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Binuclear Ruthenium(II) Carbonyl Schiff Base Complexes Containing N_2O_2 Donors and their Catalytic and Biological Activities

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An interesting series of binuclear ruthenium(II) Schiff base complexes of the type $[RuCl(CO)(EPh_3)_2(B)]_2L$ (where E=P/As; B=PPh_3/$AsPh_3$/Py; L=binucleating monobasic bidendate Schiff base ligand) have been synthesized by reacting $[RuCl(CO)(EPh_3)_2(B)]_2$ with Schiff bases derived from acetoacetanilide and salicylaldehyde/o-hydroxyacetophenone/o-vanillin/2-hydroxy-1-naphthaldehyde with benzene. The complexes were characterized by analytical, spectroscopic, and electrochemical measurements. The new diamagnetic ruthenium(II) complexes have N_2O_2 metal binding sites, which are linked to each other with a biphenyl bridge and act as potential catalyst for the oxidation of wide range of primary and secondary alcohols to corresponding aldehydes and ketones in the presence of molecular oxygen and also in C—C coupling reactions. Further, the antibacterial properties of the free ligands and their metal complexes were evaluated against certain bacteria such as Escherichia Coli and Staphylococcus aureus.

Keywords antibacterial activity, binucleating ligand, binuclear ruthenium(II) complex, catalytic activity, electrochemistry

INTRODUCTION

The coordination chemistry of binuclear transition metal complexes has received much attention in recent years.[1,2] Transition metal complexes, with bidentate ligands containing both the hard and soft donor groups, have been used extensively in coordination and organometallic chemistry. The majority of such ligands are functionalized phosphines where the phosphorus is a soft donor and either oxygen or nitrogen is the hard donor.[3,4] Currently, a considerable effort is being invested in the development of new chelating ligands; particularly, the binucleating imino ligands are versatile and they exhibit very rich coordination chemistry. Such species occupy an important position in modern inorganic chemistry.[5,6] Much research works have been published concerning the use of Schiff base ligands, which incorporate nitrogen imine, and phenolate donors seems appropriate synthesizing ruthenium complexes capable of oxidizing organic substrates.[7,8] Schiff base complexes of transition metals[9] having O and N donor atoms have shown an exponential increase as inorganic catalysts for various organic transformations. Furthermore, binuclear complexes have been found to be better catalysts than mononuclear complexes.[10] Also, transition metalphosphine/arsine complexes, especially ruthenium complexes, find application in classical catalytic processes such as hydrogenation, isomerization, decarboxylation, reductive elimination, oxidative addition, and in making C—C bonds.[11] The incorporation of binucleating Schiff base ligand into ruthenium tertiary phosphine/arsine complexes was initially aimed at promoting activity of such species towards oxidation of alcohols. Selective oxidation of alcohols to aldehydes and ketones is a key reaction in organic synthesis. The development of new products that can use air or molecular oxygen as oxidant is certainly more attractive than other traditional methods that are environmentally damaging.[12]

Metal ions in ligand-bridged binuclear complexes have gained an importance due to the intramolecular electron transfer processes that find utility in the design of photochemical molecular devices[10] or as bio-mimetic model of the photosynthetic systems in biology.[13] Bimetallic coordination complexes have numerous applications, such as in the treatment of cancer,[14] as antibacteriocide agents,[15] as antiviral agents,[16] and for other biological properties.[17] Chelation causes drastic changes in the biological properties of a ligand and also the metal moiety.

As part of our systematic study on ligand-bridged binuclear ruthenium complexes, we describe the synthesis and characterization of a series of new class of binuclear ruthenium(II) Schiff base complexes along with their catalytic and biological activity. The following binucleating Schiff base ligands (Scheme 1) containing N_2O_2 type bidentate compartments were used to synthesize a new series of binuclear ruthenium(II) Schiff base complexes.

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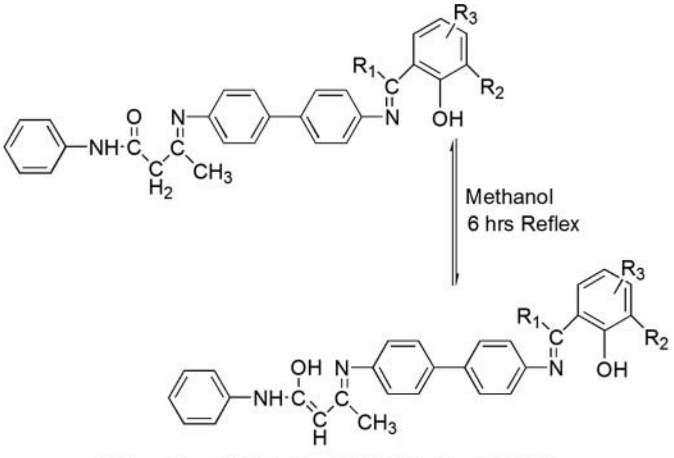


Where R_1=H/CH_3; R_2=H/OCH_3; R_3=H/C_4H_4

SCH. 1. Keto-enol tautomerism of the Schiff base ligands.

EXPERIMENTAL

Materials and Physical Measurements

All the chemicals used were chemically pure and AR grade. Solvents were purified and dried according to the standard procedure.[18] $RuCl_3.3H_2O$ was purchased from Loba Chemie and was used without any further purification. The carbon, hydrogen, nitrogen, and sulphur analyses were performed on a Vario EL III CHNS analyzer at Cochin University of Science and Technology, Kerala, India. IR spectra were recorded as KBr pellets in the 400–4000 cm^{-1} region using a Perkin Elmer FT-IR 8000 spectrophotometer. Electronic spectra were recorded in dichloromethane solution with a Systronics double beam UV-Vis spectrophotometer 2202 in the range 200–800 nm. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHZ instrument using TMS as an internal reference. ^{31}P NMR spectra were recorded on a Bruker 400 MHZ instrument using ortho phosphoric acid as an internal reference. Electrochemical studies were carried out on a BAS CV-50 electrochemical analyzer in dichloromethane solution by using a glassy carbon working electrode and $[NBu_4]ClO_4$ was used as a supporting electrolyte. Melting points were recorded on a Veego VMP-DS model heating table and were uncorrected. The starting complexes $[RuHCl(CO)(PPh_3)_3]$,[19] $[RuHCl(CO)(AsPh_3)_3]$,[20] and $[RuHCl(CO)(PPh_3)_2(Py)]$[21] were prepared according to the reported procedures. Catalytic oxidation,[22] aryl-aryl coupling experiments,[23] and antibacterial activities[24] were carried out by using reported literature methods.

Preparation of Binucleating Mono Basic Bidentate Schiff Base Ligands

To a methanolic solution of benzidine (10 mmol) salicylaldehyde/o-hydroxyacetophenone/o-vanillin/2-hydroxy-1-naphthaldehyde (10 mmol) was added and kept for stirring. Then to the above stirring solution of acetoacetanilide (10 mmol) was added. The mixture was stirred for about half an hour and then refluxed for about 6 hrs. The resultant product was washed with methanol and the purity of the ligands was checked by TLC.

Synthesis of Binuclear Ruthenium(II) Schiff Base Complexes

All the reactions were carried out under the strictly anhydrous condition. The monobasic bidentate Schiff bases (0.04–0.05 g; 0.1 mmol) were added to a solution of $[RuHCl(CO)(EPh_3)_2(B)]$, (E=P/As; B=PPh_3/$AsPh_3$/Py) in 2:1 molar ratio in benzene/chloroform (50 mL) mixture, and then refluxed for 6 hrs. The resulting compound was precipitated by the addition of small quantity of petroleum ether (60–80°C). The complexes were then filtered off, washed with petroleum ether, and recrystallized from CH_2Cl_2/petroleum ether and dried under vacuo.

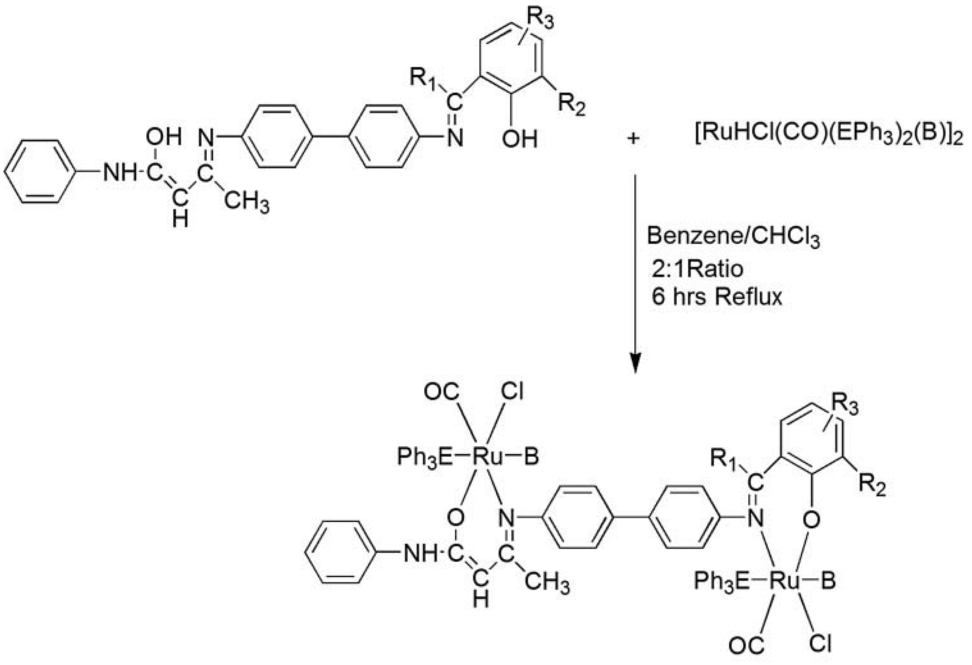
RESULTS AND DISCUSSION

A new series of binuclear ruthenium(II) Schiff base complexes of the type $[RuCl(CO)(EPh_3)_2(B)]_2L$ (E=P/As; B=PPh_3/$AsPh_3$/Py; L= monobasic bidentate Schiff base ligands) were achieved by reacting binuclear ruthenium(II) precursors $[RuHCl(CO)(EPh_3)_2(B)]$ with monobasic bidentate Schiff base ligands in 2:1molar ratio, respectively, in benzene/chloroform mixture (Scheme 2).

The synthesized binuclear ruthenium(II) Schiff base complexes are stable in air at room temperature, non-hygroscopic in nature, and soluble in common solvents such as dichloromethane, chloroform, acetonitrile, benzene, and THF. The analytical data of the complexes are in good agreement with the calculated values thus confirming the proposed binuclear composition for all the complexes (Table 1).

IR Spectroscopy

The important IR absorption bands for the synthesized complexes are shown in Table 2. The observed bands may be classified into those originating from the ligands and those arising from the bands formed between ruthenium(II) metal ion and the coordinating sites. A strong band observed around 1700 cm^{-1} in the free Schiff base ligands due to $\nu_{C=O}$ completely disappeared on complexation. This may be due to the enolization and subsequent coordination through the deprotonated enolised oxygen atom.[25] The azomethine nitrogen $\nu_{C=N}$ stretching frequency of the free ligands (H_2L^1-H_2L^4) appears at 1618–1621 cm^{-1}, which has been shifted to lower frequency in the range 1592–1606 cm^{-1} in accordance with the coordination of the azomethine function to the metal ion for all complexes.[26,27] This lowering frequency may be attributed to the decrease in electron density on the nitrogen atom of the azomethine group. In all the complexes, the bands in the region 1460–1531 cm^{-1} have been assigned to the mixed vibrational mode arising from $\nu_{C=N}$ and $\nu_{C—C}$.[28] A medium band corresponding to phenolic oxygen ν_{C-O} is observed at 1250–1283 cm^{-1} for the free ligands, respectively. On complexation, this



Where E=P/As; B=PPh3/AsPh3/Py

SCH. 2. Structure of binuclear ruthenium(II) Schiff base complexes.

band is shifted to higher frequency in the range 1309–1322 cm^{-1} for all the ruthenium(II) Schiff base complexes.[29] This is further supported by the disappearance of the ν_{OH} in the range 3027–3412 cm^{-1} in all the complexes. For all the new complexes, the IR spectra showed a strong band in the region 1938–1957 cm^{-1} due to terminally coordinated free carbonyl group. For the complexes $\{[RuCl(CO)(PPh_3)(Py)]_2L^1\}$, $\{[RuCl(CO)(PPh_3)(Py)]_2L^2\}$, $\{[RuCl(CO)(PPh_3)(Py)]_2L^3\}$ and $\{[RuCl(CO)(PPh_3)(Py)]_2L^4\}$, the IR spectra showed a medium intensity band in the region 1027–1028 cm^{-1},

TABLE 1
Analytical data for binuclear ruthenium(II) Schiff base complexes

Ligands and complexes	Color	Melting point (°C)	Calculated (found) (%) C	H	N
H_2L^1	Yellow	128	77.83 (77.86)	5.63 (5.60)	9.39 (9.37)
H_2L^2	Yellow	130	78.09 (78.02)	5.89 (5.83)	9.10 (9.13)
H_2L^3	Orange	125	75.45 (75.40)	5.69 (5.64)	8.79 (8.75)
H_2L^4	Orange	126	79.65 (79.67)	5.46 (5.42)	8.44 (8.40)
$\{[RuCl(CO)(PPh_3)_2]_2L^1\}$	Black	136	67.84 (67.86)	4.59 (4.54)	2.30 (2.31)
$\{[RuCl(CO)(AsPh_3)_2]_2L^1\}$	Green	134	61.87 (61.83)	4.18 (4.16)	2.10 (2.14)
$\{[RuCl(CO)(Py)(PPh_3)]_2L^1\}$	Green	144	63.46 (63.41)	4.36 (4.31)	4.81 (4.82)
$\{[RuCl(CO)(PPh_3)_2]_2L^2\}$	Black	172	67.97 (67.93)	4.66 (4.63)	2.29 (2.32)
$\{[RuCl(CO)(AsPh_3)_2]_2L^2\}$	Brown	138	62.04 (62.01)	4.26 (4.28)	2.09 (2.07)
$\{[RuCl(CO)(Py)(PPh_3)]_2L^2\}$	Black	164	63.67 (63.63)	4.45 (4.47)	4.76 (4.73)
$\{[RuCl(CO)(PPh_3)_2]_2L^3\}$	Green	154	67.39 (67.34)	4.62 (4.65)	2.27 (2.24)
$\{[RuCl(CO)(AsPh_3)_2]_2L^3\}$	Brown	137	61.55 (61.51)	4.22 (4.20)	2.07 (2.05)
$\{[RuCl(CO)(Py)(PPh_3)]_2L^3\}$	Green	164	63.03 (63.06)	4.34 (4.37)	4.71 (4.74)
$\{[RuCl(CO)(PPh_3)_2]_2L^4\}$	Green	142	68.59 (68.54)	4.57 (4.59)	2.24 (2.21)
$\{[RuCl(CO)(AsPh_3)_2]_2L^4\}$	Orange	139	62.70 (62.73)	4.18 (4.17)	2.05 (2.03)
$\{[RuCl(CO)(Py)(PPh_3)]_2L^4\}$	Green	155	64.54 (64.52)	4.35 (4.39)	4.65 (4.63)

TABLE 2
IR and electronic data of binuclear ruthenium(II) Schiff base complexes

Ligands and complexes	FT-IR cm^{-1} $\nu_{(C=N)}$	$\nu_{(Ph-C-O)}$	$\nu_{(C=N+C=CH)}$	$\nu_{(C\equiv O)}$	$\nu_{(Py)}$	UV-Vis λ_{max} (nm)
H_2L^1	1618	1283	—	—	—	304, 368, 411
H_2L^2	1620	1273	—	—	—	302, 369, 390, 411
H_2L^3	1621	1280	—	—	—	304, 368, 414
H_2L^4	1621	1250	—	—	—	305, 368, 412, 444, 483
$\{[RuCl(CO)(PPh_3)_2]_2L^1\}$	1605	1322	1514	1954	—	256, 291, 442
$\{[RuCl(CO)(AsPh_3)_2]_2L^1\}$	1606	1322	1517	1957	—	256,292, 366, 389
$\{[RuCl(CO)(Py)(PPh_3)]_2L^1\}$	1604	1312	1531	1940	1028	256, 293, 366, 390
$\{[RuCl(CO)(PPh_3)_2]_2L^2\}$	1600	1312	1513	1947	—	256, 296, 363, 389
$\{[RuCl(CO)(AsPh_3)_2]_2L^2\}$	1603	1310	1484	1952	—	254, 294, 358,
$\{[RuCl(CO)(Py)(PPh_3)]_2L^2\}$	1592	1311	1512	1938	1028	254, 360, 390
$\{[RuCl(CO)(PPh_3)_2]_2L^3\}$	1600	1312	1513	1948	—	254, 294, 344, 389, 467
$\{[RuCl(CO)(AsPh_3)_2]_2L^3\}$	1594	1309	1460	1950	—	254, 296, 364, 389, 456
$\{[RuCl(CO)(Py)(PPh_3)]_2L^3\}$	1602	1312	1514	1940	1028	254, 296, 350, 387, 467
$\{[RuCl(CO)(PPh_3)_2]_2L^4\}$	1601	1310	1510	1949	—	254, 293, 357, 389, 466
$\{[RuCl(CO)(AsPh_3)_2]_2L^4\}$	1600	1309	1513	1949	—	251, 338, 390
$\{[RuCl(CO)(Py)(PPh_3)]_2L^4\}$	1601	1310	1510	1944	1027	256, 296, 356, 394, 438

which has the characteristic of coordinated nitrogen base.[21] Characteristic bands for triphenylphosphine/arsine were also present in the expected region 1433–1437 cm^{-1}.[30]

Electronic Spectra

The electronic absorption spectra of the free ligands and their complexes in CH_2Cl_2 were recorded and the values are listed in Table 2. The spectra of the free ligands showed that two types of transitions appearing in the range 302–305 and 368–483 nm were due to $\pi - \pi^*$ and n-π^* transitions involving molecular orbital of the C=N, phenolic–OH and enolic-OH chromophore. These bands were shifted in the spectra of the complexes, indicating the involvement of imine group nitrogen, phenolic oxygen, and enolic oxygen in coordination with central metal atom. The spectra of the complexes showed three to five bands in the region 251–467 nm. All the Schiff base ruthenium complexes were diamagnetic, indicating the presence of ruthenium in +2 oxidation state. The ground state of ruthenium(II) in an octahedral environment is $^1A_{1g}$, arising from the t_{2g}^6 configuration, and the excited states corresponding to the $t_{2g}^5e_g^1$ configuration are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Hence, four bands corresponding to the transitions $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ are possible in order of the increasing energy. The binuclear ruthenium(II) complexes in the visible region display the high intensity band in the range 438–467 nm was assigned to be the LMCT transitions.[31–33] The band observed in the range 251–296 nm were assigned to $\pi - \pi^*$ transition from the benzene ring and the double bond of the azomethine group. The bands in the 338–394 nm regions were due to n-π^* transition of non-bonding electrons present on the nitrogen of the azomethine group in the binuclear ruthenium(II) complexes. The pattern of the electronic spectra for the complexes indicated the presence of an octahedral environment around the binuclear ruthenium(II) ion similar to that of the other ruthenium octahedral complexes.[32,33]

^{1}H, ^{31}P, and ^{13}C NMR Spectra

The ^{1}H-NMR spectra of ligands and the binuclear ruthenium(II) complexes were recorded in DMSO-d6 solution to confirm the binding mode of the Schiff base to ruthenium ion and the values are given in Table 3. The aromatic protons for all the ligands appeared as a multiplet at 6.6–7.9 ppm. The acetoacetanilide moiety of NH, CH, CH_3 and enolic-OH protons appear as a singlet at 3.5–3.9, 2.3–3.7, 1.6–2.8, and 12.2–15.5 ppm, respectively. The azomethine proton of H_2L^1, H_2L^3, and H_2L^4 ligands appear as singlet at 8.1–8.3 ppm. For the ligand H_2L^2, the methyl protons appear as singlet at 2.3 ppm. The methoxy protons for H_2L^3 ligand appears as singlet at 2.4 ppm. For all the ligands the phenolic-OH protons appear as singlet in the range 9.0–9.4 ppm. On complexation, multiplets are observed around 6.6–7.9 ppm have been assigned for aromatic protons and triphenylphosphine/arsine/pyridine protons. The NH, CH and CH_3 protons in all the complexes appears as singlet at 3.3–3.4, 2.3–3.8, and 1.4–2.9 ppm. The complexes containing the azomethine protons appear as singlet in the range 7.8–8.6 ppm. The N=C−CH_3 protons appear as singlet at 2.2 ppm in the complexes $\{[RuCl(CO)(PPh_3)_2]_2L^2\}$, $\{[RuCl(CO)(AsPh_3)_2]_2L^2\}$ and $\{[RuCl(CO)(PPh_3)(Py)]_2L^2\}$. The methoxy protons in the complexes $\{[RuCl(CO)(PPh_3)_2]_2L^3\}$, $[RuCl(CO)(AsPh_3)_2]_2L^3$

TABLE 3
^{1}H NMR spectra of binuclear ruthenium(II) Schiff base complexes

Ligands and complexes	^{1}H NMR spectra
H_2L^1	6.9–7.8 (m, Ar), 3.95 (s, NH), 12.2 (s, enolic-OH), 2.65 (s, CH), 2.19 (s, CH_3), 8.34 (s, HC=N), 9.05 (Ph-OH)
H_2L^2	6.6–7.6 (m, Ar), 3.57 (s, NH), 12.3 (s, enolic-OH), 2.63 (s, CH), 2.31 (s, CH_3), 2.13 (s, CH_3-C=N), 9.05 (Ph-OH)
H_2L^3	6.6–7.9 (m, Ar), 3.84 (s, NH), 13.3 (s, enolic-OH), 3.74 (s, CH), 2.88 (s, CH_3), 8.20 (s, HC=N), 9.45 (Ph-OH), 2.48 (s, OCH_3)
H_2L^4	6.7–7.8 (m, Ar), 3.63 (s, NH), 15.5 (s, enolic-OH), 2.33 (s, CH), 1.60 (s, CH_3), 8.13 (s, HC=N), 9.40 (Ph-OH)
$\{[RuCl(CO)(PPh_3)_2]_2L^1\}$	7.0–7.7 (m, Ar), 3.4 (s, NH), 2.65 (s, CH), 2.3 (s, CH_3), 7.85 (s, HC=N)
$\{[RuCl(CO)(AsPh_3)_2]_2L^1\}$	7.3–7.9 (m, Ar), 3.43 (s, NH), 2.64 (s, CH), 2.3 (s, CH_3), 8.34 (s, HC=N)
$\{[RuCl(CO)(Py)(PPh_3)]_2L^1\}$	7.2–7.8 (m, Ar), 3.4 (s, NH), 2.65 (s, CH), 2.2 (s, CH_3), 8.40 (s, HC=N)
$\{[RuCl(CO)(PPh_3)_2]_2L^2\}$	6.9–7.7 (m, Ar), 3.4 (s, NH), 2.60 (s, CH), 2.2 (s, CH_3), 2.2 (s, CH_3-C=N)
$\{[RuCl(CO)(AsPh_3)_2]_2L^2\}$	7.3–7.7 (m, Ar), 3.35 (s, NH), 2.65 (s, CH), 2.2 (s, CH_3), 2.2 (s, CH_3-C=N)
$\{[RuCl(CO)(Py)(PPh_3)]_2L^2\}$	7.2–7.7 (m, Ar), 3.4 (s, NH), 2.5 (s, CH), 2.2 (s, CH_3), 2.2 (s, CH_3-C=N)
$\{[RuCl(CO)(PPh_3)_2]_2L^3\}$	7.2–7.7 (m, Ar), 3.3 (s, NH), 3.8 (s, CH), 2.9 (s, CH_3), 7.85 (s,HC=N), 2.3 (s, OCH_3)
$\{[RuCl(CO)(AsPh_3)_2]_2L^3\}$	7.3–7.4 (m, Ar), 3.37 (s, NH), 3.8 (s, CH), 2.8 (s, CH_3), 8.2 (s,HC=N), 2.2 (s, OCH_3)
$\{[RuCl(CO)(Py)(PPh_3)]_2L^3\}$	7.2–7.6 (m, Ar), 3.34 (s, NH), 3.8 (s, CH), 2.8 (s, CH_3), 8.4 (s,HC=N), 2.5 (s, OCH_3)
$\{[RuCl(CO)(PPh_3)_2]_2L^4\}$	6.6–7.7 (m, Ar), 3.3 (s, NH), 2.3 (s, CH), 1.4 (s, CH_3), 7.85 (s, HC=N)
$\{[RuCl(CO)(AsPh_3)_2]_2L^4\}$	7.3–7.7 (m, Ar), 3.4 (s, NH), 2.5 (s, CH), 2.2 (s, CH_3), 8.4 (s, HC=N)
$\{[RuCl(CO)(Py)(PPh_3)]_2L^4\}$	7.2–7.7 (m, Ar), 3.34 (s, NH), 2.5 (s, CH), 2.2 (s, CH_3), 8.6 (s, HC=N)

and $\{[RuCl(CO)(PPh_3)(Py)]_2L^3\}$ appears as singlet in the range 2.2–2.5 ppm. The signals for phenolic-OH and enolic-OH proton disappeared in all the complexes, which indicate the coordination of ruthenium through the oxygen atoms. The presence of other signals in the complexes indicates that these groups do not coordinate with the ruthenium atom.

^{31}P NMR spectra were recorded for a complex in order to confirm the presence of triphenylphosphine groups and to determine the geometry of the complex. The observation of two sharp singlets at 28.4 and 30.3 ppm in the spectrum of $\{[RuCl(CO)(PPh_3)_2]_2L^2\}$ revealed that the presence of two magnetically equivalent phosphorus atoms, suggesting that the two PPh3 groups in each nuclei are trans to each other.[30]

The ^{13}C NMR data were recorded in DMSO d6 solution and the assignments of ligands and the complexes are listed in Table 4 (Figure 1). For all the ligands, the aromatic carbons appeared in the range 113–144 ppm. The acetoacetanilide moiety of enolic, CH, C=N and CH_3 carbon appeared at 86–89 ppm, 48–56 ppm, 150–160 ppm, and 15–21 ppm. For all the ligands displayed a single resonance at 162–169 ppm, which shows that the azomethine carbon atoms, which also confirms the structure of ligands. For H_2L^2 ligand, the methyl carbon appeared at 19 ppm and H_2L^3 ligand, the methoxy carbon appeared at 30 ppm. For the complexes $\{[RuCl(CO)(PPh_3)_2]_2L^1\}$, $\{[RuCl(CO)(PPh_3)_2]_2L^2\}$, $\{[RuCl(CO)(PPh_3)_2]_2L^3\}$ and $\{[RuCl(CO)(PPh_3)_2]_2L^4\}$, the aromatic carbon appeared at 120–134 ppm. For the above complexes, the acetoacetanilide

TABLE 4
^{13}C NMR spectra of binuclear ruthenium(II) Schiff base complexes

Ligands and complexes	^{13}C NMR spectra
H_2L^1	116–138 (Ar, C), 86 (enolic C), 48 (CH), 160 (C=N), 18 (CH_3), 163 (HC=N)
H_2L^2	113–144 (Ar, C), 88 (enolic C), 48 (CH), 156 (C=N), 15 (CH_3), 163 (C=N), 19.0 (CH_3)
H_2L^3	118–129 (Ar, C), 86 (enolic C), 56 (CH), 150 (C=N), 20 (CH_3), 162 (HC=N), 30.7 (OCH_3)
H_2L^4	116–130 (Ar, C), 89 (enolic C), 50 (CH), 158 (C=N), 21 (CH_3), 169 (HC=N)
$\{[RuCl(CO)(PPh_3)_2]_2L^1\}$	120–134 (Ar, C), 84 (enolic C), 46 (CH), 158 (C=N), 18 (CH_3), 161 (HC=N), 178 ($C\equiv O$)
$\{[RuCl(CO)(PPh_3)_2]_2L^2\}$	127–134 (Ar, C), 85 (enolic C), 48 (CH), 154 (C=N), 16 (CH_3), 160 (C=N), 19 (CH_3), 180 ($C\equiv O$)
$\{[RuCl(CO)(PPh_3)_2]_2L^3\}$	129–133 (Ar, C), 84 (enolic C), 54 (CH), 152 (C=N), 18 (CH_3), 162 (HC=N), 182 ($C\equiv O$), 30 (OCH_3)
$\{[RuCl(CO)(PPh_3)_2]_2L^4\}$	128–134 (Ar, C), 88 (enolic C), 50 (CH), 156 (C=N), 20 (CH_3), 166 (HC=N), 176 ($C\equiv O$)

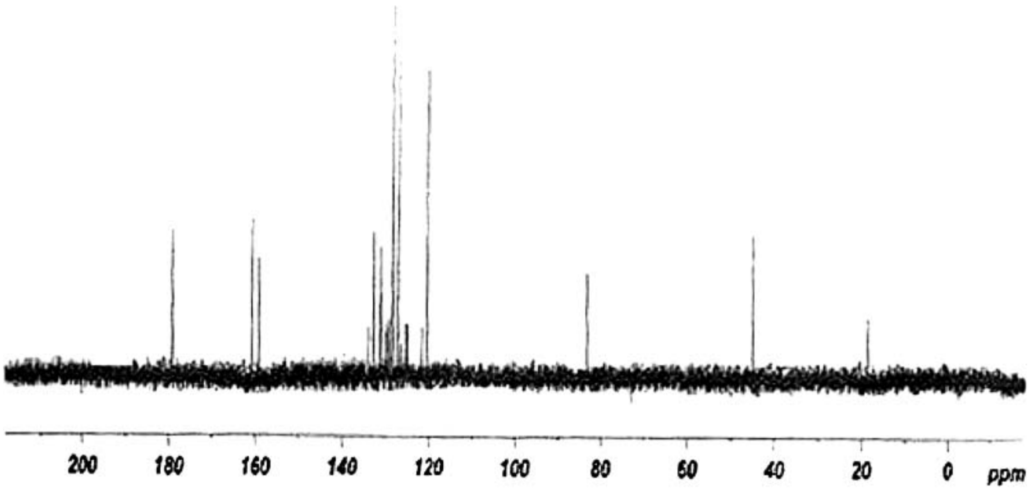


FIG. 1. ^{13}C NMR spectra of $\{[RuCl(CO)(PPh_3)_2]_2L^1\}$.

moiety of enolic, CH, C=N and CH_3 carbons appeared at 84–88 ppm, 46–54 ppm, 152–158 ppm, and 16–20 ppm. For the complexes $\{[RuCl(CO)(PPh_3)_2]_2L^2\}$ and $\{[RuCl(CO)(PPh_3)_2]_2L^3\}$, the methyl and methoxy carbons appeared at 19 ppm and 30 ppm. For all the complexes, the azomethine carbon and terminal carbonyl group C≡O appeared in the range 160–166 ppm and 176–182 ppm.

Electrochemical Studies

Electrochemical study was carried out for all the binuclear ruthenium(II) Schiff base complexes in dichloromethane solution at a glassy carbon working electrode, and all the potentials were expressed with reference to Ag-AgCl. The values are given in Table 5 (Figure 2). All the binuclear ruthenium(II) Schiff base complexes do not show any reduction wave at negative potentials, but showed two successive quasi-reversible or irreversible oxidative couples at positive potentials. The oxidation in the complexes corresponds to:

$$Ru^{II} - Ru^{II} \underset{+e-}{\overset{-e-}{\rightleftharpoons}} Ru^{II} - Ru^{III} \underset{+e-}{\overset{-e-}{\rightleftharpoons}} Ru^{III} - Ru^{III}$$

The quasireversible oxidation process occurs with peak-to-peak separations (ΔE_P) of 120–750 mV, suggesting two, single step, one electron transfer process[34] The oxidation of each complexes were characterized by well- defined waves with E_f values in the range 0.16–0.34 V corresponding to first oxidation couple and the second oxidation couple in the range 0.49–1.24 V. The first oxidation was attributed to the oxidation of one of the ruthenium(II) centers to the corresponding mixed valence complex[35,36] and the second to the ruthenium(III). The irreversible oxidation observed in the complex is presumably due to oxidative dissociation of the ligands that occurs at the ruthenium(III) center.[37] All these facts are indicative of significant electronic interactions between the two metal centers. The low difference of 200–700 mV observed for our complexes as compared to other complexes[38] is due to the fact that the distance between the two metal centers is long due to lengthy bridging ligands.

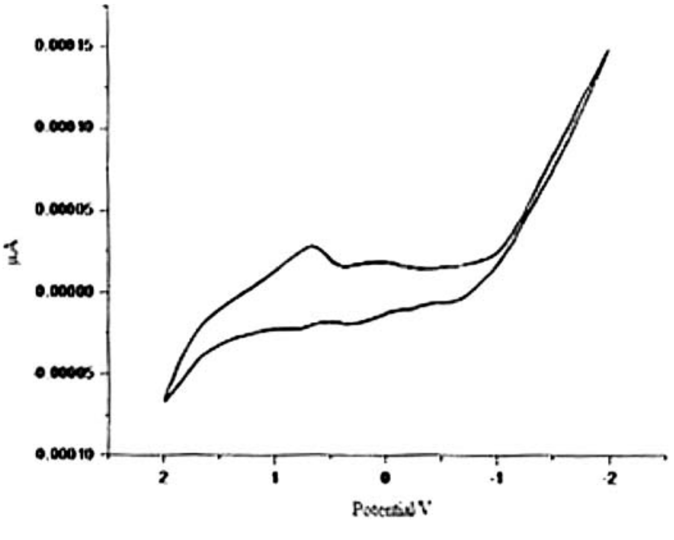


FIG. 2. Cyclic voltammogram of $\{[RuCl(CO)(AsPh_3)_2]_2L^1\}$.

CATALYTIC ACTIVITIES

Catalytic Oxidations

Catalytic oxidation of primary and secondary alcohols by free ligands, metal precursors, and binuclear ruthenium(II) Schiff base complexes were carried out in CH_2Cl_2 and stirred for about 6 hrs under an oxygen atmosphere at room temperature. The resulting carbonyl compounds were quantified as 2, 4-dinitrophenylhydrazone derivatives, and the results are summarized in Table 6. Only a very little amount of carbonyl

TABLE 5
Cyclic voltammetry[a] data of binuclear ruthenium(II) Schiff base complexes

					$Ru_2^{III,III} – Ru_2^{II,II}$			
Complexes	E_{pa} (v)	E_{pC} (v)	E_f (v)	ΔE_p (mV)	E_{pa} (v)	E_{pC} (v)	E_f (v)	ΔE_p (mV)
$\{[RuCl(CO)(PPh_3)_2]_2L^1\}$	0.23	0.35	0.29	120	0.93	1.11	1.02	180
$\{[RuCl(CO)(AsPh_3)_2]_2L^1\}$	0.28	0.03	0.16	250	0.90	0.64	0.77	260
$\{[RuCl(CO)(Py)(PPh_3)]_2L^1\}$	0.39	0.08	0.24	310	1.27	0.79	1.03	480
$\{[RuCl(CO)(PPh_3)_2]_2L^2\}$	—	—	—	—	—	—	—	—
$\{[RuCl(CO)(AsPh_3)_2]_2L^2\}$	0.48	0.03	0.26	450	1.52	0.77	1.15	750
$\{[RuCl(CO)(Py)(PPh_3)]_2L^2\}$	0.35	0.12	0.24	230	1.25	0.98	1.11	270
$\{[RuCl(CO)(PPh_3)_2]_2L^3\}$	0.52	0.04	0.28	480	1.33	0.65	0.49	330
$\{[RuCl(CO)(AsPh_3)_2]_2L^3\}$	0.46	0.06	0.26	400	1.37	0.84	1.10	530
$\{[RuCl(CO)(Py)(PPh_3)]_2L^3\}$	0.56	0.10	0.33	460	1.32	1.01	1.17	310
$\{[RuCl(CO)(PPh_3)_2]_2L^4\}$	0.52	0.15	0.34	370	1.26	1.05	1.15	210
$\{[RuCl(CO)(AsPh_3)_2]_2L^4\}$	0.48	0.09	0.29	390	1.41	1.02	1.21	390
$\{[RuCl(CO)(Py)(PPh_3)]_2L^4\}$	0.50	0.08	0.29	420	1.40	1.07	1.24	330

[a] Supporting electrolyte $[NBu_4]ClO_4$ (0.1 M); scan rate, all potentials are referenced to Ag/AgCl; $E_f = 0.5(Epa + Epc)$; Where, Epa and Epc are anodic and cathodic peak potentials, respectively; scan rate,100 mVs^{-1}.

TABLE 6
Catalytic activity data of binuclear ruthenium(II) Schiff base complexes

			Oxidation of alcohols							
	Aryl-Aryl coupling reaction Biphenyl		Benzyl alcohol → Benzaldehyde		Cyclohexanol → Cyclohexanone		Propane-1-ol → Propionaldehyde		Isobutyl alcohol → 2-Methyl-propionaldehyde	
Metal percursors, ligands and complexes	Yield (mg)	Yield (%)	Yield (%)	Turnover number[a]	Yield (%)	Turnover number[a]	Yield (%)	Turnover number[a]	Yield (%)	Turnover number[a]
$[RuHCl(CO)(PPh_3)_3]$	0.108	11.22	21.9	22.7	19.2	20.0	16.1	21.4	18.4	19.8
$[RuHCl(CO)(AsPh_3)_3]$	0.105	10.91	21.2	22.0	18.2	18.9	15.1	20.1	16.9	18.2
$[RuHCl(CO)(Py)(PPh_3)_2]$	0.100	10.39	20.2	20.9	17.5	18.2	14.1	18.7	15.8	17.0
H_2L^1	0.0382	3.96	9.0	9.08	8.0	7.9	5.0	6.7	7.0	5.3
H_2L^2	0.066	6.85	15.0	15.7	14.0	14.3	9.1	12.1	9.6	7.3
H_2L^3	0.053	5.5	12.0	12.6	11.0	11.5	8.3	11.1	9.1	6.9
H_2L^4	0.044	4.57	10.0	10.1	9.0	8.95	6.7	8.9	6.1	4.6
$\{[RuCl(CO)(PPh_3)_2]_2L^1\}$	0.280	29.09	75	76.7	69	71.6	52	69.2	53	40.5
$\{[RuCl(CO)(AsPh_3)_2]_2L^1\}$	0.253	26.28	69	69.7	62	64.5	48	63.5	49	36.8
$\{[RuCl(CO)(Py)(PPh_3)]_2L^1\}$	0.192	19.95	58	59.3	51	53.7	44	58.5	43	32.6
$\{[RuCl(CO)(PPh_3)_2]_2L^2\}$	0.485	50.39	86	87.2	71	74.5	66	87.4	67	50.8
$\{[RuCl(CO)(AsPh_3)_2]_2L^2\}$	0.463	48.10	75	76.7	70	73.1	61	81.1	61	46.7
$\{[RuCl(CO)(Py)(PPh_3)]_2L^2\}$	0.452	46.96	65	66.3	69	71.6	57	76.1	57	43.2
$\{[RuCl(CO)(PPh_3)_2]_2L^3\}$	0.463	48.10	80	81.6	72	75.2	62	82.4	62	47.2
$\{[RuCl(CO)(AsPh_3)_2]_2L^3\}$	0.447	46.44	74	75.4	71	74.1	58	77.3	59	44.5
$\{[RuCl(CO)(Py)(PPh_3)]_2L^3\}$	0.438	45.51	61	62.1	68	70.9	56	74.2	57	43.1
$\{[RuCl(CO)(PPh_3)_2]_2L^4\}$	0.259	26.91	73	74.3	67	70.2	50	66.0	52	39.1
$\{[RuCl(CO)(AsPh_3)_2]_2L^4\}$	0.245	25.45	66	70.0	65	68.4	48	63.5	49	36.9
$\{[RuCl(CO)(Py)(PPh_3)]_2L^4\}$	0.232	24.10	57	58.3	64	66.6	44	58.5	47	35.6

[a] Moles of product per mole of catalyst.

TABLE 7
Antibacterial activity of binuclear ruthenium(II) Schiff base complexes

Metal percursors, ligands, and complexes	Diameter of inhibition zone (mm)							
	S. aereus				*E. coli*			
	0.5%	1.0%	1.5%	2.0%	0.5%	1.0%	1.5%	2.0%
$[RuHCl(CO)(PPh_3)_3]$	—	5	7	9	2	5	6	6
$[RuHCl(CO)(AsPh_3)_3]$	3	5	9	9	4	7	7	8
$[RuHCl(CO)(Py)(PPh_3)_2]$	5	6	7	10	5	7	9	11
H_2L^1	—	—	3	5	—	—	2	3
H_2L^2	—	3	5	8	3	5	8	10
H_2L^3	2	4	6	9	—	3	5	8
H_2L^4	—	—	2	5	—	2	4	6
$\{[RuCl(CO)(PPh_3)_2]_2L^1\}$	5	8	12	19	8	15	19	23
$\{[RuCl(CO)(AsPh_3)_2]_2L^1\}$	—	6	11	17	—	6	12	21
$\{[RuCl(CO)(Py)(PPh_3)]_2L^1\}$	—	5	9	12	5	8	13	24
$\{[RuCl(CO)(PPh_3)_2]_2L^2\}$	8	12	18	25	5	10	13	25
$\{[RuCl(CO)(AsPh_3)_2]_2L^2\}$	5	10	16	20	3	7	11	22
$\{[RuCl(CO)(Py)(PPh_3)]_2L^2\}$	3	8	14	19	7	12	18	26
$\{[RuCl(CO)(PPh_3)_2]_2L^3\}$	8	12	19	23	3	8	13	24
$\{[RuCl(CO)(AsPh_3)_2]_2L^3\}$	10	12	17	20	6	12	16	20
$\{[RuCl(CO)(Py)(PPh_3)]_2L^3\}$	7	11	18	22	7	14	20	25
$\{[RuCl(CO)(PPh_3)_2]_2L^4\}$	6	11	13	19	—	—	—	—
$\{[RuCl(CO)(AsPh_3)_2]_2L^4\}$	5	9	11	15	7	12	18	23
$\{[RuCl(CO)(Py)(PPh_3)]_2L^4\}$	—	7	10	13	8	13	16	27
Amikacin	20–26				19–26			
DMSO-Solvent	No Activity							

compound is formed when the reaction is carried out without the catalyst. This is an insignificant amount compared with the yields of carbonyl compounds that have been obtained from the reaction catalyzed by free ligands, metal precursors, and binuclear ruthenium(II) complexes. In the catalytic oxidation, all the complexes did not show much activity for the conversion of aliphatic alcohols such as propane-1-ol (66–44%) and isopropyl alcohol (70–43%) to the corresponding aldehydes. Whereas this catalytic system works well for the oxidation of aromatic alcohols such as benzyl alcohol (86–57%) and cyclohexanol (72–51%) to corresponding aldehyde and ketone, inthe case of the catalytic efficiency of the complexes containg L^1 and L^4 was lower than that of L^2 and L^3. The essential difference between these complexes is that the hydrogen atom of the L^1 and L^4 is replaced by the methyl group of L^2 and the methoxy group of L^3. Hence, it seems that the presence of electron donating methyl and methoxy group enhances the catalytic activity of L^2 and L^3 containing complexes over the L^1 and L^4 containing complexes.[39,40] The catalytic oxidation of binuclear ruthenium(II) complexes has been found to show better catalytic activities compared with similar mono nuclear complexes.[41]

One of the complexes $\{[RuCl(CO)(PPh_3)_2]_2L^2\}$ has been tested for its reusability (Figure 3). The catalyst was recycled four times and the yield of the product was compared during the oxidation of benzyl alcohol to benzaldehyde. There is no appreciable change in the yield of the product when the catalyst was recycled. This confirms the catalytic activity of the complex. The heterogeneous nature of the catalyst has also been examined. The oxidation was completely stopped by the removal of $\{[RuCl(CO)(PPh_3)_2]_2L^2\}$ from the reaction solution.

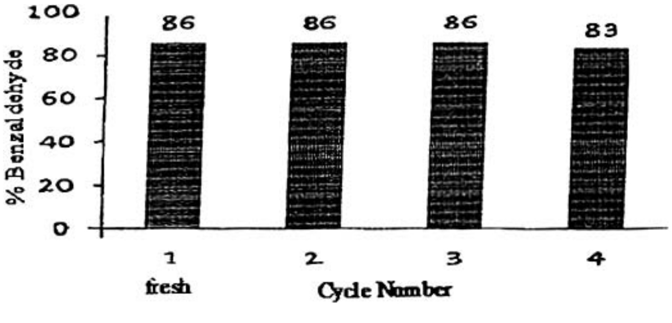


FIG. 3. Recycling of $[RuCl(CO)(PPh_3)_2]_2L^2$ catalyst for the oxidation of Benzyl alcohol.

Aryl-aryl Coupling Reaction

The free ligands, metal precursors, and the ruthenium(II) binuclear complexes have been used as catalysts in the aryl-aryl coupling reactions (Table 6). The system chosen for the study is the coupling of phenyl magnesium bromide with bromobenzene to give biphenyl as the product. Bromobenzene was first converted into the corresponding Grignard reagent. The bromobenzene, followed by the ligands and the complex chosen for the investigation, was added to the above reagent and the mixture was heated under reflux for 6 hrs. After work up, the mixture, yielded biphenyl. Only a very little amount of Ph_2 is formed when the reaction is carried out with the catalyst. This is an insignificant amount compared to the yields of Ph_2 obtained from the reactions catalysed by the ligands, metal precursors, and the binuclear ruthenium(II) complexes.[10] Ruthenium(II) binuclear complexes are better catalysts than the respective mononuclear complexes. This could be because of bicentered catalysis in binuclear complexes.[42] The yield of biphenyl obtained from the reaction catalyzed by the new binuclear ruthenium(II) complexes are low when compared to the yield obtained from the reaction catalyzed by $[NiCl_2(PPh_3)_2]$.[23] This may be due to the fact that the active species derived from ruthenium complexes are less stable compared with the active species from $[NiCl_2(PPh_3)_2]$, as the effectiveness of the catalysts is directly related to their ability to generate the corresponding active species.[43] The couplings catalysed by ruthenium complexes containing PPh_3 and $AsPh_3$ yielded biphenyl in almost equal quantity indicating non-participation of PPh_3 or $AsPh_3$ in the catalytic cycle.

Antibacterial Activities

The antibacterial activities of the free ligands, metal precursors, and binuclear ruthenium(II) Schiff base complexes were tested against certain pathogenic bacteria using disc diffusion method.[24] The zone of inhibition against the growth of bacteria for the ligands, metal precursors, and binuclear ruthenium(II) complexes is given in Table 7. It has been suggested that the ligands with N and O donor system might have inhibited enzyme production, since enzymes that require free hydroxyl groups for their activity appear to the especially susceptible to deactivation by the ions of the complexes. The complexes facilitate their diffusion through the lipid layer of spore membranes to the site of action ultimately killing them by combining with –OH groups of certain cell enzymes. The variation in the effectiveness of different biocidal agents against different organisms depends on the impermeability of the cell. Chelation reduces the polarity of the central metal atom, mainly because of partial sharing of its positive charge with the ligand. Also, the normal cell process may be affected by the formation of hydrogen bond, through the azomethine nitrogen atom with the active centers of cell constituents.[17] From the results, it is clear that binuclear ruthenium(II) carbonyl Schiff base complexes exhibit better inhibition than the other metal complexes against the same microbes.[44]

CONCLUSION

The potential binucleating monobasic bidentate Schiff base ligands had been prepared and were employed to synthesize a new class of binuclear ruthenium(II) Schiff base complexes incorporating $PPh_3/AsPh_3$ as ancillary ligands. The spectral investigation suggests the presence of an octahedral geometry around ruthenium metal. All the complexes were tested as catalyst for the oxidation of variety of alcohols in the presence of molecular oxygen. In these complexes, the complexes containing electron donating group shows more efficiency. Moreover, the reusability of the catalyst has also been proved. Finally, the antimicrobial properties of the complexes were studied and the mode of action of these complexes against the microbes was also explained.

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