Received: 26 May 2010

Revised: 23 July 2010

(wileyonlinelibrary.com) DOI 10.1002/aoc.1720

# Published online in Wiley Online Library: 27 September 2010

Applied Organometallic

Chemistry

# Synthesis, spectral characterization, C–C coupling, oxidation reactions and antibacterial activities of new ruthenium(III) Schiff base complexes

# Arumugam Manimaran<sup>a</sup>, Vaiyapuri Chinnusamy<sup>b</sup> and Chinnasamy Jayabalakrishnan<sup>b</sup>\*

A new series of hexa-coordinated stable Ru(III) Schiff base complexes of the type [RuX(EPh<sub>3</sub>)(L)] (where X = Cl/Br; E = P/As;  $L = tetradentate N_2O_2$  donor Schiff ligands) have been synthesized and characterized by elemental analysis, magnetic susceptibility measurement, FT-IR, UV-vis, <sup>13</sup>C{<sup>1</sup>H}-NMR, ESR spectra, electrochemical and powder X-ray diffraction pattern studies. The selective oxidation of alcohols to their corresponding carbonyl compounds occurred in the presence of *N*-methylmorpholin-*N*-oxide (NMO), H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> atmosphere at ambient temperature as co-oxidants and C-C coupling reactions. Further, these new Schiff base ligands and their Ru(III) complexes were also screened for their antibacterial activity against *K. pneumoniae, Shigella* sp., *M. luteus, E. coli* and *S. typhi*. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: ruthenium(III); N<sub>2</sub>O<sub>2</sub> donor; C-C coupling; oxidation reactions; antibacterial activity

#### Introduction

Selective oxidation of alcohols to the corresponding carbonyl compounds has attracted much efforts from both academic and industrial research owing to the versatile role of the carbonylic group as a building block.<sup>[1-3]</sup> Currently, considerable effort is being invested in the development of new chelating ligand systems, particularly the planarity of the N<sub>2</sub>O<sub>2</sub> ligand providing the means of creating vacant site, since their complexes may lead to active catalysts for the different organic transformations.<sup>[4–8]</sup> This is due to fact that Schiff bases offer opportunities for inducing substrate chirality, tuning metal-centered electronic factors, and enhancing the solubility and stability of either homogeneous or heterogeneous catalysts.<sup>[7-11]</sup> Further, tetradentate Schiff base complexes with transition metals are important in designing metal complexes related to synthetic and natural oxygen carriers.<sup>[12]</sup> In addition, ruthenium complexes of triphenylphosphines/arsines are of considerable interest as they find applications in classical catalytical processes, such as hydrogenation, isomerization, decarbonylation, reductive elimination, oxidative addition and in making C–C bonds  $^{[13-22]}$  and in biological activity against pathogenic microbes.<sup>[23-26]</sup> However, their use as catalysts for C-C couplings has not been discussed widely. Therefore, systematic studies that selectively change the structural and electronic features in ruthenium complexes and modulate their effect on catalytic properties could help to clarify the reactivity of those metal centers toward alcohol oxidation and coupling reactions. In connection with our ongoing interest in this field of research, we have already investigated several ruthenium (II) and ruthenium (III) complexes.<sup>[27-32]</sup> Herein, we describe the synthesis and characterization of a series of new class of ruthenium(III) Schiff base complexes along with their catalytic activity towards the selective oxidation of alcohols in the presence of O<sub>2</sub> atmosphere at ambient temperature, NMO and  $H_2O_2$  as co-oxidants and C–C coupling reactions. Further, the new Schiff base ligands and their Ru(III) complexes were also screened for their antibacterial activity against *K. pneumoniae, Shigella* sp., *M. luteus*, *E. coli* and *S. typhi*.

## Experimental

#### **Materials and Methods**

All the chemicals and solvents used were purified and dried by standard methods. IR spectra were recorded as KBr pellets with a Nicolet FT-IR spectrometer in the 4000–400 cm<sup>-1</sup> range. Electronic spectra of the complexes were recorded in CHCl<sub>2</sub> solutions using a Systronics double beam UV–vis spectrophotometer-2202 in the range 800–200 nm. Microanalyses were carried out with a Vario El AMX-400 elemental analyzer at STIC, Cochin University of Science and Technology, Kerala, India. EPR spectra of powdered samples were recorded with a Jeol TEL-100 instrument at X-band frequencies at room temperature. Cyclic voltammetric studies were carried out with a BAS CV-27 model electrochemical analyzer in acetonitrile using a glassy carbon working electrode and the potentials were referenced to an Ag–AgCl electrode. Powder XRD were recorded using Shimadzu model XRD6000

b Post Graduate and Research Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore-20, Tamil Nadu, India

Correspondence to: Chinnasamy Jayabalakrishnan, Post Graduate and Research Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore-20, Tamil Nadu, India. E-mail: vcsrkv@gmail.com

a Department of Physical Sciences, Bannari Amman Institute of Technology, Sathyamangalam, Erode-638 401, Tamil Nadu, India



**Scheme 1.** Structure of N<sub>2</sub>O<sub>2</sub> donor Schiff base ligands.

instrument with CuK<sub>α</sub> radiation ( $\lambda = 1.54060$  Å) from a Cu target. Magnetic moments were measured on an EG&G PARC vibrating sample magnetometer. Melting points were recorded with a Veego VMP-DS model heating table and were uncorrected. The starting complexes [RuCl<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>],<sup>[33]</sup> [RuBr<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sup>[34]</sup> and [RuCl<sub>3</sub>(AsPh<sub>3</sub>)<sub>3</sub>]<sup>[35]</sup> and the Schiff base ligands (Scheme 1) were prepared by the following procedure. The analytical data, FT-IR, <sup>13</sup>C{<sup>1</sup>H}-NMR spectral data confirm the proposed molecular formula and the structure of the Schiff base ligands.

#### Synthesis of N<sub>2</sub>O<sub>2</sub> Donor Schiff Base Ligands

To an ethanolic solution of *o*-phenylenediamine (1.8 g; 10 mmol) and salicylaldehyde / 2-hydroxy-1-naphthaldehyde / *o*-hydroxyacetophenone / *o*-vanillin (10 mmol) were added and stirred for an hour. Then to the above stirring solution about 10 mmol of isatin was added. The mixture was stirred for about half an hour and then refluxed for about 4 h. The resultant product was washed with ethanol and dried in *vacuo* and the reactions were monitored by TLC.

#### Synthesis of New Ruthenium(III) Schiff Base Complexes

To a solution of  $[RuX_3(EPh)_3]$  (where X = CI/Br; E = P/As) (0.20 mmol) in  $CH_2CI_2$ -methanol, an appropriate Schiff base ligand (molar ratio of ruthenium complex to Schiff base was 1:1) was added. The solution was heated under reflux for 6–8 h (Scheme 2) and then it was concentrated to 5 cm<sup>3</sup>. The new complex was separated from it by addition of 10 cm<sup>3</sup> of petroleum ether (60–80 °C). The product was filtered, washed with petroleum ether and recrystallized from CH<sub>3</sub>CN/methanol and dried *in vacuo*, then the reactions were monitored by TLC (yield 76–88%).

#### **Catalytic Reactions**

#### **C-C** Coupling Reactions

Magnesium turnings (0.320 g) were placed in a flask equipped with a CaCl<sub>2</sub> guard tube. A crystal of iodine was added. PhBr (0.75 cm<sup>3</sup> of total 1.88 cm<sup>3</sup>) in anhydrous  $Et_2O$  (5 cm<sup>3</sup>) was added with stirring



Where, R1=H/CH3; R2=H/C4H4; R3=H/OCH3; X=Cl/Br; E=P/As

Scheme 2. Formation of new Ru(III) Schiff base complexes.

and the mixture was heated under reflux. The remaining PhBr in Et<sub>2</sub>O (5 cm<sup>3</sup>) was added dropwise and the mixture was refluxed for 40 min. To this mixture, 1.03 cm<sup>3</sup> (0.01 mol) of PhBr in anhydrous Et<sub>2</sub>O (5 cm<sup>3</sup>) and the Ru(III) Schiff base complex (0.05 mmol) 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<sub>4</sub>Cl and the ether extract on evaporation gave a crude product, which was chromatographed to obtain pure biphenyl and compared well with an authentic sample.<sup>[27–32,36,37]</sup>

#### Selective Oxidation of Alcohols to its Carbonyl Compounds

#### In the presence of NMO and $H_2O_2$ as co-oxidants

Catalytic oxidation of alcohols to corresponding carbonyl compounds by new Ru(III) Schiff base complexes containing triphenylphosphine / triphenylarsine as co-ligands was studied in the presence of *N*-methylmorpholin-*N*-oxide and H<sub>2</sub>O<sub>2</sub> as co-oxidants. A typical reaction using the complexes {[(EPh<sub>3</sub>)(X)Ru]L} as a catalyst and alcohols as substrates at a 1 : 100 molar ratio is described as follows. A solution of new Ru(III) Schiff base complex (0.01 mmol) in 20 cm<sup>3</sup> CH<sub>2</sub>Cl<sub>2</sub> was added to the solution of alcohol (1 mmol) in the presence of NMO (3 mmol) / H<sub>2</sub>O<sub>2</sub> (6 mmol). The solution mixture was refluxed for 6 h and the solvent was then evaporated from the mother liquor under reduced pressure. The resulting carbonyl compounds were then extracted with petroleum ether (60–80 °C; 20 cm<sup>3</sup>). The extracts were combined, dried over anhydrous MgSO<sub>4</sub> and evaporated to dryness. The carbonyl derivative was quantified as 2,4-dinitrophenylhydrazone derivative.<sup>[28,36,37]</sup>

#### In the presence of O<sub>2</sub> atmosphere at ambient temperature

To a solution of alcohol (1 mmol) in  $CH_2CI_2$  (20 cm<sup>3</sup>), a solution of the ruthenium complex in  $CH_2CI_2$  (0.01 mmol) was added and the mixture was stirred under an oxygen atmosphere at ambient temperature for 6 h and the solvent was then evaporated from the mother liquor under reduced pressure. The resulting carbonyl compounds was then extracted with petroleum ether (60–80 °C; 20 cm<sup>3</sup>) and was then quantified as 2, 4-dinitrophenylhydrazone derivative.<sup>[27–32]</sup> The oxidation products are known and are commercially available. These products were monitored by TLC and confirmed from FT-IR spectrometer and UV–vis spectrophotometer.

Table 1. Analytical, IR and UV-vis spectral data of new ruthenium(III) Schiff base complexes

		Melting	Elementa	ll analysis o (found) (%	alculated			IR			UV-vis
Sample no.	Complexes	Point (°C)	С	Н	N	$\nu_{C=N}$ (cm <sup>-1</sup> )	$\frac{v_{Ph-C}=0}{(cm^{-1})}$	$(cm^{-1})^{\nu_{Ru-N}}$	$\frac{\nu_{Ru-O}}{(cm^{-1})}$	Bands due to PPh <sub>3</sub>	λ <sub>max</sub> (nm)
1.	[RuCl(PPh <sub>3</sub> )(L <sup>1</sup> )]	140	63.3 (63.2)	4.1 (4.0)	5.7 (5.7)	1597	1421	490	473	690, 1080, 1430	253, 296, 352, 456, 636
2.	$C_{39}H_{30}CIN_3O_2PRu$ $[RuCl(PPh_3)(L^2)]$	115	65.4 (65.3)	4.1 (4.0)	5.3 (5.3)	1600	1443	543	457	690, 1089, 1432	253, 296, 368, 402, 669
3.	$C_{43}H_{32}CIN_3O_2PRu$ [RuCl(PPh <sub>3</sub> )(L <sup>3</sup> )]	110	63.7 (63.7)	4.3 (4.2)	5.6 (5.5)	1599	1402	540	460	692, 1088, 1435	247, 319, 494, 643
4.	$\begin{array}{l} C_{40}H_{32}CIN_3O_2PRu\\ [RuCl(PPh_3)(L^4)] \end{array}$	130	62.4 (62.2)	4.2 (4.1)	5.5 (5.5)	1608	1426	544	470	694, 1086, 1436	258, 338, 350, 388, 622
5.	$C_{40}H_{32}CIN_3O_3PRu$ $[RuBr(PPh_3)(L^1)]$	70	59.7 (59.6)	3.9 (3.9)	5.4 (5.4)	1598	1412	542	471	691, 1080, 1430	247, 297, 357,
6.	$C_{39}H_{30}BrN_3O_2PRu$ $[RuBr(PPh_3)(L^2)]$	78	61.9 (61.8)	3.9 (3.8)	5.0 (4.9)	1605	1444	541	474	694, 1082, 1434	254, 295, 362, 390, 474, 643
7.	$C_{43}H_{32}BrN_3O_2PRu$ $[RuBr(PPh_3)(L^3)]$	102	60.2 (60.1)	4.0 (4.1)	5.3 (5.3)	1607	1442	541	471	693, 1089, 1438	250, 308, 357, 388, 501, 672
8.	$\begin{array}{l} C_{40}H_{32}BrN_3O_2PRu\\ [RuBr(PPh_3)(L^4)] \end{array}$	88	59.0 (58.9)	4.0 (4.0)	5.2 (5.1)	1600	1440	543	470	692, 1082, 1435	253, 295, 338, 616
9.	$\begin{array}{l} C_{40}H_{32}BrN_{3}O_{3}PRu\\ [RuCl(AsPh_{3})(L^{1})] \end{array}$	70	59.7 (59.7)	3.9 (3.9)	5.4 (5.4)	1600	1462	492	472	691, 1083, 1435	252, 297, 362, 388, 628
10.	C <sub>39</sub> H <sub>30</sub> AsCIN <sub>3</sub> O <sub>2</sub> Ru [RuCl(AsPh <sub>3</sub> )(L <sup>2</sup> )]	81	61.9 (62.0)	3.9 (3.8)	5.0 (5.1)	1604	1398	542	481	692, 1084, 1486	249, 292, 354, 392, 489
11.	$\begin{array}{l} C_{43}H_{32}AsCIN_3O_2Ru\\ [RuCl(AsPh_3)(L^3)] \end{array}$	96	60.2 (60.1)	4.0 (4.0)	5.3 (5.2)	1607	1460	540	490	690, 1058, 1439	253, 320, 354, 390, 494, 645
12.	$\begin{array}{l} C_{40}H_{32}AsCIN_3O_2Ru\\ [RuCI(AsPh_3)(L^4)] \end{array}$	89	59.0 (59.0)	4.0 (4.0)	5.2 (5.2)	1598	1453	471	522	682, 1078,	252, 315, 385,
13.	$C_{40}H_{32}AsCIN_3O_3Ru$ $H_2L^1$	176	73.5 (73.5)	5.0 (5.0)	12.2 (12.2)	1614	1252	_	_	-	240, 278, 360,
14.	$C_{21}H_{17}N_3O_2$ $H_2L^2$	118	76.3 (76.2)	4.9 (5.0)	10.7 (10.7)	1625	1353	_	_	_	424 242, 268, 390,
15.	$C_{25}H_{19}N_3O_2 \\ H_2L^3$	265	73.9 (73.7)	5.4 (5.3)	11.8 (11.7)	1630	1296	_	_	_	447 242, 269, 389,
16.	$C_{22}H_{19}N_3O_2$ $H_2L^4$	215	70.8 (70.7)	5.1 (5.1)	11.3 (11.3)	1632	1327	_	_	_	442 241, 270, 380,
	C <sub>22</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub>										432

## **Results and Discussions**

All the complexes were isolated in high yields and are stable both in solid state and in solution. The analytical data (C, H, N) of all the Schiff base ligands (Scheme 1) and their Ru(III) complexes (Scheme 2) are in good agreement with the calculated values, thus confirming the proposed Mononuclear composition for all the complexes (Table 1). The complexes were obtained in powder form. Various attempts have been made to obtain the single crystals of the complexes but it has been unsuccessful. Therefore all the ligands and their complexes are stable at room temperature,

Applied Organometallic Chemistry non-hygroscopic and insoluble in water, methanol and ethanol and soluble in  $CH_2Cl_2$ ,  $CHCl_3$ , DMF, DMSO and  $CH_3CN$ .

#### **IR Spectra**

The IR spectra of the Schiff base ligands were compared with those of ruthenium complexes to obtain the information about binding mode of the ligands to ruthenium metal in the complexes listed in Table 1. The IR spectra of all the free Schiff base ligands exhibit strong bands in the 1614–1632 cm<sup>-1</sup> region, which is characteristic of the azomethine  $\nu_{(C=N)}$  group. It is expected that the coordination of the nitrogen to the metal atom could reduce the electron density in the azomethine group and thus lower  $\nu_{(C=N)}$  absorption. In the IR spectra of all the complexes this band is shifted to lower frequency at 1597–1608 cm<sup>-1</sup>, indicating the coordination of Schiff bases through azomethine nitrogen atom.<sup>[7,8,23,24]</sup> A strong band was obtained at 1252-1353 cm<sup>-1</sup> in the free Schiff base ligands, which has been assigned to phenolic-C-O absorption. On complexation, this band was shifted to a higher frequency range of 1398–1462 cm<sup>-1</sup>, indicating the other coordination of Schiff bases through the phenolic oxygen atom.<sup>[8,34,35]</sup> This is further confirmed by the disappearance of the  $v_{ph-C-OH}$  band in Ru(III) complexes at 3298-3442 cm<sup>-1</sup>. In addition the spectra of Schiff base ligands show bands at 3180 and 1680 cm<sup>-1</sup>, which are assigned to  $\nu_{N-H}$  and  $\nu_{C=0}$  vibrations of isatin moiety.<sup>[38,39]</sup> These bands disappear in ruthenium(III) complexes, possibly due to enolization of the keto group. This is further confirmed by the appearance of new bands at 1580 cm<sup>-1</sup> and in the 1535–1562 cm<sup>-1</sup> region, assignable to newly formed  $\nu_{\rm C}$  and  $\nu_{\rm NCO}$  groups. Further, bands in the 471–544 and 457–522 cm<sup>-1</sup> regions are probably due to formation of  $v_{Ru-N}$  and  $v_{Ru-O}$  bonds, respectively.<sup>[27]</sup>

#### UV-Vis Spectra and Magnetic Susceptibility

The electronic spectra of all the complexes in  $CH_2Cl_2$  showed four to six bands in the region 247–672 nm and their assignments



**Figure 1.** Electronic spectra of new Ru(III) Schiff base complexes: C1 =  $[RuCl(PPh_3)(L^1)]$ ; C2 =  $[RuCl(PPh_3)(L^2)]$ ; C3 =  $[RuCl(PPh_3)(L^3)]$ ; C4 =  $[RuCl(PPh_3)(L^4)]$ ; C6 =  $[RuBr(PPh_3)(L^2)]$ ; C7 =  $[RuBr(PPh_3)(L^3)]$ ; C8 =  $[RuBr(PPh_3)(L^4)]$ ; C9 =  $[RuCl(AsPh_3)(L^1)]$ ; C10 =  $[RuCl(AsPh_3)(L^2)]$ ; C11 =  $[RuCl(AsPh_3)(L^3)]$ .

are summarized in Table 1 and Fig. 1. The ground state of ruthenium(III) ( $t_{2g}^{5}$  configuration) is  ${}^{2}T_{2g}$ , while the first excited doublet levels in the order of increasing energy are  ${}^{2}A_{2g}$  and  ${}^{2}T_{1g}$ , which arise from  $t_{2g}^{4}e_{1g}^{1}$  configuration. In most of the ruthenium(III) complexes, the electronic spectra show only charge transfer bands. In a d<sup>5</sup> system and especially in ruthenium(III), which has relatively high oxidation properties, the charge transfer bands of the type  $L_{y} \rightarrow t_{2g}$  are prominent in the low-energy region and obscure the weaker bands due to d–d transition at 616–672 nm. Therefore, it becomes difficult to assign conclusively the bands in the visible region. Hence all the bands that appear in this region

Table 2. EPR spe	ctral da	ta, cyclio	voltam	metry <sup>a</sup> ar	id magnet	ic momen	its of new	/ Ru(III) Schiff	base cata	ysts			
		EPF	R data					Cyclic volta	ammetry d	ata			
						Ru <sup>l</sup>	<sup>II</sup> /Ru <sup>IV</sup>			Ru	<sup>III</sup> /Ru <sup>II</sup>		
Complexes	g <sub>x</sub>	$g_y$	g <sub>z</sub>	< <i>g</i> >*	<i>E</i> <sub>pa</sub> (V)	$E_{\rm pc}$ (V)	$E_{\rm f}$ (V)	$\Delta E_{\rm p}$ (mV)	$E_{\rm pa}$ (V)	$E_{\rm pc}$ (V)	$E_{\rm f}$ (V)	$\Delta E_{\rm p}$ (mV)	$\mu_{\mathrm{eff}}$ (BM)
[RuCl(PPh <sub>3</sub> )(L <sup>1</sup> )]	1.60	2.23	2.60	2.14	0.900	0.400	0.650	500	-0.400	-0.800	-0.600	400	1.74
[RuCl(PPh <sub>3</sub> )(L <sup>2</sup> )]	1.66	2.26	2.86	2.26	0.600	0.200	0.400	200	-0.500	-0.700	-0.600	200	1.72
[RuCl(PPh <sub>3</sub> )(L <sup>3</sup> )]	1.58	2.20	2.74	2.17	1.000	0.400	0.700	600	-0.300	-0.600	-0.450	300	1.72
[RuCl(PPh <sub>3</sub> )(L <sup>4</sup> )]	1.60	2.29	2.71	2.20	0.800	0.200	0.500	600	-0.500	-0.800	-0.650	300	1.74
[RuBr(PPh <sub>3</sub> )(L <sup>1</sup> )]	1.62	2.21	2.50	2.11	0.953	0.526	0.736	427	-1.030	-1.515	-1.273	485	1.73
[RuBr(PPh <sub>3</sub> )(L <sup>2</sup> )]	1.64	2.18	2.80	2.21	0.910	0.570	0.740	340	-1.120	-1.624	-1.372	504	1.72
[RuBr(PPh <sub>3</sub> )(L <sup>3</sup> )]	1.69	2.29	2.84	2.27	0.925	0.663	0.794	262	-1.085	-1.205	-1.145	120	1.76
[RuBr(PPh <sub>3</sub> )(L <sup>4</sup> )]	1.57	2.15	2.65	2.12	0.974	0.687	0.831	287	-1.218	-1.649	-1.434	431	1.74
[RuCl(AsPh <sub>3</sub> )(L <sup>1</sup> )]	1.62	2.26	2.67	2.18	0.829	0.314	0.572	515	-0.727	-1.123	-0.925	396	1.78
[RuCl(AsPh <sub>3</sub> )(L <sup>2</sup> )]	1.61	2.24	2.80	2.22	0.740	0.416	0.578	324	-0.810	-1.252	-1.031	442	1.69
[RuCl(AsPh <sub>3</sub> )(L <sup>3</sup> )]	1.59	2.28	2.77	2.21	0.786	0.350	0.601	436	-0.852	-1.276	-1.064	424	1.70
[RuCl(AsPh <sub>3</sub> )(L <sup>4</sup> )]	1.64	2.24	2.69	2.19	0.734	0.362	0.548	372	-0.816	-1.295	-0.479	479	1.68

<sup>a</sup> Working electrode, glassy carbon electrode; reference electrode, Ag–AgCl electrode; supporting electrolyte [NBu<sub>4</sub>]ClO<sub>4</sub> (0.01 M); concentration of the complex, 0.001 M; scan rate, 100 mV s<sup>-1</sup>;  $E_{\rm f} = 0.5(E_{\rm pa} + E_{\rm pc})$ ,  $\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc}$ , where  $E_{\rm pa}$  and  $E_{\rm pc}$  are anodic and cathodic potentials.  $<g>^* = [1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2]^{1/2}$ .

Table 3.	<sup>13</sup> C{ <sup>1</sup> H}-NMR spectra of Schiff ba	ase ligands		
Ligand	11	H-NMR (δ ppm)	13	<sup>2</sup> C-NMR (δ ppm)
H <sub>2</sub> L <sup>1</sup>	6.9-8.4	m, aromatic (12 H)	124.0–156.5	Phenyl carbons
	9.8	s, Ph-CH=N (1 H)	25.0	Ph-C=N-Carbon
	12.0	s, Ph-OH (1 H)	163.0	Enolic N=C <sup>1</sup> -OH
	15.2	s, Enolic N=C-OH (1 H)	164.0	Enolic N=C <sup>1</sup> -C <sup>2</sup> =N
$H_2L^2$	6.9-7.8	m, aromatic (14 H)	123.0–154.6	Naphthyl/phenyl carbons
	10.4	s, Ph-CH=N (1 H)	28.0	Ph-C=N-carbon
	13.4	s, Ph-OH (1 H)	163.0	Enolic N=C <sup>1</sup> -OH
	15.2	s, Enolic N=C-OH (1 H)	164.0	Enolic N=C <sup>1</sup> -C <sup>2</sup> =N
H <sub>2</sub> L <sup>3</sup>	6.9-8.2 12.0 15.2 2.5	m, aromatic (12 H) s, Ph–OH (1 H) s, Enolic N=C–OH (1 H) s, CH <sub>3</sub> (3 H)	122.0–158.0 28.0 18 163.0 164.0	Phenyl carbons Ph-C=N-Carbon Methyl carbon Enolic N= $C^1$ -OH Enolic N= $C^1$ - $C^2$ =N
H <sub>2</sub> L <sup>4</sup>	7.2-8.1	m, aromatic (12 H)	123.0-156.0	Phenyl carbons
	9.7	s, Ph-CH=N (1 H)	25.0	Ph-C=N-carbon
	12.0	s, Ph-OH (1 H)	68.0	Methoxy carbon
	15.2	s, Enolic N=C-OH (1 H)	163.0	Enolic $N=C^{1}-OH$
	3.3	s,-OCH <sub>3</sub> (3 H)	164.0	Enolic $N=C^{1}-C^{2}=N$



**Figure 2.** <sup>1</sup>H-NMR spectra of Schiff base ligands.

Appl. Organometal. Chem. 2011, 25, 87-97

have been assigned to charge transfer transitions which are in conformity with the assignment made for similar ruthenium(III) complexes.<sup>[28]</sup> The room temperature magnetic moments show that the ruthenium(III) catalysts are one electron paramagnetic (Table 2), in the range 1.68–1.76 BM, which corresponds to the +3 state of ruthenium, suggesting a low spin 4d<sup>5</sup>, S = 1/2 configuration around the Ru(III) ion in the octahedral environment.

#### <sup>13</sup>C{<sup>1</sup>H}-NMR Spectra of Schiff Base Ligands

The proton magnetic resonance spectra of the Schiff base ligands have been recorded in DMSO<sup>•</sup>d<sub>6</sub>. The different proton magnetic resonance signals are given in Table 3 and Fig. 2. The intensities of all the resonance lines were determined by planimetric integration. The spectra are complicated by coupling between



Figure 3. EPR spectra of the Ru(III) complexes: (a)  $[RuCI(PPh_3)(L^3)]$  and (b)  $[RuBr(PPh_3)(L^1)]$ .

various groups of the Schiff base ligands, leading to the following conclusions:

- (1) The proton signals of the enolic N=C-OH group was seen as a singlet at  $\delta = 15.2$  (1 H) and Ph-C-OH group in the region  $\delta = 12.0-13.4$  (1 H) for all the Schiff base ligands.
- (2) The chemical shift due to aromatic ring protons appeared as a multiplet at  $\delta = 6.9-8.4$  ppm in the Schiff base ligands.
- (3) The methyl protons and the methoxy protons were observed as a singlet at 2.5 and 3.3 ppm for  $H_2L^3$  and  $H_2L^4$  ligands.

The <sup>13</sup>C-NMR spectra of Schiff base ligands were recorded in DMSO<sup>•</sup>d<sub>6</sub> (Table 3). The ligands showed phenolic–C–OH and ph–C=N at  $\delta$  = 161.0 and  $\delta$  = 160.0, respectively. The significant shift in the position of enolic N=C<sup>1</sup>-OH at 163.0 ppm and N=C<sup>1</sup>(OH)-C<sup>2</sup>=N at 164.0 ppm may be due to the enolization of the keto group and formation of a new azomethine linkage.

#### ESR Spectra

The solid-state EPR spectra of the complexes exhibited an anisotropic spectra with axial distortion and the *g* values were measured in the range of  $g_x = 1.57-1.69$ ,  $g_y = 1.15-2.29$  and  $g_z = 2.50-2.86$  with  $g_{av} = 2.11-2.27$ , which derived from  $\langle g \rangle^* = [1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2]^{1/2}$ , and a three-line spectrum (Fig. 3) showing three different *g* values indicates that all complexes are rhombic in nature from the data obtained. The rhombicity of the spectra reflects the asymmetry of the electronic environment around ruthenium in the complexes.<sup>[7,8,40]</sup>

#### **Powder X-ray Diffraction**

Powder X-ray diffraction was performed to obtain further evidence about the structure of the metal complexes. The diffractograms obtained for the Schiff base metal complexes are given in Fig. 4 and the XRD patterns indicate a crystalline nature for the Schiff

Table 4.	X-ray powder diffract	tion data of [RuCl(PPh <sub>3</sub> )(L <sup>4</sup> )	] complex
Peak	20	Lattice spacing (d) (Å)	h k l
1	5.174	17.0049	136
2	13.623	6.5423	142
3	15.783	5.6104	412
4	19.146	4.6320	104
5	23.042	3.8557	246
6	30.003	2.7119	214
7	35.653	2.5162	326
8	39.951	2.2543	401
9	41.895	2.1546	260
10	63.439	1.7132	304
11	73.000	1.2950	215

base ligands and their Ru(III) complexes. The 'd' values,  $2\theta$  angles and (*h k I*) values are listed in Table 4. The complex crystallizes in an orthorhombic type of lattice with dimensions of a = 1.102, b = 1.245 and c = 1.206 Å. On the basis of above studies, an octahedral geometry for Ru(III) complexes has been proposed.<sup>[27,29,31,41-43]</sup>

#### **Electrochemical Studies**

The electron transfer properties of the Ru(III) Schiff base complexes were studied by cyclic voltammetry. Voltammograms of these complexes exhibited a range from 0 to 2.0 V (Ru<sup>III</sup>/Ru<sup>IV</sup>) and from 0 to -2.0 V (Ru<sup>III</sup>/Ru<sup>II</sup>), respectively, vs Ag-AgCI (Table 2 and Fig. 5). Since the ligands used in this study are not reversibly oxidized or reduced in the applied potential range, it is assumed that all redox processes are metal-centered only. These are compared with [FeCp<sub>2</sub>]<sup>0/+</sup>,  $E_{1/2} = +0.44$  V,  $\Delta E = 70$  mV for the cell used under the same conditions. The voltammogram reveals a pair of redox waves for these complexes, which corresponds to Ru<sup>III</sup>/Ru<sup>IV</sup> (oxidation) and Ru<sup>III</sup>/Ru<sup>II</sup> (reduction) at the positive and negative potentials, respectively. The peak separation ( $\Delta E$ ) for each complex is close to that anticipated for a Nernstian one-electron process.<sup>[44]</sup> Hence, it is inferred from the electrochemical data that the present ligand system is highly suitable for stabilizing the higher oxidation state of ruthenium.

We conclude that, in all the ruthenium complexes, the ruthenium trivalent state is highly stabilized, which is reflected in the low  $E_{1/2}$  value for the Ru<sup>III</sup>/Ru<sup>II</sup> couple. This result also indicates that the chelation by O,O-donors alone cannot stabilize the +2 state of ruthenium, and in order to have a stable complex containing an O,O-donor ligand for ruthenium(II), at least one of these Schiff base ligands in ruthenium complex needs to be replaced by strong  $\pi$ -acid ligand, e.g. the H<sub>2</sub>L<sup>2</sup> ligand which is a familiar stabilizer of ruthenium(II) and causes a positive potential shift to the E<sub>1/2</sub> for Ru<sup>II</sup>/R<sup>III</sup> couple.<sup>[45]</sup>

#### Catalytic Activity of Ru(III) Schiff Base Complexes

#### C-C coupling reaction

The new Ru(III) Schiff base complexes have been used as catalysts in the aryl-aryl coupling (Table 5). The system chosen for our study is the coupling of phenylmagnesium bromide with bromobenzene first converted into the corresponding Grignard



Figure 4. Powder X-ray diffraction pattern of the Schiff base ligand and corresponding Ru(III) complex: (a) H<sub>2</sub>L<sup>2</sup> ligand and (b) [RuBr(PPh<sub>3</sub>)(L<sup>2</sup>)] complex.

reagent. Then bromobenzene, followed by the complex chosen for the investigation, was added to the above reagent and the mixture was heated under reflux for 6 h. After work-up, the mixture yielded biphenyl. Only a very small amount of biphenyl was formed when the reaction was carried out without the catalyst. This is an insignificant amount compared with the yields of biphenyl obtained from the reactions catalyzed by ruthenium complexes. The optimum quantity of ruthenium catalyst (0.00012 mmol) required for the coupling of phenylmagnesium bromide with bromobenzene was investigated by performing a series of experiments using different mole ratios of phenylmagnesium bromide and the ruthenium catalyst already reported. The catalytic properties of the new mononuclear complexes were also

compared with those already reported mono nuclear complexes. It has been observed that the Ru(III) Schiff base complexes are better catalysts than the already reported mononuclear complexes.<sup>[21,22,33]</sup> The possible mechanism for the coupling of PhMgBr with PhBr catalysed by Ru(III) complexes has already been reported.<sup>[33]</sup>

#### Oxidation of primary and secondary alcohols

The use of environmentally friendly co-xidants in selective organic oxidations is of current interest. We describe the catalytic oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones by the synthesized ruthenium(III) tetradentate Schiff base complexes [RuCl(PPh<sub>3</sub>)(L)],



Figure 5. Cyclic voltammogram of Ru(III) complexes:  $C7 = [RuBr(PPh_3)(L^3)];$  $C8 = [RuBr(PPh_3)(L^4)]; C9 = [RuCI(AsPh_3)(L^1)].$ 

carried out in the presence of *N*-methyl morpholine-*N*-oxide and  $H_2O_2$  as co-oxidants and dioxygen atmosphere; the results of this

study are listed in Table 5. The primary and secondary alcohols (1 mmol) were efficient catalyzed using 0.01 mmol of the catalyst in the coexistence of dioxygen, 3 mmol of NMO and 6 mmol of H<sub>2</sub>O<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>. All the complexes oxidized the primary alcohols and secondary alcohols to their corresponding aldehydes and ketones with high yield. This reaction provides an environmentally friendly route to the conversion of alcoholic functions to carbonyl groups and water is the only by product during the course of the reaction which is removed using molecular sieves. The aldehydes and ketones formed after 6 h of stirring were isolated and guantified as their 2,4-dinitrophenylhydrazone derivatives. Control experiments were carried out without the ruthenium catalyst under the same reaction conditions and in no case was there any detectable oxidation of alcohols using NMO as co-oxidant, and only a very small amount of carbonyl compound is formed when the reaction was carried out without the catalyst in the presence of dioxygen and H<sub>2</sub>O<sub>2</sub> at ambient temperature. This is an insignificant amount compared with the yields of carbonyl compounds that have been obtained from the reaction catalyzed by ruthenium complexes. The results of the present investigation suggest that the complexes are able to react efficiently with NMO,  $^{[35-38]}$  H<sub>2</sub>O<sub>2</sub> and dioxygen to

	C–C cc	oupling			Oxidatio	on of alcoho	ls			
					In	NMO	In	$H_2O_2$	ln (	D <sub>2</sub> atm
Catalyst	Yield of Ph– Ph (in mg)	Percentage (%)	Substrate	Product	Yield <sup>a</sup> (%)	Turnover number <sup>b</sup>	Yield <sup>a</sup> (%)	Turnover number <sup>b</sup>	Yield <sup>a</sup> (%)	Turnover number <sup>b</sup>
[RuCl(PPh <sub>3</sub> )(L <sup>1</sup> )]	382	40	Cinnamy alcohol	Cinnamaldehyde	89	88	78	77	68	67
			Benzyl alcohol	Benzaldehyde	65	67	59	60	50	51
			Cyclohexanol	Cyclohexanone	85	85	77	77	66	66
			Butan-2-ol	Butanone	65	86	58	78	70	94
			Propan-2-ol	Propanone	69	115	60	100	52	71
			Butan-1-ol	Butraldehyde	60	81	62	83	60	101
			Propan-1-ol	Propionaldehyde	68	113	61	102	55	89
$[RuCl(PPh_3)(L^2)]$	408	42	Cinnamy alcohol	Cinnamaldehyde	96	95	91	89	79	78
			Benzyl alcohol	Benzaldehyde	74	76	68	70	56	57
			Cyclohexanol	Cyclohexanone	95	95	88	88	75	75
			Butan-2-ol	Butanone	90	123	77	104	62	84
			Propan-2-ol	Propanone	83	138	73	122	66	108
			Butan-1-ol	Butraldehyde	78	114	66	89	60	91
			Propan-1-ol	Propionaldehyde	90	150	76	126	68	112
[RuCl(PPh <sub>3</sub> )(L <sup>3</sup> )]	302	31	Cinnamy alcohol	Cinnamaldehyde	68	67	59	58	82	81
			Benzyl alcohol	Benzaldehyde	49	51	39	39	32	33
			Cyclohexanol	Cyclohexanone	60	60	52	52	41	41
			Butan-2-ol	Butanone	33	44	25	33	16	26
			Propan-2-ol	Propanone	35	58	26	44	21	30
			Butan-1-ol	Butraldehyde	28	38	20	28	18	26
			Propan-1-ol	Propionaldehyde	50	83	41	68	27	42
[RuCl(PPh <sub>3</sub> )(L <sup>4</sup> )]	356	37	Cinnamy alcohol	Cinnamaldehyde	88	87	80	79	66	65
			Benzyl alcohol	Benzaldehyde	69	71	61	62	53	54
			Cyclohexanol	Cyclohexanone	92	92	83	83	70	70
			Butan-2-ol	Butanone	86	116	68	92	56	78
			Propan-2-ol	Propanone	79	132	74	123	61	102
			Butan-1-ol	Butraldehyde	76	102	66	89	60	101
			Propan-1-ol	Propionaldehyde	88	147	76	126	64	106

<sup>b</sup> Moles of product per mole of catalyst



										Ц	hibitio	n Zone	concen	tration	(mm)									
		К. р	neumor	niae			Shig	<i>jella</i> sp.				M.	luteus				E.c	ili				S.typh	!	
Ligand/complex	0.5%	1.0%	1.5%	2.0%	2.5%	0.5%	1.0%	1.5% 2	.0% 2	.5% 0	.5%	.0%0.1	1.5%	2.0%	2.5% 0	.5% 1.	0% 1.5	% 2.C	% 2.5	% 0.5%	1.0%	1.5%	2.0%	2.5%
H <sub>2</sub> L <sup>1</sup>	8	8	10	10	1	8	8	8	6	10	8	6	10	10	12	10	10 10		6	6	10	10	10	11
H <sub>2</sub> L <sup>2</sup>	8	80	8	6	6	00	6	6	6	7	8	6	6	6	10	6	6	•	9 12	6	6	6	11	12
H <sub>2</sub> L <sup>3</sup>	8	8	8	6	10	6	6	10	10	11	10	10	10	11	12	6	6	~	6	8	6	6	6	12
H <sub>2</sub> L <sup>4</sup>	10	10	10	10	12	6	6	6	8	6	11	11	11	11	1	10	10 1	-	0 12	6	6	6	11	12
[RuCl(PPh <sub>3</sub> )(L <sup>1</sup> )]	10	10	12	14	14	11	12	12	14	14	14	14	14	16	16	12	12 1	 +	4 14	12	13	13	14	15
[RuCl(PPh <sub>3</sub> )(L <sup>2</sup> )]	12	13	13	13	14	13	13	14	14	15	14	14	14	16	16	13	13 13	1	5 15	14	14	14	16	16
[RuCl(PPh <sub>3</sub> )(L <sup>3</sup> )]	12	13	13	15	17	12	14	16	16	16	13	13	14	15	16	13	14	10	5 14	12	13	14	16	16
[RuCl(PPh <sub>3</sub> )(L <sup>4</sup> )]	12	12	14	15	16	12	13	15	16	16	14	14	14	16	15	14	14		5 16	13	15	16	16	15
[RuBr(PPh <sub>3</sub> )(L <sup>1</sup> )]	14	14	14	15	15	15	15	14	15	14	18	16	14	14	14	14	16 10	1	5 16	14	16	14	17	15
[RuBr(PPh <sub>3</sub> )(L <sup>2</sup> )]	16	16	16	15	15	14	14	14	16	16	14	14	15	16	16	16	16 10	-	4 15	16	15	16	16	16
[RuBr(PPh <sub>3</sub> )(L <sup>3</sup> )]	16	14	15	15	16	14	15	16	16	16	14	15	14	16	17	15	15 10	-	5 16	14	14	16	16	18
[RuBr(PPh <sub>3</sub> )(L <sup>4</sup> )]	14	14	14	15	16	16	16	14	12	13	15	16	16	16	16	14	15 1	10	5 13	16	15	16	16	16
[RuCl(AsPh <sub>3</sub> )(L <sup>1</sup> )]	14	14	15	15	16	16	16	16	17	17	12	12	14	14	15	15	15 15	-	5 16	16	16	16	18	18
[RuCl(AsPh <sub>3</sub> )(L <sup>2</sup> )]	12	12	14	14	14	12	14	14	14	14	15	15	15	15	16	12	12 1:	~ 	3 15	15	14	15	15	16
[RuCl(AsPh <sub>3</sub> )(L <sup>3</sup> )]	16	16	16	17	15	14	14	14	15	15	14	14	14	12	15	16	13 13	2	3 13	14	15	15	16	16
[RuCl(AsPh <sub>3</sub> )(L <sup>4</sup> )]	14	14	14	14	15	15	15	15	14	14	14	14	18	18	18	16	16 1	1	5 12	12	13	12	15	16
Standards	Δ	ш	A <sub>×</sub>	$A_k$	S	۵	ш	A <sub>×</sub>	$A_k$	S	Δ	$A_{k}$	A <sub>×</sub>	S	ш	D	Ē	Å	~	$A_k$	A <sub>×</sub>	ш	S	۵
	I	12	8	23	17	I	16	10	21	10	I	15	I	6	16	I	1	I	I	16	I	10	I	8
D = DMSO; E = eŋ	ythron	ycin; A <sub>x</sub>	= amo	vxycilin;	$A_k = ar$	npicillin	and S =	strepto	mycin.															

yield a high valency ruthenium-oxo species, capable of oxygen atom transfer to alcohols. This was further supported by spectral changes that occur by addition of NMO,  $H_2O_2$  and in presence of dioxygen to a dichloromethane solution of the ruthenium(III) complexes and it was monitored using a UV-vis spectrophotometer and the appearance of the peak at 390 nm.

The relatively higher product yield obtained for the oxidation of cinnamyl alcohol is due to the presence of a more acidic  $\alpha$ -CH unit in cinnamyl alcohol. Further, the oxidation of cinnamyl alcohol to cinnamaldehyde takes place with retention of a C=C double bond, which is an important characteristic of a ruthenium – NMO or H<sub>2</sub>O<sub>2</sub> or dioxygen system. The primary and secondary aliphatic alcohols were effectively oxidized into their corresponding aldehydes and ketones with high yield. These reactions were also studied without using catalysts to determine the effect of catalyst in oxidation of primary and secondary alcohols to its carbonyl compounds. The amount of reaction products was compared with percentage conversion of these alcohols. The oxidation products of hydrozones showed separation peaks corresponding to the alcohols in the FT-IR spectrometer; hence, the carboxylic acid formed in the oxidation of alcohols was discarded.

#### **Antibacterial Activities**

The Schiff base ligands and their ruthenium(III) complexes were tested in vitro to access their growth inhibitory activity against K. pneumoniae, Shigella sp., M. luteus, E. coli and S. typhi by the Kirby Bauer method.<sup>[46]</sup> The test organisms were grown on nutrient agar medium in Petri plates. The compounds to be tested were dissolved in DMSO and soaked on a filter paper disk of 5 mm diameter and 1 mm thickness. The concentrations used in this study were 0.5, 1.0, 1.5, 2.0 and 2.5% (Table 6). The disks were placed on the previously seeded plates and incubated at 37  $^{\circ}$ C for 24 h. Amoxycilin, ampicillin, erythromycin and streptomycin were used as standards with different concentrations. The variation in the effectiveness of the different compounds against different organisms depends on their impermeability of the microbial cells or on the difference in the ribosome of the microbial cells.<sup>[47]</sup> In general, the complexes are more active than those of the parent ligands and ruthenium(III) starting complexes. The increase in the antibacterial activity of the metal chelates with increase in concentration is due to the effect of metal ion on normal cell process. Such an increase in activity of the metal chelates can be explained on the basis of Overtone's  $\mathsf{concept}^{[48]}$  and chelation theory.<sup>[49,50]</sup> According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only rapid soluble materials, due to which liposolubility is an important factor that controls the antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of  $\pi$ -electrons over the whole chelate ring and enhances the liphophilicity, which enhances the penetration of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocks the metal binding sites on enzymes of microorganism. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts the further growth of the organism. Furthermore, the mode of action of the complexes may involve formation of a hydrogen bond through an azomethine group with the active centers of cell constituents, resulting in interference with the normal cell process.<sup>[51,52]</sup>

#### Conclusion

In conclusion, we have synthesized and characterized a series of ruthenium(III) Schiff base complexes of N<sub>2</sub>O<sub>2</sub> donor ligands and these complexes were developed as a new and efficient catalyst for the C-C coupling and oxidation reactions of primary and secondary alcohols into their corresponding carbonyl compounds in the presence of NMO/H<sub>2</sub>O<sub>2</sub> co-oxidants and in O<sub>2</sub> atmosphere at ambient temperature. It was shown that complexes of the type [RuX(EPh<sub>3</sub>)(L)] (where, X = CI/Br; E = P/As;  $L = N_2O_2$ donors of Schiff bas ligands) can be turned from moderate to good catalysts with proper modification of their ligands under the usually applied concentrations (1:100 catatlyst:substrate). Furthermore, the organometallic ruthenium systems allow easy ligand modifications, which may lead to further improvements of their catalytic performance. Superior selectivity combined with a high activity and easy synthetic modifications are the advantages of the ruthenium catalysts described here in comparison to previously described coupling and oxidation catalysts. From antibacterial activity study, it was found that the activity of the ruthenium(III) Schiff base complexes almost reaches the effectiveness of the conventional bacteriocide standards such as Amoxycilin, ampicillin, erythromycin and streptomycin, for which the concentrations used in this study were 0.5, 1.0, 1.5, 2.0 and 2.5%.

#### Acknowledgment

We are thankful to NMR Research Centre, Indian Institute of Science (IISc), Bangalore, India for providing  $^{13}C\{^{1}H\}$ -NMR spectra.

#### References

- [1] T. Mallat, A. Baiker, Chem. Rev. 2004, 104, 3037.
- [2] A. S. K. Hashmi, Chem. Rev. 2007, 107, 3180.
- [3] A. Corma, H. Garcia, *Chem. Soc. Rev.* **2008**, *37*, 2096.
- [4] G. A. Morris, H. Zhou, L. C. Stern, S. T. Nguyen, *Inorg. Chem.* **2001**, 40, 3222.
- [5] K. Jitsukawa, H. Shizaki, H. Masuda, *Tetrahedron Lett.* **2002**, *43*, 1491.
- [6] A. Yeori, S. Genler, S. Groysman, I. Goldberg, M. Kol, Inorg. Chem.
- Commun. **2004**, 7, 280.
- [7] R. Ramesh, Inorg. Chem. Commun. 2004, 7, 274.
- [8] G. Venkatachalam, R. Ramesh, Inorg. Chem. Commun. 2005, 8, 1009.
- [9] S. N. Pal, S. Pal, Inorg. Chem. **2001**, 40, 4807.
- [10] B. De Clercq, F. Verpoort, *Adv. Synth. Catal.* **2002**, *34*, 639.
- [11] B. De Clercq, F. Lefebvre, F. Verpoort, Appl. Catal. 2003, A247, 345.
- [12] P. J. McCarthy, R. Hovey, K. Ueno, A. E. Martell, J. Am. Chem. Soc. 1955, 77, 5820.
- [13] W. H. Leung, C. M. Che, Inorg. Chem. 1989, 28, 4619.
- [14] W. K. Wong, X. P. Chen, J. P. Gao, Y. G. Chi, W. X. Pan, W. Y. Wang, J. Chem. Soc. Dalton Trans. 2002, 113.
- [15] J. Y. Kim, M. J. Jun, W. Y. Lee, J. Organomet. Chem. 2003, 665, 87.
- [16] Y.-G. Zhou, W. Tang, W.-B. Wang, W. Li, X. Zhang, J. Am. Chem. Soc. 2002, 124, 4952.
- [17] J. G. De Vries, G. Roelfes, R. Green, Tetrahedron Lett. 1998, 39, 8329.
- [18] H. Dai, X. Hu, H. Chen, C. Bai, Z. Zheng, *Tetrahedron Assym.* 2003, 14, 1467.
- [19] S. Priya, M. S. Balakrishna, S. M. Mobin, R. McDonald, J. Organomet. Chem. 2003, 688, 227.
- [20] K. M. Sung, S. Huh, M. J. Jun, Polyhedron. 1999, 18, 469.
- [21] D. Chatterjeea, A. Mitra, B. C. Roy, J. Mol. Catal. Chem. 2000, 161A, 17.
- [22] A. S. Goldstein, R. H. Beer, R. S. Drago. J. Am. Chem. Soc. 1994, 116, 2424.
- [23] R. Ramesh, S. Maheshwaran, J. Inorg. Biochem. 2003, 96, 457.
- [24] T. D. Thangadurai, S. K. Ihm, Synth. React. Inorg. Met.-Org and Nano-Met. Chem. 2006, 36, 435.

- [25] A. A. Ensafi, H. A. Soleymani, E. Mirmomtaz, Microchem. J. 2008, 89, 108
- [26] T. D. Thangadurai, S. Jeong, S. Yun, S. Kim, C. Kim, Y.-I. Lee, Microchem. J. 2010, (in press).
- [27] N. Sathya, A. Manimaran, G. Raja, P. Muthusamy, K. Deivasigamani, C. Jayabalakrishnan, Trans. Met. Chem. 2009, 34, 7.
- [28] N. Padma Priya, S. Arunachalam, A. Manimaran, D. Muthupriya, V. Chinnusamy, C. Jayabalakrishnan, Spectrochim Acta part A. 2009, 72,670.
- [29] A. Manimaran, C. Jayabalakrishnan, Appl. Org. Met. Chem. 2010, 24, 71.
- [30] N. Thilagavathi, A. Manimaran, N. Padma Priya, N. Sathya, C. Jayabalakrishnan, Trans. Met. Chem. 2009, 34, 725.
- [31] A. Manimaran, C. Jayabalakrishnan, Synth. React. Met.-Org. Nano-Metal Chem. 2010, 40, 116.
- [32] N. Thilagavathi, A. Manimaran, N. Padma Priya, N. Sathya, C. Jayabalakrishnan, Appl. Org. Met. Chem. 2010, 24, 301.
- [33] J. Chatt, G. Leigh, D. M. P. Mingos, R. J. Paske, J. Chem. Soc. 1968, A, 2636.
- [34] K. Natarajan, R. K. Poddar, U. Agarwala, J. Inorg. Nucl. Chem. 1977, 39, 431.
- [35] P. Viswanathamurthi, K. Natarajan, Ind. J. Chem. 1999, 38A, 797.
- [36] A. I. Vogel, Text Book of Practical Organic Chemistry, 5th edn, Longman: London, 1989, p. 264.
- [37] P. Viswanathamurthi, K. Natarajan, Synth. React. Met.-Org. Chem. 2006, 36, 415.

- [38] G. A. Bain, D. X. West, J. Krecji, J. Vald'es-Martinez, S. Hernandez-Ortega, R. Toscano, Polyhedron 1997, 16, 855.
- A. Rai, S. K. Sengupta, P. Pandey, Spectrochim. Acta Pt A. 2005, 61, [39] 2761.
- [40] S. Priyarega, R. Prabhakaran, K. R. Aranganayagam, R. Karvembu, K. Natarajan, Appl. Organomet. Chem. 2007, 21, 788.
- [41] S. K. Chattopadhyay, S. Ghosh, Inorg. Chim. Acta 1989, 163, 245.
- [42] M. M. T. Khan, R. I. Kureshy, N. H. Khan, Tetrahedron Assym. 1991, 2,
- 1015. [43]
- S. C. Singh Jadon, D. Singh, R. V. Singh, Ind. J. Chem. 1996, 35A, 1107.
- [44] R. S. Nicholson, I. Shain, Anal. Chem. 1964, 36, 706.
- [45] A. M. El-Handawy, S. Y. Alqaradawi, H. A. Al-Madfa, Trans. Met. Chem. 2000, 25, 572.
- A. W. Bauer, W. M. M. Kirby, J. C. Sherries, M. Truck, Am. J. Clin. Pathol. [46] 1996, 45, 493.
- [47] C. Perez, M. Pauli, P. Bazerque, Acat. Biol. Et. Med. Exper. 1990, 15, 113.
- M. Thilagavathi, R. Karvembu, [48] R. Prabhakaran, A. Geetha, V. Krishnan, H. Bertagnolli, K. Natarajan, J. Inorg. Biochem. 2004, 98, 2131.
- [49] T. D. Thangadurai, K. Natarajan, Ind. J. Chem. 2002, 41A, 741.
- [50] R. Maruvada, S. Pal, G. Balakrish Nair. J. Micro. Biol. Meth. 1994, 20, 115.
- [51] S. C. J. Singh, N. Gupta, R. V. Singh, Ind. J. Chem. 1995, 34A, 733.
- [52] N. Dharmaraj, P. Viswanthamurthi, K. Natarajan, Trans. Met. Chem. 2001, 26, 105.