	93
$[RuH(CO)(PPh_3)(L_1)]$	Acetophenone	1-Phenylethanol	86
	4-Methylpentane-2-one	4-Methylpentane-2-ol	76
	Cyclohexanone	Cyclohexanol	96
$[RuH(CO)(PPh_3)(L_2)]$	Acetophenone	1-Phenylethanol	87
	4-Methylpentane-2-one	4-Methylpentane-2-ol	76
	Cyclohexanone	Cyclohexanol	98

[a] Conversion determined by GC and comparing with the analysis of authentic sample.

Conclusions

Several ruthenium(II) complexes of the composition [RuX(-CO)(B)(L)] (where X=H or Cl, B = PPh_3, $AsPh_3$ or Py, L = ligand) have been synthesized by reacting ruthenium(II) starting complexes [$RuHX(CO)(EPh_3)_2(B)$] (where X=H or Cl, E = P or As, B = PPh_3, $AsPh_3$ or Py) with ligand under reflux. The new complexes obtained were characterized on the basis of elemental analysis and spectral (FT-IR, electronic, ^1H, ^{13}C NMR, ^{31}P NMR and ESI-MS) data. An octahedral structure has been tentatively proposed for all the complexes. The complexes showed efficient catalytic property for oxidation of both primary and secondary alcohols to the corresponding carbonyl compounds in the presence of NMO and also for transfer hydrogenation of aliphatic and aromatic ketones with high conversions. The complexes also efficiently cleaved the DNA, even at low concentration.

Acknowledgements

The authors express their sincere thanks to Council of Scientific and Industrial Research (CSIR), New Delhi [Grant No. 01(2437)/10/EMR-II] for financial support. One of the authors (PA) thanks CSIR for the award of Senior Research Fellowship.

References

[1] (a) D.M. Wiles, B.A. Gingras, T. Suprunchuk, Can. J. Chem. 45 (1967) 469–473;
(b) A.G. Bingham, H. Bogge, A. Muller, E.W. Ainscoing, A.M. Brodie, J. Chem. Soc. Dalton Trans. (1987) 493–499;
(c) D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, P.B. Sonawane, A.S. Kumbhar, R.G. Yerande, Coord. Chem. Rev. 123 (1993) 49–71;
(d) D.X. West, G.A. Bain, J. Butcher, J.P. Jasinski, Y. Li, Y. Pozdniakv, J. Valdes-Martınez, A.R. Toscano, S. Hernandez-Ortega, Polyhedron 15 (1996) 665–674.
[2] (a) F. Basuli, S.M. Peng, S. Bhattacharya, Inorg. Chem. 39 (2000) 1120–1127;
(b) S. Kannan, M. Sivagamasundari, R. Ramesh, Y. Liu, J. Organomet. Chem. 693 (2008) 2251–2257.
[3] (a) D.X. West, S.B. Padhye, P.B. Sonawane, Struct. Bonding 76 (1991) 1–50;
(b) J.M. Vila, T. Pereira, J.M. Ortigueira, M. Lopez-Torres, A. Castineiras, D. Lata, J.J. Fernandez, A. Fernandez, J. Organomet. Chem. 556 (1998) 21–30;
(c) J.M. Vila, M.T. Pereira, J.M. Ortigueira, M. Grana, D. Lata, A. Suarez, J.J. Fernandez, A. Fernandez, M. Lopez-Torres, H. Adams, J. Chem. Soc. Dalton Trans. (1999) 4193–4201.
[4] W. Kaim, M. Wanner, A. Knodler, S. Zalis, Inorg. Chim. Acta 337 (2002) 163–172.
[5] B.I. Kharisov, M.A. Mendez-Rojas, A.D. Garnovskii, E.P. Ivakhnenko, U. Ortiz-Mendez, J. Coord. Chem. 55 (2002) 745–770.
[6] X.X. Liu, W.T. Wong, Eur. J. Inorg. Chem. (2001) 511–520.
[7] I. Banerjee, M. Sivakumar, A. Chakravorty, Polyhedron 21 (2002) 2761–2765.
[8] C.G. Pierpont, C.W. Lange, Prog. Inorg. Chem. 41 (1994) 331–442.
[9] (a) J.N. Lopes, F.S. Cruz, R. Docampo, Ann. Trop. Med. Parasitol. 72 (1978) 523–531;
(b) M.P. Molina Portela, S.H. Fernandez Villamil, L.J. Perissinotti, A.O. Stoppani, Biochem. Pharmacol. 52 (1996) 1875–1882.
[10] D.K. Saha, S. Padhye, E. Sinn, K. Newton, Ind. J. Chem. 41 (2002) 279–283.
[11] A.S. Kumbhar, S.B. Padhye, D. Ross, Biometals 9 (1996) 235–240.
[12] Z. Afrasiabi, E. Sinn, J. Chen, Y. Ma, A.L. Rheingold, L.N. Zakharov, N. Rath, S. Padhye, Inorg. Chim. Acta 357 (2004) 271–278.
[13] N.G. Gokhale, S.B. Padhye, C.J. Newton, R. Pritchard, Met. Based Drugs 7 (2000) 121–128.
[14] Z. Afrasiabi, E. Sinn, S. Padhye, S. Dutta, S.B. Padhye, C. Newton, C.E. Anson, A.K. Powell, J. Inorg. Biochem. 95 (2003) 306–314.
[15] Z. Afrasiabi, E. Sinn, W. Lin, Y. Ma, C. Campana, S. Padye, J. Inorg. Biochem. 99 (2005) 1526.
[16] E.P. Kelson, P.P. Phengsy, J. Chem. Soc. Dalton Trans. (2000) 4023–4024.
[17] (a) S.M.J. Samec, A.H. Ell, J.E. Backvall, Chem. Commun. (2004) 2748–2749;
(b) G. Venkatachalam, R. Ramesh, Inorg. Chem. Commun. 9 (2006) 703–707.
[18] R. Noyori, H. Takaya, Acc. Chem. Res. 23 (1990) 345–350.
[19] R.L. Chowdhury, J.E. Backvall, J. Chem. Soc. Chem. Commun. (1991) 1063–1064.
[20] I.W.C.E. Arends, T. Kodama, R.A. Sheldon, Topics in Organometallic Chemistry, Springer, Berlin, 2004.
[21] M. Pagliaro, S. Campestrini, R. Ciriminna, Chem. Soc. Rev. 34 (2005) 837–845.
[22] P.K. Bhattacharya, J.K. Barton, J. Am. Chem. Soc. 123 (2001) 8649–8656.
[23] A.I. Vogel, Text book of Practical Organic Chemistry, fifth ed., Longman, London, 1989.
[24] N. Ahmed, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 45–64.
[25] S. Gopinathan, I.R. Unny, S.S. Deshpande, C. Gopinathan, Ind. J. Chem. (1986) 1015–1017.
[26] R.A. Sanchez-Delgado, W.Y. Lee, S.R. Choi, Y. Cho, J. Jun, Trans. Met. Chem. 16 (1991) 241–244.
[27] J. Sambrook, E.F. Fritsch, T. Maniatis, Molecular cloning, A laboratory Manual, Second ed., Cold Spring, Harbor Laboratory, Cold Spring Harbor, New York, 1989.
[28] M. Wang, L. Wang, Y.Z. Li, Q.X. Li, Z.D. Xu, D.M. Qu, Trans. Met. Chem. 26 (2001) 307–310.
[29] G. Ibrahim, E. Chebli, M.A. Khan, G.M. Bouet, Trans. Met. Chem. 24 (1999) 294–298.
[30] S.Y. He, J.L. Chen, R. Yang, W.T. Wu, J.S. Zhao, Q.Z. Shi, R.X. Wang, Chin. J. Org. Chem. 23 (2003) 1387–1392.
[31] E.M. Jouad, A. Riou, M. Allain, M.A. Khan, G.M. Bouet, Polyhedron 20 (2001) 67–74.
[32] L.J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen, London, 1985.
[33] D.M. Boghaei, S. Mohebi, J. Mol. Cat. A: Chem. 179 (2002) 41–51.
[34] K. Nareshkumar, R. Ramesh, Polyhedron 24 (2005) 1885–1892.
[35] K. Nareshkumar, R. Ramesh, Spectrochim. Acta A 60 (2004) 2913–2918.
[36] M.S. El-Shahawi, A.F. Shoair, Spectrochim. Acta A 60 (2004) 121–127.
[37] M.V. Kaveri, R. Prabhakaran, K. Natarajan, Spectrochim. Acta A 61 (2005) 2915–2918.
[38] (a) M.C. Rodriguez-Arguelles, M.B. Ferrari, G.G. Fava, C. Pelizzi, G. Pelosi, R. Albertini, A. Bonati, P.P. Dall_Aglio, P. Lunghi, S. Pinelli, J. Inorg. Biochem. 66 (1997) 7–17;
(b) J.S. Cassas, A. Castineiras, M.C. Rodriguez-Arguelles, A. Sanchez, J. Sordo, A. Vazquez- Lopez, E.M. Vazquez-Lopez, J. Chem. Soc. Dalton Trans. (2000) 4056–4063.
[39] K. Singh, B.V. Agarwala, G.A. Naganagowda, Ind. J. Chem. A 35 (1996) 66–68.
[40] J. Matthes, S. Grundemann, A. Toner, Y. Guari, B. Donnadieu, J. Spandl, S. Sabo-Etienne, E. Clot, H.H. Limbach, B. Chaudret, Organometallics 23 (2004) 1424–1433.
[41] K.P. Balasubramaniun, R. Karvembu, R. Prabhakaran, V. Chinnusamy, K. Natarajan, Spectrochim. Acta A 65 (2006) 678–683.
[42] A.M. El-Hendaey, A.H. Alkubaisi, A.E. Koursahy, M.M. Shanab, Polyhedron 12 (1993) 2343–2350.
[43] M.M.T. Khan, Ch. Sreelatha, S.A. Mizra, G. Ramachandraiah, S.H.R. Abdi, Inorg. Chim. Acta 154 (1988) 103–108.
[44] M. Sivagamasundari, R. Ramesh, Spectrochim. Acta A 67 (2007) 256–262.
[45] R.K. Rath, M. Nethaji, A.R. Chakravarty, Polyhedron 20 (2001) 2735–2739.
[46] G. Venkatachalam, R. Ramesh, Tetrahedron Lett. 46 (2005) 5215–5218.
[47] J.K. Barton, A.L. Raphael, J. Am. Chem. Soc. 106 (1984) 2466–2468.