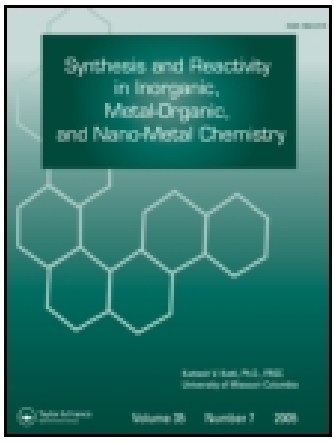

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Ruthenium(II) Complexes Derived from Substituted Cyclobutane and Substituted Thiazole Schiff Base Ligands: Synthetic, Spectral, Catalytic and Antimicrobial Studies

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Published online: 31 Jan 2012.

To cite this article: T. Daniel Thangadurai & Son-Ki Ihm (2005) Ruthenium(II) Complexes Derived from Substituted Cyclobutane and Substituted Thiazole Schiff Base Ligands: Synthetic, Spectral, Catalytic and Antimicrobial Studies, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 35:6, 499-507, DOI: 10.1081/SIM-200067062

To link to this article: http://dx.doi.org/10.1081/SIM-200067062

Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry, 35:499–507, 2005

ISSN: 0094-5714 print / 1532-2440 online
DOI: 10.1081/SIM-200067062

Ruthenium(II) Complexes Derived from Substituted Cyclobutane and Substituted Thiazole Schiff Base Ligands: Synthetic, Spectral, Catalytic and Antimicrobial Studies

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Ruthenium(II) complexes of the type $[Ru(CO)(L)_2(B)]$ (L = novel bidentate Schiff base ligand; B = PPh_3, pyridine (py), piperidine (pip), morpholine (morph) or $AsPh_3$) have been prepared by reacting $[RuHCl(CO)(PPh_3)_2(B)]$ (B = PPh_3, py, pip or morph) or $[RuHCl(CO)(AsPh_3)_3]$ with two novel bidentate Schiff base ligands derived from 4-(1-methyl-1-mesitylcyclobutane-3-yl)-2-aminothiazole in 1 : 2 molar ratio in benzene. Complexes have been characterized by analytical, spectroscopic (IR, UV, ^1H, ^{13}C- and ^{31}P NMR) and magnetic data. An octahedral structure has been tentatively proposed for all the new complexes. The thermal properties of the ligands and their complexes have been studied by TGA. The new complexes have been used as catalyst in aryl-aryl coupling and also subjected to antibacterial and antifungal activity studies.

Keywords Ruthenium(II), Schiff base, catalyst, aryl–aryl coupling, antimicrobial

INTRODUCTION

Schiff bases derived from the salicylaldehyde are well known as polydentate ligands, coordinating as deprotonated or neutral forms. Several adducts of non-transition, early transition and f-block metals with such bases acting neutral ligands (Kawakami et al., 1971; Bullock et al., 1978), have been studied.

It is well known that 3-substituted cyclobutane carboxylic acid derivatives exhibit antiinflamatory and antidepressant activities and liquid crystal properties. Various thiazole derivatives showed herbicidal, antiinflamatory, antimicrobial or antiparasitic activity (Slip et al., 1974). However, the syntheses and physicochemical properties of 1,1,3-trisubstituted cyclobutane substituted thiazoles and its Schiff base derivatives containing the mesityl group have not been reported many so far. These compounds containing cyclobutane, thiazole and Schiff base functions in their chemical modifications may be pharmacologically active and useful as ligands in coordination chemistry.

Ruthenium complexes, by virtue of their wide range of reversible and accessible oxidation states, have proved to be useful catalysts in many reactions such as hydrogenation, oxidation, carbonylation, hydroformylation, etc. (Sung et al., 1999; Chatterjee et al., 2000; Goldstein et al., 1994), But their use as catalyst for aryl-aryl couplings has not been discussed widely. Mild and efficient aromatic cross-couplings, catalyzed by various transition metal complexes, have been developed recently (Bringmann et al., 1990; Watanabe et al., 1992; Cox et al., 1992). Besides natural product synthesis, construction of large organic receptors in host-guest chemistry (Kelly et al., 1990), elaboration of dendrimers (Miller et al., 1992), or one-dimensional polymers (Wallow and Novak, 1991), aromatic couplings can be used to build multi-site ligands able to incorporate two or several transition metals (Beley et al., 1993).

The ligands used in this work have characteristic properties of cyclobutane, thiazole and Schif bases. The extensive synthetic possibilities of this type of heterocycle, due to the presence of several reaction sites, hold promise for the preparation of new thiazole derivatives. As part of our systematic investigations on the reactions of substituted cyclobutane and

Received 30 December 2004; accepted 8 April 2005.
We gratefully acknowledge financial support from the Brain Korea 21 Project and National Research Laboratory for Environmental Catalysis.
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related ligand with transition metal complexes, we report the synthesis, spectral studies, catalytic and antimicrobial activites of mononuclear ruthenium(II) carbonyl complexes of the type $[Ru(CO)(L)_2(B)]$.

EXPERIMENTAL

Commercially available $RuCl_3 \cdot 3H_2O$ was used without further purification. The solvents were purified and dried according to the standard procedures (Vogel, 1989). Salicylaldehyde, 2-hydroxy-5-bromobenzaldehyde and thiosemicarbazide were purchased and were used without further purification. 1-methyl-1-mesityl-3-(2-chloro-1-oxoethyl)cyclobutane was prepared and purified by column chromatography, 1-(2-hydroxybenzylidene)thiosemicarbazide and 1-(2-hydroxy-5-bromobenzylidene) thiosemicarbazide were prepared by the reported methods (Daniel Thangadurai and Ihm, 2004; Cukurovali et al., 2001).

Elemental analyses were carried out by using Carlo Erba 1106 analyzer. IR spectra were recorded with Nexus FTIR spectrophotometer in the range $4000-300\,cm^{-1}$. Electronic spectra were recorded in CH_2Cl_2 on Hitachi-Elmer model 20/200 spectrophotometer. Melting points were recorded on micro heating table and are uncorrected. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Brucker 400 MHz instrument using TMS, TMS and *o*-phosphoric acid as an internal reference, respectively. Magnetic susceptibilities were determined on a Sherwood scientific magnetic susceptibility balance (Model MK1) at room temperature (25°C) using Hg[Co $(SCN)_2$] as calibrant; diamagnetic corrections were calculated from Pascal's constants. Thermal analysis curves were recorded on a Shimadzu TG-50 thermobalance. The starting complexes (Daniel Thangadurai and Natarajan, 2001a) and ligands (Cukurovali et al., 2001) have been prepared by the following literature procedures. The following reaction scheme will represent the preparation of the Schiff base ligands [HL^1(**1**), color: pale yellow, m. pt.: 225°C, yield: 84% and HL^2(**7**), color: pale yellow, m. pt.: 230°C, yield: 87%] (Scheme 1).

Preparation of the Complexes (2–6 and 8–12)

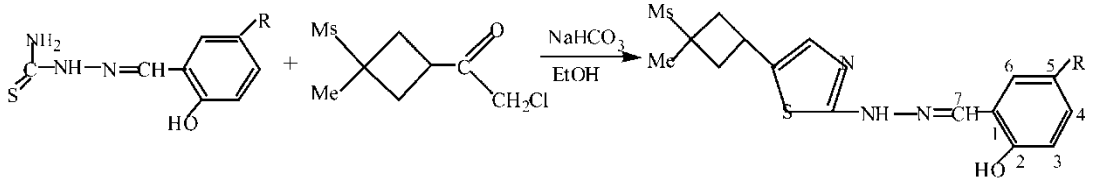
All the preparations were carried out under strictly anhydrous conditions. To a solution of $[RuHCl(CO)(PPh_3)_2(B)]$ (B = PPh_3, py, pip or morph) (0.095–0.077 g, 0.01 mmol) or $[RuHCl(CO)(AsPh_3)_3]$ (0.108 g, 0.01 mmol) in benzene (20 mL), the appropriate Schiff base ligands (0.075–0.126 g; 0.02 mmol) were added (molar ratio of the ruthenium complex : ligand = 1 : 2). The resulting mixture was heated under reflux for 5 h. The completion of the reaction was checked by TLC, concentrated on rotavapor to 3 mL and precipitated by addition of petroleum ether (60–80°C). The complexes were filtered, washed with petroleum ether and recrystallized from CH_2Cl_2/petroleum ether (60–80°C) mixture and dried in vacuo. (color: green, yield: 81–87%)

Catalytic Activity

In two necked round-bottom flask with a $CaCl_2$ guard tube, magnesium turnings (0.320 g; 0.013 g atom) were placed. To the above, bromobenzene [0.746 g of total 1.884 g (0.012 mol)] in anhydrous Et_2O (5 mL) was added with stirring. A crystal of iodine was added to activate magnesium and the mixture was heated under reflux. The appearance of turbidity after 5 min. indicated initiation of the reaction. The remaining bromobenzene in Et_2O (5 mL) was added dropwise and the mixture was refluxed for 40 min. To this mixture, 1.03 mL (0.01 mol) of bromobenzene in anhydrous Et_2O (5 mL) and the ruthenium complex (0.05 mol) chosen for investigation were added and heated under reflux for 6 h. The reaction mixture was cooled and hydrolyzed with a saturated solution of aqueous NH_4Cl. The Et_2O extract, on evaporation of the solvent, gave the crude product, which was chromatographed on a silica gel column. Petroleum ether (60–80°C) eluted pure biphenyl which compared well with an authentic sample (TLC plates), (M. p. 69–72°C).

Qualitative Antimicrobial Assay

In this work, *Bacillus megaterium* (B.m.), *Candida albicans* (C.a.), *Enterobacter aeroginosa* (E.a.), *Aspergillus flavus*



HL^1, R = H

HL^2, R = Br

SCH. 1. Preparation of novel Schiff base ligands.

(A.f.), *Fusarium oxysporium* (F.o.) and *Rhizoctonia solani* (R.s.) were used to investigate the antibacteriological and antifungal activities of ligands and their appropriate ruthenium(II) complexes. Nutrient agar medium for bacteria and Saburoud dextrose agar medium for fungi was poured into the sterilized Petri plates and allowed to solidify, and the plates were inoculated with a spore suspension to test micro organisms, respectively. The compounds to be tested were dissolved in DMF and soaked in filter paper discs (Whatmann no. 4, 5 mm diameter). The discs were placed on the already seeded plates [incubation period: 24°C for bacteria (24 h); 26°C for fungi (36 h)]. After 2 days, the inhibition zone, which appeared around the discs in each plate, was measured. To avoid the activity of the solvent used in the test solutions, a solvent-only treated plate was maintained. An untreated control plate was also maintained in order to calculate the percentage of inhibition.

RESULTS AND DISCUSSION

1-methyl-1-mesityl-3-(2-chloro-1-oxoethyl)cyclobutane is very soluble in polar organic solvents, such as EtOH, $CHCl_3$, MeOH, and in nonpolar organic solvents, such as Et_2O and benzene. The compound is not stable for long under ordinary laboratory conditions. It is highly affected by direct sunlight and decomposed within two months. Hence, it was used as prepared, without delay. Substituted benzaldehyde derivatives of thiosemicarbazide were freshly prepared in excellent yields according to the well known Schiff base methods. The ligands HL^1(**1**) and HL^2 (**7**) were obtained in excellent yield. The hot solutions of the ligands were used during complexation. Attempts to crystallize the complexes in different solvents failed.

The bidentate Schiff bases react with the ruthenium(II) starting complexes of the type $[RuHCl(CO)(PPh_3)_2(B)]$ (B = PPh_3, py, pip or morph) or $[RuHCl(CO)(AsPh_3)_3]$ to yield complexes of the type $[Ru(CO)(L)_2(B)]$ (L = novel bidentate Schiff base ligand; B = PPh_3, py, pip, morph or $AsPh_3$).

In general, reactions of the ligands HL^1 and HL^2, with starting ruthenium complexes were quick and gave good yields (81–87%) of mononuclear complexes (**2–6** and **8–12**). The new complexes are air- and light-stable and soluble in most common organic solvents. Molecular weight determination (Rast method) and elemental analyses data confirm the complexes to be hexa-coordinated. Table 1 lists the analytical data for the ligands and their ruthenium metal complexes.

Infrared Spectra

The IR spectral data of the ligands and their metal complexes are listed in Table 2. Since there are no C═O, C–Cl and $-NH_2$ absorptions in the IR spectra of the ligands HL^1 and HL^2, these peaks indicate the formation of the expected compounds. The strong bands observed at 3130 cm^{-1} for each ligand can be attributed to the –NH-group vibration. This absorption remains unaltered in complexes showing the non-involvement of this group upon coordination. The ligands exhibit broad medium intensity bands in the 2700–2550 cm^{-1} range, which are assigned to the intramolecular hydrogen-bonding vibrations (O-H $\cdots$ N). This situation is common for aromatic azomethine compounds containing *o*-OH groups (Tumer et al. 1999), and in the complexes, these bands disappear completely. The azomethine group vibrations of the free ligands occur at 1630 and 1625 cm^{-1}, respectively, and these bands were not observed at the same frequencies in the spectra of all the complexes. They shifted

TABLE 1
Analytical and physical data of Schiff base ligands and ruthenium(II) complexes

S. no.	Compound	M.p. (°C)	Found (calcd.) (%) C	H	N	S
(1)	$(C_{24}H_{27}N_3SO)$	225	71.10 (71.07)	6.72 (6.70)	10.30 (10.36)	7.87 (7.90)
(2)	$[Ru(CO)(C_{24}H_{26}N_3SO)_2(PPh_3)]$	187	66.89 (67.02)	5.65 (5.63)	7.02 (7.00)	5.40 (5.33)
(3)	$[Ru(CO)(C_{24}H_{26}N_3SO)_2(py)]$	176	63.89 (63.75)	5.65 (5.65)	9.22 (9.64)	6.40 (6.30)
(4)	$[Ru(CO)(C_{24}H_{26}N_3SO)_2(pip)]$	180	63.39 (63.44)	6.65 (6.12)	9.52 (9.59)	6.30 (6.27)
(5)	$[Ru(CO)(C_{24}H_{26}N_3SO)_2(morph)]$	157	62.09 (62.08)	6.05 (6.00)	9.62 (9.56)	6.22 (6.25)
(6)	$[Ru(CO)(C_{24}H_{26}N_3SO)_2(AsPh_3)]$	163	64.90 (64.66)	5.45 (5.43)	7.02 (6.75)	5.20 (5.15)
(7)	$(C_{24}H_{26}N_3SOBr)$	230	58.98 (59.49)	5.55 (5.41)	8.72 (8.70)	6.60 (6.60)
(8)	$[Ru(CO)(C_{24}H_{25}N_3SOBr)_2(PPh_3)]$	178	59.19 (59.23)	4.65 (4.79)	6.20 (6.19)	4.70 (4.72)
(9)	$[Ru(CO)(C_{24}H_{25}N_3SOBr)_2(py)]$	153	55.19 (55.18)	4.69 (4.72)	8.02 (8.34)	5.40 (5.45)
(10)	$[Ru(CO)(C_{24}H_{25}N_3SOBr)_2(pip)]$	169	54.90 (54.95)	5.15 (5.13)	8.20 (8.31)	5.41 (5.43)
(11)	$[Ru(CO)(C_{24}H_{25}N_3SOBr)_2(morph)]$	180	53.79 (53.79)	4.85 (4.86)	8.30 (8.29)	5.47 (5.41)
(12)	$[Ru(CO)(C_{24}H_{25}N_3SOBr)_2(AsPh_3)]$	171	57.29 (57.40)	4.65 (4.64)	6.02 (6.00)	4.51 (4.57)

TABLE 2
IR spectral data of the ligands and ruthenium(II) complexes

S.No.	ν(OH)[a]	ν(N-H)[a]	$\nu(CH_3)/\nu(CH_2)$[a]	ν(C=N)[a] thiazole	ν(C=N)[a] azomethine	ν(C-O)[a]	ν(C≡O)[a]
(1)	3289	3130 s	2979–2927 m	1627 s	1650 vs	1170	—
(2)	—	3130 s	2979–2927 m	1626 s	1623 vs	1186	1950 s
(3)	—	3132 s	2979–2927 m	1627 s	1622 vs	1189	1952 s
(4)	—	3131 s	2979–2927 m	1627 s	1622 vs	1192	1950 s
(5)	—	3130 s	2979–2927 m	1625 s	1620 vs	1188	1950 s
(6)	—	3130 s	2979–2927 m	1627 s	1621 vs	1191	1951 s
(7)	3290	3132 s	2979–2927 m	1627 s	1625 vs	1170	—
(8)	—	3130 s	2979–2927 m	1626 s	1601 vs	1190	1950 s
(9)	—	3131 s	2979–2927 m	1627 s	1599 vs	1192	1954 s
(10)	—	3130 s	2979–2927 m	1627 s	1600 vs	1189	1951 s
(11)	—	3132 s	2979–2927 m	1625 s	1602 vs	1190	1950 s
(12)	—	3131 s	2979–2927 m	1627 s	1600 vs	1193	1952 s

[a]cm^{-1}; s = strong, m = medium, vs = very strong.

to lower frequency region, indicating coordination of Schiff bases through azomethine nitrogen. In the free ligands, bands at 1170 cm^{-1} can be attributed to the phenolic (C–OH) group vibration, and in the metal complexes, these bands are shifted to higher frequencies indicating coordination of oxygen to the metal atom (Daniel Thangadurai and Natarajan 2001b). The spectra of all the complexes show a very strong absorption at 1950 cm^{-1} due to the coordinated terminal carbonyl group (Daniel Thangadurai et al., 2002). In the complexes containing a coordinated nitrogen base, a medium intensity band is observed in the 1000–1020 cm^{-1} region characteristic of the coordinated pyridine, piperidine and morpholine (Plytazanopoubs et al. 1977). The bands in the 550–480 and 460–430 cm^{-1} range in the complex spectrum have been assigned to the ν(Ru-N) and ν(Ru-O) bands.

Electronic Spectra

All the ruthenium(II) complexes are diamagnetic, indicating the presence of ruthenium in its +2 oxidation state. The ground state of ruthenium(II) in octahedral environment is $^1A_{1g}$ arising from t_{2g}^6 configuration. The excited states corresponding to the $t_{2g}^5\ e_g^1$ configuration are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Hence, four bands corresponding to the transitions $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ are possible in the order of increasing energy. The electronic spectra of all the complexes (Table 3) in dichloromethane showed two bands in the 600–300 nm region. The bands in the 600–510 nm region have been assigned to the spin-allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transition (Daniel Thangadurai and Natarajan, 2001a). The other high intensity bands in the 375–300 nm region have been assigned charge transfer bands on the basis of high extinction coefficient value (ε = 7,540–9,190 $dm^3\ mol^{-1}\ cm^{-1}$). The nature of the electronic spectra of all the complexes indicate an octahedral geometry around ruthenium ion in the complexes, and the spectra are very similar to the ones observed for other

TABLE 3
Electronic spectra and magnetic moment data of ruthenium(II) complexes

S.no.	λ_{max}[a]	(ε)[b]	Assignment
(2)	586	892	$^1A_{1g} \rightarrow {}^1T_{1g}$
	367	7612	charge transfer
(3)	600	991	$^1A_{1g} \rightarrow {}^1T_{1g}$
	375	7540	charge transfer
(4)	524	901	$^1A_{1g} \rightarrow {}^1T_{1g}$
	354	8723	charge transfer
(5)	510	873	$^1A_{1g} \rightarrow {}^1T_{1g}$
	349	9190	charge transfer
(6)	537	804	$^1A_{1g} \rightarrow {}^1T_{1g}$
	357	8345	charge transfer
(8)	596	798	$^1A_{1g} \rightarrow {}^1T_{1g}$
	300	7781	charge transfer
(9)	561	865	$^1A_{1g} \rightarrow {}^1T_{1g}$
	375	8127	charge transfer
(10)	581	917	$^1A_{1g} \rightarrow {}^1T_{1g}$
	344	9099	charge transfer
(11)	573	832	$^1A_{1g} \rightarrow {}^1T_{1g}$
	323	8993	charge transfer
(12)	559	934	$^1A_{1g} \rightarrow {}^1T_{1g}$
	312	7998	charge transfer

[a]nm.
[b]$dm^3\ mol^{-1}\ cm^{-1}$.

TABLE 4
^{1}H NMR spectral data of ligands and ruthenium(II) complexes

S.no.	HC═N	> C–H	CH_3	Ms-CH_3, *ortho*	Ms-CH_3, *para*	CH_2	C–H, *thiazole*	–NH–	–OH	Aromatics
(1)	8.11 (s)	3.69 (q)	1.48 (s)	2.16 (s)	2.42 (s)	2.56 (d)	6.06 (s)	10.02 (s)	10.12 (s)	6.80–7.39 (m)
(2)	8.10 (s)	3.68 (q)	1.48 (s)	2.16 (s)	2.42 (s)	2.56 (d)	6.06 (s)	10.02 (s)	—	6.80–7.39 (m)
(3)	8.11 (s)	3.69 (q)	1.48 (s)	2.16 (s)	2.42 (s)	2.56 (d)	6.06 (s)	10.02 (s)	—	6.80–7.39 (m)
(4)	8.12 (s)	3.69 (q)	1.48 (s)	2.16 (s)	2.42 (s)	2.56 (d)	6.06 (s)	10.02 (s)	—	6.80–7.39 (m)
(5)	8.09 (s)	3.68 (q)	1.48 (s)	2.16 (s)	2.42 (s)	2.56 (d)	6.06 (s)	10.02 (s)	—	6.80–7.39 (m)
(6)	8.11 (s)	3.69 (q)	1.48 (s)	2.16 (s)	2.42 (s)	2.56 (d)	6.06 (s)	10.02 (s)	—	6.80–7.39 (m)
(7)	8.01 (s)	3.29 (q)	1.49 (s)	2.15 (s)	2.40 (s)	2.55 (d)	5.98 (s)	10.10 (s)	10.26 (s)	6.84–7.38 (m)
(8)	8.02 (s)	3.30 (q)	1.49 (s)	2.15 (s)	2.40 (s)	2.55 (d)	5.98 (s)	10.10 (s)	—	6.84–7.38 (m)
(9)	8.01 (s)	3.29 (q)	1.49 (s)	2.15 (s)	2.40 (s)	2.55 (d)	5.98 (s)	10.10 (s)	—	6.84–7.38 (m)
(10)	8.00 (s)	3.30 (q)	1.49 (s)	2.15 (s)	2.40 (s)	2.55 (d)	5.98 (s)	10.10 (s)	—	6.84–7.38 (m)
(11)	8.03 (s)	3.30 (q)	1.49 (s)	2.15 (s)	2.40 (s)	2.55 (d)	5.98 (s)	10.10 (s)	—	6.84–7.38 (m)
(12)	8.01 (s)	3.29 (q)	1.49 (s)	2.15 (s)	2.40 (s)	2.55 (d)	5.98 (s)	10.10 (s)	—	6.84–7.38 (m)

(s) = singlet, (d) = doublet, (q) = quteret, (m) = multiplet.

ruthenium(II) complexes (Daniel Thangadurai and Natarajan, 2001a).

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

The ^{1}H NMR spectra assignments are detailed in Table 4. It is important to emphasize that the ^{1}H resonance of the O–H group at 10.00–10.89 ppm is due to the presence of intramolecular hydrogen bonding (Lindoy et al., 1977). The single proton resonances in the ^{1}H NMR spectra of these ligands, which occur at 8.11 ppm for HL^1 and 8.01 ppm for HL^2, have been assigned to the azomethine group proton. The aromatic ring resonances in the ligands and all the complexes are observed as multiplets. The detailed ^{1}H NMR spectral data of the ligands and ruthenium(II) complexes are given in Table 4, and more detailed spectral investigation of cyclobutane compounds can be found in the literature (Daniel Thangadurai and Ihm, 2004).

The ^{13}C NMR spectral data of the ligands confirm the ^{1}H NMR spectral results. Azomethine carbon atoms are observed at 153.17 and 158.71 ppm, respectively, for HL^1 and HL^2.

Characteristic ^{13}C NMR peaks for *(*HL^1*)* ($CDCl_3$, TMS, δ ppm): 120.06 (C_1), 132.24 (C_2), 121.52 (C_3), 132.96 (C_4), 118.87 (C_5), 159.82 (C_6), 153.17 (C_7), 171.40 (C_8), 101.63 (C_9), 148.38 (C_{10}), 32.06 (C_{11}), 42.88 (C_{12}), 45.15 (C_{13}), 26.46 (C_{14}), 145.63 (C_{15}), 135.38 (C_{16}), 132.44 (C_{17}), 137.00 (C_{18}), 22.42 (C_{19}), 23.38 (C_{20}).

Characteristic ^{13}C NMR peaks for *(*HL^2*)* ($CDCl_3$, TMS, δ ppm): 121.80 (C_1), 152.29 (C_2), 121.73 (C_3), 136.69 (C_4), 113.04 (C_5), 135.82 (C_6), 158.71 (C_7), 171.24 (C_8), 101.69 (C_9), 148.35 (C_{10}), 32.20 (C_{11}), 42.88 (C_{12}), 45.15 (C_{13}), 26.45 (C_{14}), 145.63 (C_{15}), 135.38 (C_{16}), 132.44 (C_{17}), 137.00 (C_{18}), 22.42 (C_{19}), 23.38 (C_{20}).

^{31}P NMR spectra were recorded in order to confirm whether the PPh_3 group or the heterocyclic base is present in the complex. A singlet at δ 26.74 and 26.54 ppm in the spectrum of (**2**) and (**8**), respectively, confirmed the presence of triphenylphosphine group in these complexes. However, the complexes (**3**–**5** and **9**–**11**) exhibited no such signal confirming the absence of triphenylphosphine in the complex (Table 4). This observation revealed the presence of coordinated pyridine or piperidine or morpholine in the complexes even after the coordination of bidentate Schiff bases (Daniel Thangadurai and Natarajan, 2002).

Thermal Studies

The TGA curves were studied in the 20–500°C range and the curves showed that the thermal decomposition of the complexes take place in several steps. It is possible that the different groups in ligands lead to a decrease in the stability of all the complexes. Furthermore, it is known that the electronegativity and the atomic radius of the central metal atom also affects the thermal stability.

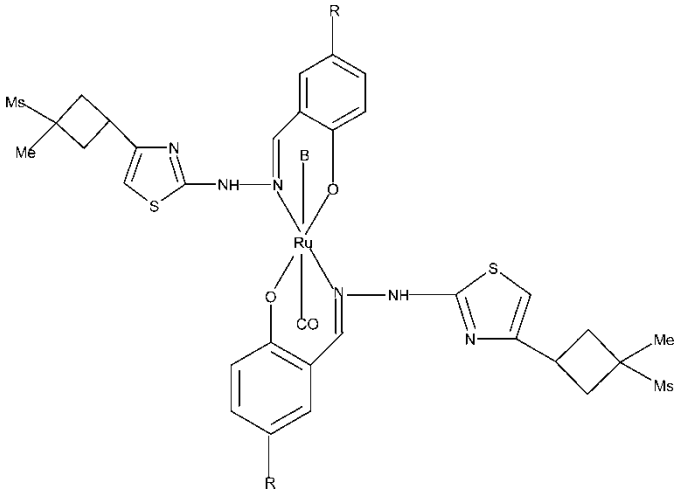


FIG. 1. Suggested structure of the ruthenium(II) Schiff base ligand (R and B groups are as previously described).

Based on elemental analyses, spectral (IR, UV, ^{1}H, ^{13}C and ^{31}P NMR), magnetic moment and thermal studies, the suggested structure for the complexes is shown in Figure 1.

APPLICATIONS OF NEW RUTHENIUM(II) COMPLEXES

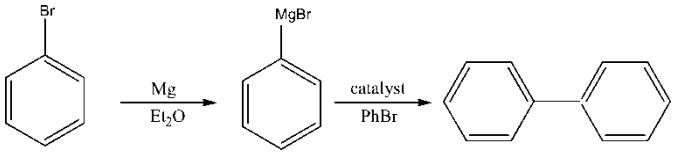
Catalytic Studies

The synthesized ruthenium(II) complexes have been used as catalysts in aryl-aryl coupling (Table 5). The system chosen for our study is the coupling of phenylmagnesium bromide with bromobenzene to give biphenyl as the product (Scheme 2). Bromobenzene was first converted into the corresponding Grignard reagent. Then bromobenzene, followed by the complex chosen for the investigation, were added to the above reaction medium, and the mixture was heated under reflux for 7 h. After work up, the mixture yielded biphenyl. Only a very little amount of biphenyl was formed when the reaction was carried out without the catalyst. This is

TABLE 5
Yields of biphenyl with different mole ratios of PhMgBr and ruthenium(II) complex

S. no.	$[Ru(CO)(L^1)_2(PPh_3)]$	PhMgBr[a]	Yield[b]
1	0.0001	0.03	10.7
2	0.0003	0.03	26.1
3	0.0005	0.03	18.4
4	0.0007	0.03	11.1
5	0.0009	0.03	13.5

[a]in mole
[b]in (%).



SCH. 2. Formation of biphenyl.

TABLE 6
Yields of biphenyl with ruthenium(II) complexes as catalyst

S. no.	Catalyst	Yield of Ph-Ph (in g)	Yield of Ph-Ph (%)
1	**(2)**	0.410	26.1
2	**(3)**	0.383	24.4
3	**(4)**	0.376	23.9
4	**(5)**	0.431	27.4
5	**(6)**	0.416	26.5
6	**(8)**	0.503	32.0
7	**(9)**	0.407	25.9
8	**(10)**	0.425	27.1
9	**(11)**	0.404	25.7
10	**(12)**	0.495	31.5

an insignificant amount compared to the yields of biphenyl obtained from the reactions catalyzed by ruthenium complexes.

The optimum quantity of catalyst required for the coupling of phenylmagnesium bromide with bromobenzene has been investigated by performing a series of experiments using different mole ratios of phenylmagnesium bromide and $[Ru(CO)(L^1)_2(PPh_3)]$ (**3**), and the results are presented in Table 6. This study revealed the optimum mole ratio of the Grignard reagent to ruthenium complex 100 : 1 in good agreement with a recent observation (Gnanasoundari and Natarajan, 2004).

The yield of biphenyl obtained from the reactions catalyzed by the new ruthenium(II) complexes are low when compared to the yield obtained from the reaction catalyzed by $NiCl_2(PPh_3)_2$. (Gnanasoundari and Natarajan, 2004). The couplings catalyzed by ruthenium complexes containing triphenylphosphine/triphenylarsine yielded biphenyl in almost equal quantity indicating non-participation of triphenylphosphine/triphenylarsine in the catalytic cycle.

Quantitative Antimicrobial Assay

The antimicrobial activities of the ligands and their ruthenium(II) complexes have been screened against six different bacteria and fungal by disc diffusion method (Daniel Thangadurai and Ihm, 2004) (Table 7). Different concentrations of the complex in DMF solution (0.25 and 0.50%) were used for the studies. The percentage inhibition was calculated as $100(C\text{-}T)/C$, where C is the average diameter of bacteria or fungal growth on the control plate (DMF only) and T is the average diameter of bacteria or fungal growth on the test plate.

It has also been observed from the antimicrobial screening studies that the ruthenium chelates have higher activity than the corresponding free ligands against the same microorganism

TABLE 7
Antimicrobial effects of the ligands and ruthenium(II) complexes

	Inhibition (%)											
	B.M.		C.a.		E.a		A.f.		F.o.		R.s.	
Compound	0.25	0.50	0.25	0.50	0.25	0.50	0.25	0.50	0.25	0.50	0.25	0.50
Streptomycin	18	21	19	21	21	25	—	—	—	—	—	—
Bavistin	—	—	—	—	—	—	17	20	19	23	16	22
(1)	5	7	8	9	6	10	7	9	8	11	9	10
(2)	7	8	—	—	9	12	9	13	12	14	11	14
(3)	6	9	7	9	—	—	15	12	12	13	11	15
(5)	7	8	9	11	7	13	10	14	—	—	11	13
(6)	7	9	9	12	8	12	9	13	9	15	11	14
(7)	6	9	7	9	7	10	8	12	7	10	10	12
(8)	7	11	—	—	8	13	10	14	9	12	13	15
(9)	8	11	10	13	9	12	10	15	11	14	—	—
(10)	8	12	9	13	—	—	10	15	9	13	13	16
(12)	—	—	10	13	8	11	12	13	11	13	12	16

under identical experimental conditions, which is consistent with earlier reports (Srivastva, 1980). It has been suggested that the ligands with the N and O donor system might have inhibited enzyme production, since enzymes which require a free hydroxy group for their activity appear to the especially susceptible to deactivation by the ions of the complexes. Chelation reduces the polarity of the central ion mainly because of the partial sharing of its positive charge with the donor groups and possible π-electron delocalization within the whole chelate ring, this chelation increases the lipophilic nature of the central atom, which favors its permeation through lipid layers of the cell membrane (Daniel Thangadurai et al., 2002; Daniel Thangadurai and Natarajan, 2002; Maruvada et al., 1994). Furthermore, the mode of action of the compounds may involve the formation of hydrogen bonds through the azomethine (>C═N) group of the complexes with the active centers of cell constituents resulting in the interference with normal cell processes (Singh et al., 1995). Though the complexes possess activity, it could not reach the effectiveness of the standard drugs such as *Streptomycin* and *Bavistin.* Few compounds were inactive against different organisms, the variation in the effectiveness of different compounds against different organisms depends either on the imper1eability of the cells of the microbes or differences in ribosomes of microbial cells (Thangadurai and Ihm, 2003). The toxic activity of the new compounds increases with increase in the concentration of the solution.

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