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Ru(III) complexes containing 3,5-pyrazole dicarboxylic acid and triphenylphosphine/triphenylarsine: Synthesis, characterization and catalytic activity

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ABSTRACT

New hexa-coordinated Ru(III) complexes of the type $[Ru(H_2Pzdc)(EPh_3)_3X_2]$ have been synthesized by reacting 3,5-pyrazole dicarboxylic acid (H₃Pzdc) with the appropriate starting complexes $[RuX_3(EPh_3)_3]$ (where X = Cl or Br; E = P or As). The ligand behaves as a bidentate monobasic chelate. All the complexes have been characterized by analytical and spectroscopic (IR, electronic and EPR) data. Single-crystal X-ray analysis of the complex $[Ru(H_2Pzdc)(PPh_3)_2Cl_2]\cdot C_6H_6\cdot C_2H_5OH$ revealed that the coordination environment around the ruthenium center consists of an NOP₂Cl₂ octahedron. The planar ligand occupies the equatorial position along with two chlorine atoms, while the triphenylphosphine groups occupy the axial positions. The electrochemical behavior of the new complexes was studied using cyclic voltammetry. The new mononuclear ruthenium complexes are capable of acting as catalysts for the oxidation of alcohols. © 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The use of transition metal complexes as catalysts has become indispensable and reactions being environmentally benign are mandatory. In recognition of their widespread importance over the years, many synthetic metal complexes have been employed as catalysts for simple single step reactions to complicated multistep processes [1-8]. The cross coupling reaction is found to be one of the efficient methods for the easy synthesis of certain compounds which would otherwise be tedious [9-11]. The new synthetic methods that have emerged for the formation of C--C bonds play an important role in pharmacological industries. A number of ruthenium metal complexes have been found to catalyze such aryl-aryl coupling reactions [12-15]. Another industrially important reaction is the oxidation of organic compounds, ranging from simple alcohols to complicated compounds. Ruthenium complexes can also act as versatile catalysts in the oxidation of alcohols to aldehydes or ketones [1,16–18].

With this background in mind, we aimed at developing metal complexes that can act as a dual catalyst for both aryl-aryl coupling and oxidation. Herein we report the synthesis, characterization and catalytic activity of hexacoordinated ruthenium(III) complexes containing 3,5-pyrazole dicarboxylic acid and $PPh_3/ASPh_3$.

2. Experimental work

2.1. Materials

 $RuCl_3$ ·3H₂O purchased from Hi-media and 3,5-pyrazole dicarboxylic acid purchased from Acros chemicals were used as such, without further purification. Solvents were dried before use. The starting complexes $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$, $[RuBr_3-(AsPh_3)_3]$ and $[RuBr_3(PPh_3)_3]$ were prepared as reported earlier [19–22].

2.2. Physical measurements

The infrared spectra of the ligand and the complexes have been recorded on a Nicolet Avatar model FT-IR spectrophotometer using KBr discs in the range 4000–400 cm⁻¹. Electronic spectra were recorded on a Systronics 119 UV–Vis spectrophotometer using methanol as the solvent. Elemental analyses were performed with a Vario EL III Elementar analyzer. Room temperature electron paramagnetic resonance (EPR) spectra were recorded with an ER 200 D-SRC Bruker spectrometer. Cyclic voltammetric experiments were carried out using a BAS CV-27 electrochemical analyzer with a glassy carbon working electrode. A platinum wire and a silver–



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silver chloride electrode were used as counter and reference electrodes respectively. Melting points were recorded with a Lab India apparatus.

2.3. Crystallography

Single crystals of $[Ru(H_2Pzdc)(PPh_3)_2Cl_2] \cdot C_6H_6 \cdot C_2H_5OH$ suitable for X-ray diffraction studies were obtained from slow evaporation of a solution of the complex in a benzene/ethanol mixture.

2.3.1. Data collection

A Bruker SMART 1000 three-circle X-ray diffractometer (Mo K α radiation, 50 kV, 40 mA) fitted with a graphite monochromator and a CCD detector (CCD-PXL-KAF2, SMART 1000, 512 \times 512 pixel) was employed [23]. The crystal, coated with rotectant (mineral oil), was mounted on a nylon loop and was maintained at 110 K using a cold nitrogen stream. The crystal to detector distance was set at 5.0 cm.

2.3.2. Data reduction, structure solution and refinement

SAINTPLUS [24] was used for data integration and data were corrected for Lorentz and polarization factors. SADABS [25] was employed to correct the absorption effects. Systematic reflection conditions for the data set suggest the space group $Pca2_1$ for $[Ru(H_2Pzdc)(PPh_3)_2Cl_2] \cdot C_6H_6 \cdot C_2H_5OH$. The structure was solved readily by Patterson map interpretation. All non-hydrogen atoms were located with the Fourier difference map analysis and refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions. The structure was refined (weighted least squares refinement on F^2) to convergence [26]. Table 1 gives further details of the data collection, refinement and the structural details of $[Ru(H_2Pzdc)(PPh_3)_2Cl_2] \cdot C_6H_6 \cdot C_2H_5OH$.

2.4. Synthesis of $[Ru(H_2Pzdc)(EPh_3)_2X_2]$ (X = Cl or Br; E = P or As)

All the new mononuclear ruthenium(III) complexes were prepared by the following general procedure: a benzene (20 ml) solu-

Table 1

Crystal data and structure refinement parameters for $[Ru(H_2Pzdc)(PPh_3)_2Cl_2]\cdot C_6H_6-C_2H_5OH$ (1).

Crystal data	1
Empirical formula	C49H45Cl2N2O5P2Ru
Formula weight	975.78
T (K)	110(2)
Wavelength (Å)	0.71073
Crystal system, space group	orthorhombic, Pca2(1)
Unit cell dimensions	
a (Å)	20.972(2)
b (Å)	11.9684(11)
<i>c</i> (Å)	18.0511(17)
V (Å ³)	4530.8(7)
Z, D_{calc} (Mg/m ³)	4, 1.431
Absorption coefficient (mm ⁻¹)	0.584
F(000)	2004
Crystal size (mm)	$0.29 \times 0.19 \times 0.16$
θ Range for data collection (°)	1.70–27.52
Limiting indices	$-27\leqslant h\leqslant 27$, $-10\leqslant k\leqslant 15$,
	$-20 \leqslant l \leqslant 23$
Reflections collected/unique	33 976/10 055 [R _{int} = 0.0433]
Completeness (to θ = 24.98) (%)	99.4
Absorption correction	SADABS
Maximum and minimum	0.9129 and 0.8495
transmission	
Refinement method	full-matrix least-squares on F ²
Data/restraints/parameters	10 055/4/558
Goodness-of-fit (GOF) on F^2	1.036
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0345, wR_2 = 0.0715$
R indices (all data)	$R_1 = 0.0391, wR_2 = 0.0729$
Largest difference in peak and hole	0.847 and -0.363
(e A ⁻³)	

tion of $[RuX_3(EPh_3)_3]$ (where E = P or As; X = Cl or Br) (0.1 mmol) was added to a refluxing solution of 3,5-pyrazole dicarboxylic acid monohydrate (0.1 mmol) in ethanol (20 ml). The solution was filtered while hot, reduced to half of its volume and left for slow evaporation. The crystalline product that separated out was filtered off, washed with ethanol and dried under vacuum. The product was recrystallized from a benzene/ethanol mixture. The individual syntheses are given below.

2.4.1. [Ru(H₂Pzdc)(PPh₃)₂Cl₂]·C₆H₆·C₂H₅OH (1)

 $[\text{Ru}(\text{H}_2\text{Pzdc})(\text{PPh}_3)_2\text{Cl}_2] \cdot \text{C}_6\text{H}_6 \cdot \text{C}_2\text{H}_5\text{OH} (1) \text{ was prepared from } [\text{RuCl}_3(\text{PPh}_3)_3] (0.0994 \text{ g}, 0.1 \text{ mmol}) \text{ and } 3,5\text{-pyrazole dicarboxylic } acid monohydrate (0.017 \text{ g}, 0.1 \text{ mmol}) \text{ as dark green crystals. Yield: } 70\%.$ *Anal.* $Calc. for <math>\text{RuC}_{41}\text{H}_{33}\text{N}_2\text{O}_4\text{Cl}_2\text{P}_2 \cdot \text{C}_6\text{H}_6 \cdot \text{C}_2\text{H}_5\text{OH}$: C, 60.31; H, 4.65; N, 2.87. Found: C, 60.28; H, 4.71; N, 2.82\%. IR (cm⁻¹): 3332, 1715, 1652, 1482, 1434, 1091, 694. UV λ_{max} (nm (L mol⁻¹ cm⁻¹)): 248(25,200), 270(17,260), 289(18,450), 301(19,220). M.p.: >200 °C^d (d = decomposition).

2.4.2. $[Ru(H_2Pzdc)(AsPh_3)_2Cl_2]$ (2)

[Ru(H₂Pzdc)(AsPh₃)₂Cl₂] (**2**) was prepared from [RuCl₃(AsPh₃)₃] (0.112 g, 0.1 mmol) and 3,5-pyrazole dicarboxylic acid monohydrate (0.017 g, 0.1 mmol) as dark green crystals. Yield: 75%. *Anal.* Calc. for RuC₄₁H₃₃N₂O₄Cl₂As₂: C, 52.40; H, 3.53; N, 2.98. Found: C, 52.16; H, 3.35; N, 2.63%. IR (cm⁻¹): 3334, 1724, 1652, 1481, 1434, 1076, 692. UV λ_{max} (nm (L mol⁻¹ cm⁻¹)): 284(24,610), 306(24,950). M.p.: >190 °C^d.

2.4.3. $[Ru(H_2Pzdc)(AsPh_3)_2Br_2]$ (3)

[Ru(H₂Pzdc)(AsPh₃)₂Br₂] (**3**) was prepared from [RuBr₃(AsPh₃)₃] (0.125 g, 0.1 mmol) and 3,5-pyrazole dicarboxylic acid monohydrate (0.017 g, 0.1 mmol) as reddish brown crystals. Yield: 75%. *Anal.* Calc. for RuC₄₁H₃₃N₂O₄Br₂As₂: C, 47.87; H, 3.23; N, 2.72. Found: C, 47.62; H, 3.11; N, 2.83%. IR (cm⁻¹): 3326, 1720, 1652, 1482, 1434, 1076, 692. UV λ_{max} (nm (L mol⁻¹ cm⁻¹)): 268(4236), 306(16,910). M.p.: >200 °C^d.

2.4.4. $[Ru(H_2Pzdc)(PPh_3)_2Br_2]$ (4)

[Ru(H₂Pzdc)(PPh₃)₂Br₂] (**4**) was prepared from [RuBr₃(PPh₃)₃] (0.1128 g, 0.1 mmol) and 3,5-pyrazole dicarboxylic acid monohydrate (0.017 g, 0.1 mmol) as dark green crystals. Yield: 80%. *Anal.* Calc. for RuC₄₁H₃₃N₂O₄Br₂P₂: C, 52.35; H, 3.53; N, 2.97. Found: C, 52.06; H, 3.93; N, 2.72%. IR (cm⁻¹): 3324, 1713, 1651, 1481, 1434, 1090, 693. UV λ_{max} (nm (L mol⁻¹ cm⁻¹)): 248(25,000), 268(16,450), 306(14,590). M.p.: >230 °C^d.

2.5. Application studies

2.5.1. Catalytic oxidation

To a solution of the alcohol (1 mmol) in CH_2Cl_2 (20 ml), *N*-methyl morpholine-oxide (1 mmol) and the ruthenium complex (0.01 mmol) were added. The solution was heated under reflux for 3 h. The mixture was evaporated to dryness and extracted with petroleum ether (60–80 °C). The combined petroleum ether mixture was filtered and evaporated to give the corresponding aldehyde, which was then quantified as the 2,4-dinitrophenyl hydrazone derivative [27].

2.5.2. Aryl-aryl coupling

Magnesium turnings (0.320 g; 0.013 g atom) were placed in a two necked round bottomed flask with a calcium chloride guard tube. A crystal of iodine was added to activate the magnesium. Bromobenzene [0.746 g of a total 1.884 g (0.012 mol)] in anhydrous diethylether (5 ml) was added with stirring and the mixture was heated under reflux. The appearance of turbidity after 5 min indicated initiation of the reaction. The remaining bromobenzene in

diethylether (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 diethylether (5 ml) and the ruthenium 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 ammonium chloride. The diethylether extract, on evaporation of the solvent, gave the crude product which was chromatographed on a silica gel column. Light petroleum (60–80 °C) eluted the pure biphenyl, which compared well with an authentic sample (TLC plates, IR and ¹H NMR M.p. 69–72 °C) [28].

3. Results and discussion

New hexa-coordinated Ru(III) complexes of the type [Ru(H₂Pzdc)(EPh₃)₂X₂] have been prepared by reacting 3,5-pyrazole dicarboxylic acid (H₃Pzdc) with [RuCl₃(PPh₃)₃], [RuCl₃(AsPh₃)₃], [RuBr₃(AsPh₃)₃] and [RuBr₃(PPh₃)₃] in a 1:1 ratio (Scheme 1). The ligand replaces one EPh₃ and one X atom (E = As or P; X = Cl or Br) from the starting complex to yield [Ru(H₂Pzdc)(EPh₃)₂X₂], and the analytical data conform to this stoichiometry.

3.1. Infrared spectroscopy

The IR spectrum of the free ligand (H₃Pzdc) shows a strong band around 1700 cm⁻¹ assignable to $v_{(C=0)}$ of the —COOH moiety [29]. In all the complexes, new bands due to v_{as} (COO⁻) were observed in the region 1652–1651 cm⁻¹ and that due to v_s (COO⁻) at about 1480 cm⁻¹. A large difference of 171–170 cm⁻¹ between the v_{as} and v_s vibrations indicates a monodentate coordination of the carboxylic group in all the complexes [30]. A broad band observed in the region 3400–3000 cm⁻¹ due to $v_{(OH)}$ of the carboxyl group and that due to $v_{(C=O)}$ around 1700 cm⁻¹ in the free ligand remains as such in the new complexes, indicating that one —COOH group remains uncoordinated [31]. All the characteristic peaks due to PPh₃/ AsPh₃ were observed in the usual regions [32].

3.2. EPR spectroscopy

The EPR spectra of all the complexes have been recorded in the solid state and in DMF solution at room temperature. The nature of the spectra revealed the absence of any hyperfine splitting due to interactions with any other nuclei present in the complexes. All the complexes exhibit a single isotropic resonance with *g* values in the range 2.21–2.35. EPR spectra of all the complexes in DMF solution indicate that the complexes retain their structures in the solution state. Although the complexes have some distortion in their octahedral geometries, the observation of isotropic lines in the EPR spectra may be due to intermolecular spin exchange and due to the occupancy of the unpaired electron in a degenerate orbi-



Fig. 1. EPR spectrum of $[Ru(H_2Pzdc)(PPh_3)_2Br_2]$ (**4**) in the solid state (solid line) and in DMF solution (dotted line) at room temperature.

tal [33]. The nature of spectra obtained is in good agreement with that of previously reported ruthenium(III) complexes [33,34]. A representative spectrum is depicted in Fig. 1.

3.3. Electrochemistry

The redox behavior of the complexes was studied using cyclic voltammetry at a glassy carbon working electrode at a scan rate of 100 mV s⁻¹. [NBu₄]ClO₄ (0.1 M) was used as supporting electrolyte in an acetonitrile solution of 0.001 M of the complexes. The cyclic voltammetric data are given in Table 2. The $E_{1/2}$ of the oxidation process was in the range from 0.82 to 0.99 V and reduction process was in the range from -0.79 to -0.82 V. The oxidation and reduction waves are due to the metal centered Ru(III) \rightarrow Ru(IV) and Ru(III) \rightarrow Ru(I) processes respectively. Moreover, the potential difference between the two successive oxidation processes is \approx 1.5 V, which agrees well with the average potential difference between the redox processes of the ruthenium center (Ru^{II/III}–Ru^{III/IV}) (\approx 1.0–2.0 V) observed for other mononuclear complexes [35]. All the complexes exhibit quasi-reversible oxidative couples with peak to peak separations (ΔE_p) of 180–280 mV [36].

3.4. Crystal structure of [Ru(H₂Pzdc)(PPh₃)₂Cl₂]·C₆H₆·C₂H₅OH

The ORTEP diagram of $[Ru(H_2Pzdc)(PPh_3)_2Cl_2]$ is shown in Fig. 2. Selected bond lengths and bond angles are given in Table 3. The bite angles around Ru(III) are N(1)–Ru(1)–O(1) = 76.07(9); N(1)– Ru(1)–Cl(2) = 89.52(7); O(1)–Ru(1)–Cl(1) = 96.36(6) and Cl(2)– Ru(1)–Cl(1) = 98.04(3)°, summing up the in-plane angles to be 360.09°. This shows the high planarity of the two Cl, N and O atoms. The ligand occupies the equatorial position, along with



Scheme 1. Synthesis of [Ru(H₂Pzdc)(EPh₃)₂X₂].

Table 2
Cyclic voltammetric data ^a of new Ru(III) complexes.

Complex	Ru(III)-Ru(IV)			Ru(III)-Ru(II)	Ru(III)-Ru(II)			
	$E_{\rm pc}$ (V)	$E_{\rm pa}$ (V)	$E_{\rm f}\left({\sf V}\right)$	$\Delta E_{\rm p}~({\rm mV})$	$E_{\rm pc}\left(V\right)$	$E_{\rm pa}\left({\sf V}\right)$	$E_{\rm f}$ (V)	$\Delta E_{\rm p}~({\rm mV})$
1	0.78	1.05	0.91	270	-0.88	-0.70	-0.79	180
2	0.72	0.93	0.82	210	-0.91	-0.71	-0.81	200
3	0.89	1.10	0.99	210	-0.91	-0.70	-0.80	210
4	0.79	1.07	0.93	280	-0.92	-0.72	-0.82	200

^a Supporting electrolyte: [NBu₄]ClO₄ (0.1 M); complex concentration: 0.001 M; scan rate: 100 mV s⁻¹; all the potentials are referenced to Ag/AgCl.



Fig. 2. ORTEP diagram of [Ru(H₂Pzdc)(PPh₃)₂Cl₂]·C₆H₆·C₂H₅OH (1). Hydrogen atoms and solvent molecules have been omitted for clarity.

the two chlorine atoms. The P(2)-Ru(1)-P(1) bond angle is 175.41(3)°, showing that the two PPh₃ groups are trans to each other, occupying the axial positions. The Ru–O [33], Ru–N [6], Ru–P [37] and Ru–Cl [38] bond lengths found in the complex agree well with those reported for similar ruthenium complexes. Since the 3,5-pyrazole dicarboxylic acid moiety has both hydrogen bond donors and hydrogen bond acceptors, the species provide the possibility of forming hydrogen bonds in the crystal. The complexes are joined through hydrogen bonds involving the O2 and O3 oxygen atoms of 3,5-pyrazole dicarboxylic acid, giving a complex three dimensional lattice for $[Ru(H_2Pzdc)(PPh_3)_2Cl_2]$.

3.5. Catalytic activity

The oxidation of alcohols was carried out with the new ruthenium(III) complexes as catalysts in the presence of *N*-methyl morpholine-*N*-oxide (NMO) as a co-oxidant in CH_2Cl_2 , and the results are summarized in Table 4. In no case was there any detectable oxidation of alcohols in the presence of NMO alone, without the Ru(III) complexes. All the complexes oxidize primary alcohols to the corresponding aldehyde and secondary alcohols to the corresponding ketone in high yield. The results of the present investigation suggest that the complexes efficiently react with NMO to yield

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Bond distances (Å)	
Ru(1) - N(1)	2.073(2)
Ru(1)-O(1)	2.084(2)
Ru(1)-Cl(2)	2.3145(7)
Ru(1)-Cl(1)	2.3226(7)
Ru(1)-P(2)	2.4027(8)
Ru(1) - P(1)	2.4137(7)
Bond angles (°)	
N(1)-Ru(1)-O(1)	76.07(9)
N(1)-Ru(1)-Cl(2)	89.52(7)
O(1)-Ru(1)-Cl(2)	165.55(6)
N(1)-Ru(1)-Cl(1)	172.41(7)
O(1)-Ru(1)-Cl(1)	96.36(6)
Cl(2)-Ru(1)-Cl(1)	98.04(3)
N(1)-Ru(1)-P(2)	93.21(7)
O(1)-Ru(1)-P(2)	89.86(6)
Cl(2)-Ru(1)-P(2)	89.96(3)
Cl(1)-Ru(1)-P(2)	86.19(3)
N(1)-Ru(1)-P(1)	90.31(7)
O(1)-Ru(1)-P(1)	88.13(6)
Cl(2)-Ru(1)-P(1)	93.01(3)
Cl(1)-Ru(1)-P(1)	89.93(3)
P(2)-Ru(1)-P(1)	175.41(3)

Table 3Selected geometrical parameters for 1.

Table 4	
Catalytic activity of new Ru(III) complete	xes.

Complex	Substrate	Yield ^a (%)	Turnover number ^b
1	benzyl alcohol	74	75
	cinnamyl alcohol	82	80
	cyclohexanol	26	25
2	benzyl alcohol	54	53
	cinnamyl alcohol	75	74
	cyclohexanol	16	16
3	benzyl alcohol	65	67
	cinnamyl alcohol	80	79
	cyclohexanol	18	17
4	benzyl alcohol	73	74
	cinnamyl alcohol	83	82
	cyclohexanol	25	26

^a Yield based on substrate.

^b Moles of product per mole of catalyst.

high valent Ru(V)=O species [39], capable of oxygen atom transfer to alcohols. This was supported by spectral changes that occur on the addition of NMO to a CH₂Cl₂ solution of the Ru(III) complexes. The appearance of a peak at 390 nm is attributed to the formation of Ru(V)=0, which is in conformity with other Ru(V) complexes [39,40]. Further support in favor of the formation of such a species has been identified from the IR spectrum of the solid mass (obtained by evaporation of the resultant solution to dryness) which showed a band at 860 cm^{-1} , characteristic of Ru(V)=0 species [18,39,41]. It has already been established that the catalytic cycle passes through a Ru(V)=O species [41]. The relatively higher yield for oxidation of cinnamyl alcohol than benzyl alcohol or cyclohexanol is due to the presence of the α -CH unit in cinnamyl alcohol, which is more acidic than benzyl alcohol or cyclohexanol. An unsaturated alcohol like cinnamyl alcohol is selectively oxidized at the alcoholic group with high yield, without affecting the double bond. This is an important characteristic of the ruthenium/NMO system. It has been observed that these Ru(III) complexes have better catalytic efficiency in the case of oxidation of benzyl alcohol, cinnamyl alcohol and cyclohexanol when compared to the earlier reports [18,39–41] on similar ruthenium complexes as catalysts in the presence of NMO/t-BuOOH. From the comparative yields, it is evident that triphenylphosphine complexes possess more catalytic activity than triphenylarsine complexes because the Ru—P bond is more labile than the Ru—As bond.

The new complexes have been used as catalysts for the coupling of phenyl magnesium bromide with bromobenzene to give biphenyl. An insignificant amount of biphenyl was formed when the reaction was carried out without the catalyst. The percentage yield of biphenyl obtained from the reactions catalyzed by the new Ru(III) complexes are low compared to NiCl₂(PPh₃)₂ [42]. This may be due to the fact that the lifetime of the active species (d⁷) formed from ruthenium(III) complexes is less than that of the d¹⁰ species formed from the nickel(II) complexes, as the effectiveness of the catalysts is directly related to their ability to generate the corresponding active species [43,44]. The nature of the ligand was found to have no positive effect on the reaction rate when compared to our previously reported binuclear Ru(III) complexes containing an O,N donor ligand and PPh₃/AsPh₃ [28].

4. Conclusion

Some new hexa-coordinated ruthenium(III) complexes containing 3,5-pyrazole dicarboxylic acid and PPh₃/AsPh₃ have been synthesized. The new complexes have been characterized by analytical and spectral (IR, electronic and EPR) studies. The redox behavior of the complexes has been studied by cyclic voltammetry. The new complexes were found to catalyze the oxidation of alcohols to give reasonably good yields, but were not effective catalysts for aryl–aryl coupling.

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Appendix A. Supplementary data

CCDC 621596 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.ac.uk.

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