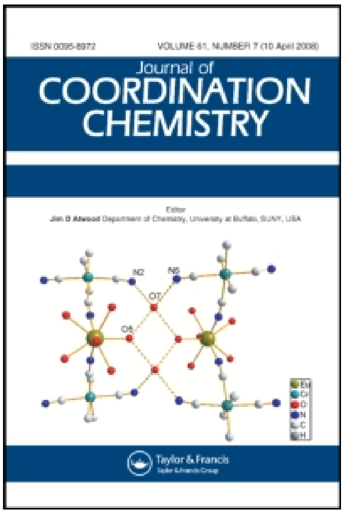

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SYNTHESIS AND CATALYTIC ACTIVITY OF RUTHENIUM(II) COMPLEXES CONTAINING ACETYLACETONATE

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Synthesis and characterisation of complexes of ruthenium(II), $[RuBr(acac)L_2]_2$ (L = PPh_3, $AsPh_3$, py; L_2 = bipy or phen) and $M_2[RuBr_3(acac)]$ (M = Me_4N, Cs or Rb) are described. Catalytic oxidations of PPh_3 and $AsPh_3$ using $[RuBr(acac)(PPh_3)_2]_2$ and $[RuBr(acac)(AsPh_3)_2]_2$ have been carried out by molecular oxygen.

KEYWORDS: ruthenium, acetylacetone, complexes, oxidation, catalysis

INTRODUCTION

Some reports exist on ruthenium(III) complexes containing acetylacetonate, neutral donor ligand(s) and halide (chloride or bromide). These describe $[RuX_2(acac)(MPh_3)_2]$ (X = Cl or Br; M = P or As),[1-3] $[RuCl_2(acac)(acacH)]$[4] and $[RuCl_2(acac)L_2]$ (L = PPh_3, $AsPh_3$, py, Me_2SO, MeCN or *o*-phenylenediamine; L_2 = bipy or phen)[4]. Similarly, ruthenium(II) complexes containing acetylacetonate, neutral donor ligand(s) and chloride described in the literature are $[RuCl(CO)(acac)(PPh_3)_2]$[5] and $[RuCl(acac)(MPh_3)_2]$ (M = P or As).[6] No report on ruthenium(II) complexes containing acetylacetonate, neutral donor ligand(s) and bromide is in the literature. Further, a ruthenium(II) complex containing bromide and neutral donor ligands, *viz*, $[RuBr_2(Me_2SO)_4]$ has been found to have better activity compared to the chloro analogue *cis*-$[RuCl_2(Me_2SO)_4]$, as a molecular oxygen oxidation catalyst towards thioethers to give corresponding sulphoxides.[7,8]

In view of the above, the present work describes the synthesis and characterisation of some ruthenium(II) complexes containing acetylacetonate, neutral donor ligand(s) and bromide as co-ligand. Preliminary studies on the catalytic activity of $[RuBr(acac)(PPh_3)_2]_2$ and $[RuBr(acac)(AsPh_3)_2]_2$ towards molecular oxygen oxidation of PPh_3 and $AsPh_3$ are described.

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EXPERIMENTAL

All solvents were freshly distilled before use. $RuCl_3 \cdot 3H_2O$ was obtained from Arora Mathey Ltd., Calcutta. $[RuCl_2(acac)(acacH)]$ was prepared according to the reported method.[4] Analyses for bromide were carried out by a standard method.[9] C, H and N analyses were obtained from the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow (Table 1). IR, ^1H NMR, electronic absorption spectra, magnetic susceptibility, conductivity and electrochemical measurements were carried out as reported earlier.[4]

[RuBr(acac)L₂]₂ (L = PPh₃, AsPh₃, py or 3Mepy; L₂ = bipy or phen)

Lithium bromide (0.2 g) was added to a solution of $[RuCl_2(acac)(acacH)]$ (0.2 g) in ethanol (15 cm^3) and the mixture was refluxed on a water bath for 1 h. To the hot solution, a solution of the ligand (L) was added and the mixture was further refluxed for a few hours and then cooled to room temperature. Compounds which separated out were centrifuged, washed with ethanol and then with diethylether and dried *in vacuo*. Specific reaction conditions for each ligand are given in Table 2.

M₂[RuBr₃(acac)] (M = Me₄N, Cs or Rb)

To a solution of $[RuCl_2(acac)(acacH)]$ (0.2 g) in ethanol (15 cm^3), lithium bromide (0.2g) was added and the mixture refluxed for 1 h. A solution of MBr (M = Me_4N, Cs or Rb) in ethanol (15 cm^3) (molar ratio, Ru : MBr = 1:2) was added to the hot solution. The reaction mixture was further refluxed on a water bath for one and one half hours. Compounds were collected, washed with ethanol, then acetone and dried *in vacuo*. Yield, 55–60%.

Catalytic Oxidation of PPh₃ using [RuBr(acac)(PPh₃)₂]₂

A suspension of $[RuBr(acac)(PPh_3)]_2$ (0.05 g) in acetonitrile (15 cm^3) was refluxed on a waterbath for 1 h, when a pale yellow solution was obtained. A solution of triphenylphosphine (0.33 g) in acetonitrile (10 cm^3) was added to the hot solution. Oxygen was bubbled slowly through the solution and the mixture was refluxed on a waterbath for 10 hrs. The solution was evaporated to dryness and the residue dissolved in acetone when a brown compound separated out. The acetone solution was evaporated to dryness and the residue washed with dry ether several times. Crude triphenylphosphine oxide (0.23 g, 65%) was obtained.

Table 1 Reaction conditions for the preparation of the Ru(II) complexes.

Ligand	Molar ratio Comp.: Ligand	Reflux time (h)	Product
PPh_3	1 : 2	1/2	$[RuBr(acac)(PPh_3)_2]$
$AsPh_3$	1 : 2	1	$[RuBr(acac)(AsPh_3)_2]$
py	1 : 2	1	$[RuBr(acac)(py)_2]$
3-Mepy	1 : 2	1	$[RuBr(acac)(3Mepy)_2]$
bipy	1 : 1	2	$[RuBr(acac)(bipy)]$
phen	1 : 1	2	$[RuBr(acac)(phen)]$

Table 2 Physical and analytical data for the Ru(II) complexes.

Compound	Colour	Melting point (°C)	Found (calcd)%			
			C	H	N	Br
$[RuBr(acac)(PPh_3)_2]_2$	Brown	220	61.0 (61.2)	4.5 (4.6)		9.5 (9.9)
$[RuBr(acac)(AsPh_3)_2]_2$	Brown	295	55.1 (55.1)	4.3 (4.1)		
$[RuBr(acac)(py)_2]_2$	Red	305	41.0 (41.1)	3.8 (3.9)	6.3 (6.4)	
$[RuBr(acac)(3\text{-}Mepy)_2]_2$	Red	325	43.2 (43.8)	4.6 (4.5)	5.7 (6.0)	
$[RuBr(acac)(bipy)]_2$	Dark brown	>360	41.1 (41.3)	3.6 (3.4)	6.3 (6.4)	17.8 (18.3)
$[RuBr(acac)(phen)]_2$	Dark brown	>360	43.4 (43.3)	3.3 (3.3)	6.0 (6.1)	
$(Me_4N)_2[RuBr_3(acac)]$	Violet	>360	26.1 (26.5)	5.7 (5.3)	5.0 (4.8)	39.9 (40.8)
$Cs_2[RuBr_3(acac)]$	Violet	>360	8.1 (8.5)	1.5 (1.0)		33.2 (34.0)
$Rb_2[RuBr_3(acac)]$	Dark brown	>360	10.4 (9.8)	1.8 (1.8)		38.7 (39.3)

Catalytic Oxidation of $AsPh_3$ using $[RuBr(acac)(AsPh_3)_2]_2$

A reaction similar to the above was carried out with $[RuBr(acac)(AsPh_3)_2]_2$ (0.05 g) and $AsPh_3$ (0.36 g). The solution obtained after oxidation was evaporated to dryness and washed with dry ether. A brown product separated out. The ether extract was evaporated at room temperature, and the components of the mixture, $AsPh_3$ and $OAsPh_3$, were separated by column chromatography. Yield of $OAsPh_3$, 0.09 g (25%).

RESULTS AND DISCUSSION

$[RuBr(acac)L_2]_2$ ($L = PPh_3$, $AsPh_3$, py, 3Mepy; L_2 = bipy or phen)

Reported methods for the synthesis of ruthenium(III) complexes containing acetylacetonate, bromide and other neutral donor ligand(s) involve reaction of acetylacetone with $[RuBr_2(PPh_3)_3]$, $[RuBr_3(PPh_3)_2(MeOH)]$ or $[RuBr_3(AsPh_3)_3]$.[1] We attempted to synthesise ruthenium(III) complexes containing acetylacetonate, bromide and neutral donor ligand(s) by the metathesis of $[RuCl_2(acac)(acacH)]$ with LiBr followed by its reaction with neutral donor ligand. However, the products obtained analysed for ruthenium(II) complexes, *viz*, $[RuBr(acac)L_2]$. It is likely that bromide ion present in excess reduces Ru(III) to Ru(II), besides substituting the chloride in $[RuCl_2(acac)(acacH)]$. Molecular weight determinations of $[RuBr(acac)L_2]$ ($L = PPh_3$ or py) in bromoform by the cryoscopic method gave values close to that of a dimeric structure, which can be interpreted by assuming bromide bridges between the two ruthenium centres as in $[RuCl(acac)(PPh_3)_2]$.[6] These complexes are non-electrolytes (Λ_M = 5–8 $\Omega^{-1}cm^2mol^{-1}$ in MeCN).

All the complexes $[RuBr(acac)L_2]$ ($L = PPh_3$, $AsPh_3$, py, 3Mepy; L_2 = bipy or phen) are diamagnetic at room temperature, characteristic of low-spin

d^6-configuration for ruthenium(II). Cyclic voltammogram of $[RuBr(acac)L_2]_2$ (L = py or 3Mepy) for 10^{-3} M solutions in acetonitrile (Figure 1) using tetraethylammoniumperchlorate as a supporting electrolyte show one *quasi*-reversible (ΔE = 80–140 mV) oxidation wave at $E_{1/2}$ = 0.30–0.34 V (*versus* SCE), which corresponds to ruthenium(II)/ruthenium(III) oxidation.

IR spectra of $[RuBr(acac)L_2]$ (L = PPh_3, $AsPh_3$, py, 3Mepy; L_2 = bipy or phen) in KBr show two sharp bands in the region 1555–1510 cm^{-1} (Table 3), characteristic of a chelated *O*-bonded acetylacetonato group.[10] Other absorption bands due to acetylacetonato and the ligand(s) are also observed. The ^1H NMR spectrum of $[RuBr(acac)(py)_2]_2$ in $CDCl_3$ showed one singlet at δ 2.05 corresponding to methyl protons of coordinated acetylacetonate. A doublet at δ 9.0 and two triplets at δ 7.2 and δ 7.8 were also observed. The former could be assigned to the *ortho* protons and the other two due to *meta* and *para* protons respectively of the coordinated pyridine molecules.[11] The ^1H NMR spectrum of $[RuBr(acac)(PPh_3)_2]_2$ in $CDCl_3$ showed one sharp singlet at δ 2.17, a broad singlet at δ 5.86 and a sharp doublet centered at δ 7.57. The singlets are assigned to the methyl and methine proton(s), respectively, of the acetylacetonato group and the doublet is due to the aromatic protons of triphenylphosphine molecules. The area under the signals correspond to the appropriate number of protons.

$M_2[RuBr_3(acac)]$ (M = Me_4N, Rb or Cs)

Metathesis of chloride in $[RuCl_2(acac)(acacH)]$ by bromide followed by reaction with MBr (Me_4N, Rb or Cs) resulted in the formation $M_2[RuBr_3(acac)]$ (M = Me_4N, Rb or Cs). These complexes are diamagnetic, confirming low spin d^6 configurations for ruthenium(II). Molar conductance values at 28°C (Λ_M = 262–280 $\Omega^{-1}cm^2mol^{-1}$) for aqueous millimolar solutions correspond to 2:1 electrolytes. IR spectra in KBr showed two sharp bands in 1535–1510 cm^{-1} region, characteristic of the *O*-bonded acetylacetonato group.

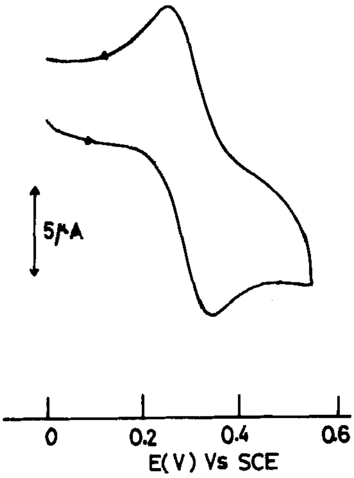

Figure 1 C.V. of $[RuBr(acac)(3\text{-}Mepy)_2]_2$ (10^{-3} M) in MeCN with 0.1 M TEAP as supporting electrolyte.

Table 3 Characteristic IR and electronic absorption bands for the Ru(II) complexes.

Compound	Infrared bands (cm^{-1})	Electronic absorptions λ_{max},nm(ε)*
$[RuBr(acac)(PPh_3)_2]_2$	1550, 1518	^{a}620(305), 487(1320), 415^{sh}, 300(10630)
$[RuBr(acac)(AsPh_3)_2]_2$	1542, 1513	^{a}490(590), 325^{sh} 318(18500)
$[RuBr(acac)(py)_2]_2$	1549, 1515	^{a}495(1485), 400(1660), 350(4145), 310(4870)
$[RuBr(acac)(3\text{-}Mepy)_2]_2$	1543, 1512	^{a}500(875), 395(12010), 318(4070)
$[RuBr(acac)(bipy)]_2$	1555, 1520	^{a}580(1130), 500(2420), 447(4040)
$[RuBr(acac)(phen)]_2$	1534, 1510	^{a}595^{sh}, 490(1770), 400 (3840)
$(NMe_4)_2[RuBr_3(acac)]$	1535, 1517	^{b}490(645), 408(1420), 310^{sh}
$Rb_2[RuBr_3(acac)]$	1536, 1511	^{b}490(990), 408(1160), 310(5230), 275(12035)
$Cs_2[RuBr_3(acac)]$	1534, 1513	

*M^{-1} cm^{-1}. ^{a}In chloroform; ^{b}In water; sh = shoulder.

Electronic Spectra

Electronic absorption spectra of $[RuBr(acac)L_2]_2$ (L = PPh_3, $AsPh_3$, py, 3Mepy; L_2 = bipy or phen; Table 3) generally show three or four absorption bands in the 620–300 nm region. The first at 620–500 nm with ε = 10^2–10^3 M^{-1}cm^{-1} may be assigned to a combination of $^1A_{1g} \rightarrow {}^1T_{1g}$ or $^1T_{2g}$ and a Ru(t_{2g}) → ligand charge transfer transition.[6] Other bands in the 500–350 nm region, with ε = 10^3 to 10^4 may be assigned to the Ru(t_{2g}) → ligand (PPh_3, $AsPh_3$, py, 3Mepy, bipy or phen) and Ru($t_{2g} \rightarrow \Pi^*$ (acac) charge transfer transition. The highest energy band around 300 nm with ε = 10^3–10^4 is an intra-ligand Π-Π^* (acac) transition.[12] Electronic absorption spectra of $M_2[RuBr_3(acac)]$ (M = Me_4N or Rb) are superimposable, showing absorptions in the 500–250 nm region. The two highest energy transitions at 310 and 275 nm may be assigned to the intra-ligand Π-Π^* (acac) and Br (Π)→Ru(σ^*) transitions, respectively.[12] The lowest energy band at 490 nm (ε = 10^2) may be assigned to a combination of $^1A_{1g} \rightarrow {}^1T_{1g}$ or $^1T_{2g}$ and Ru(t_{2g}) → ligand charge transfer transition, whereas the band at 400 nm is a Ru(t_{2g}) → Π^* (acac) transition.

Catalytic Oxidation of PPh_3 and $AsPh_3$

Oxidation of PPh_3 and $AsPh_3$ with molecular oxygen using $[RuBr(acac)L_2]_2$ (L = PPh_3 or $AsPh_3$) catalysts in acetonitrile resulted in the formation of $OPPh_3$ and $OAsPh_3$, respectively. Reactions were carried out with Ru : PPh_3 or $AsPh_3$ in the molar ratio 1 : 20 for a period of 10 hrs. A conversion of 65% in case of PPh_3 and 25% in case of $AsPh_3$ was observed. Triphenylphosphine oxide and triphenylarsine oxide were characterised by carbon and hydrogen analyses, melting point, infrared and electronic spectra.[10,13]

Complexes isolated after the oxidation of PPh_3 or $AsPh_3$ using $[RuBr(acac)L_2]_2$ (L = PPh_3 or $AsPh_3$) showed the presence of acetonitrile coordinated to the metal ion (ν_{CN} observed at 2275 cm^{-1}). Perhaps acetonitrile helps in cleaving the bromo bridges of the dimer and forms the monomer [RuBr(acac)L_2(CH_3CN)] which further loses coordinated ligands to give catalytic species in solution. Reaction carried out in *n*-butanol medium did not oxidise PPh_3. This may be attributed to preservation of the bromo bridges of the dimeric species.

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