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Reactivity and catalytic activity of [$RuBr_2(Me_2SO)_3$]

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Abstract

[$RuBr_2(Me_2SO)_3$] has been used as precursor for the synthesis of many ruthenium(II) complexes containing bromide ion and other ligands. The complexes, thus synthesised are: [$RuBr_2L_4$] (L = PPh_3, L_2 = phen or bpy); [$RuBr_2(Me_2SO)_2L_2$] (L = py, $AsPh_3$; L_2 = phen, bpy or *o*-phenylenediamine); [$RuBr_2(CS)(PPh_3)_3$]; [$RuBr_2(CS)(Me_2SO)_2$]; [$RuBr_2(CS)(AsPh_3)_2(Me_2SO)$] and [$RuBr(C_2O_4H)(Me_2SO)_2$]. These compounds have been characterised with the help of analytical data and various physical methods. [$RuBr_2(Me_2SO)_3$] has been used as a catalyst for the oxidation of PPh_3 by molecular oxygen.

Introduction

Ruthenium(II) and ruthenium(III) complexes containing Me_2SO are found to be precursors for the synthesis of many Ru(II) and Ru(III) complexes. Some of the complexes of this type are: *cis*-[$RuCl_2(Me_2SO)_4$], *trans*-[$RuBr_2(Me_2SO)_4$, [$Ru_2Cl_6(Me_2SO)_4$], *fac*- and *mer*-[$RuCl_3(Me_2SO)_3$] and [$RuBr_3(Me_2SO)_3$] [1–13]. The synthesis and characterisation of [$RuBr_2(Me_2SO)_3$] has been reported recently by our group [11]. The present work describes the synthesis of many new Ru(II) complexes containing ligands like $OPPh_3$, $AsPh_3$, CS, py, bpy, phen, *o*-phenylenediamine and oxalate, from [$RuBr_2(Me_2SO)_3$]. *cis*-[$RuCl_2(Me_2SO)_4$], *trans*-[$RuBr_2(Me_2SO)_4$], [$RuCl_2(Me_2SO)_2(PPh_3)$], and [$RuBr_2(Me_2SO)_3L$] (L = PPh_3, PBu_3, $P(OBu)_3$, $AsPh_3$) have been reported for their catalytic activity towards molecular oxygen oxidation of thioethers to sulfoxides [14, 15]. We report here the catalytic activity of [$RuBr_2(Me_2SO)_3$] towards molecular oxygen oxidation of triphenylphosphine to triphenylphosphine oxide.

Experimental

Rutheniumtrichloride trihydrate was obtained from Aurora Matthey Ltd, Calcutta. [$RuBr_2(Me_2SO)_3$] was prepared according to the reported method [11]. The analyses for bromide were carried out by a standard method [16]. Carbon, hydrogen and nitrogen analyses were obtained from the Regional Sophisticated Instrumentation Centre, C.D.R.I., Lucknow and the Microanalytical section of the Department of Chemistry, N.E.H.U., Shillong. The analytical data are presented in Table 1. Physical measurements, viz. IR, ^1H NMR and electronic absorption spectra, magnetic and conductivity measurements were carried out as reported earlier [10].

Reactions of [$RuBr_2(Me_2SO)_3$]

(i) With triphenylphosphine

(a) To a solution of [$RuBr_2(Me_2SO)_3$] (0.2 g) in methanol (10 cm^3), a solution of PPh_3 (0.5 g) in methanol (10 cm^3) was added and the mixture was stirred at room temperature for 2 h. A reddish brown compound separated out. It was centrifuged, washed with ether and dried *in vacuo*. The compound analysed as [$RuBr_2(PPh_3)_4$]. Yield 0.45 g (85%).

(b) A reaction similar to (a) above was carried out, where the reaction mixture was refluxed for 1 h on a water-bath in the presence of oxygen. A deep violet crystalline compound separated out, which was isolated as in (a) above. It analysed as [$RuBr_2(OPPh_3)_3$]. Yield 0.30 g (68%).

(ii) With triphenylarsine

To a solution of [$RuBr_2(Me_2SO)_3$] (0.2 g) in methanol (10 cm^3), a solution of triphenylarsine (0.24 g) in methanol (molar ratio 1:2) was added and the mixture was stirred at room temperature for 2 h. A reddish brown compound separated out, which was centrifuged, washed with methanol and dried

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TABLE 1. Some physical and analytical data of ruthenium(II) complexes

Compounds	Colour	Melting point (°C)	Analysis[a] (%) C	H	N	Br
$[RuBr_2(OPPh_3)_3]$	violet	125–128	58.72	3.78		
			(59.17)	(4.01)		
$[RuBr_2(Me_2SO)_2(AsPh_3)_2]$	reddish brown	230	46.69	3.63		
			(46.65)	(4.08)		
$[RuBr_2(AsPh_3)_2(CS)(Me_2SO)]$	dark brown	180	46.80	3.32		
			(47.04)	(3.62)		
$[RuBr_2(CS)(PPh_3)_3]$	red	295	59.53	3.55		
			(60.49)	(4.12)		
$[RuBr_2(CS)(Me_2SO)_2]$	black	>360	12.82	2.77		
			(13.02)	(2.60)		
$[RuBr(C_2O_4H)(Me_2SO)_2]$	brown	330–340[d]	16.2	3.4		18.8
			(16.9)	(2.99)		(18.8)
$[RuBr_2(Py)_2(Me_2SO)_2]$	dark yellow	185–190[d]	29.0	3.5	4.6	
			(29.2)	(3.8)	(4.9)	
$[RuBr_2(bpy)(Me_2SO)_2]$	dark brown	200–205[d]	29.0	3.0	4.5	
			(29.3)	(3.5)	(4.9)	
$[RuBr_2(phen)(Me_2SO)_2]$	yellow	230–235[d]	31.8	3.0	4.3	
			(32.1)	(3.3)	(4.7)	
$[RuBr_2(PDA)(Me_2SO)_2]$	light yellow	210–215	22.96	4.08	4.99	
			(22.8)	(3.8)	(5.3)	

[a] Calculated values are in parentheses, d: decomposes.

in vacuo. The compound analysed as $[RuBr_2(Me_2SO)_2(AsPh_3)_2]$. Yield 0.28 g (67%).

(iii) With pyridine (py)

(a) Pyridine (0.5 cm^3) was added to a solution of $[RuBr_2(Me_2SO)_3]$ (0.2 g) in methanol (10 cm^3) and the mixture was stirred at room temperature for 3 h. A yellow compound separated out. It was centrifuged, washed with ether and dried *in vacuo*. The compound analysed as $[RuBr_2(py)_2(Me_2SO)_2]$. Yield 0.2 g (90%).

(b) Pyridine (0.5 cm^3) was added to a solution of $[RuBr_2(Me_2SO)_3]$ (0.2 g) in methanol (10 cm^3) and the solution was refluxed for 1 h. From the solution on concentration (~5 cm^3) and cooling to room temperature, a brown crystalline compound of composition, $[RuBr_2(py)_4]$ separated out. This was centrifuged, washed with methanol and then with diethyl ether and dried *in vacuo*. Yield 0.18 g (85%).

(iv) With 1,10-phenanthroline (phen)

(a) $[RuBr_2(Me_2SO)_3]$ (0.2 g) was dissolved in methanol (10 cm^3) and a solution of 1,10-phenanthroline (0.08 g) in methanol (5 cm^3) was added to it. The solution was stirred at room temperature for 10 min. A yellow compound separated out. This was centrifuged, washed with methanol and ether and dried *in vacuo*. The compound analysed as $[RuBr_2(phen)(Me_2SO)_2]$. Yield 0.16 g (68%).

(b) A reaction similar to (iv)(a) above, with excess of 1,10-phenanthroline (0.24 g) was carried out by refluxing on a water-bath for 1 h. A dark orange solution was obtained, which was concentrated to small volume (~2 cm^3). Diethyl ether was added to precipitate a dark orange coloured compound, which was isolated as in (iv)(a) above. It analysed as $[Ru(phen)_2Br_2]$. Yield 0.18 g (70%).

(v) With 2,2′-bipyridine (bpy)

(a) To a solution of $[RuBr_2(Me_2SO)_3]$ (0.2 g) in methanol (10 cm^3), a solution of 2,2′-bipyridine (0.065 g) in methanol (5 cm^3) was added and the mixture was stirred at room temperature for 2 h. The volume of the solution was reduced (~1 cm^3) under vacuum at room temperature and diethyl ether was added to precipitate a dark brown coloured compound. The compound was centrifuged, washed with methanol followed by diethyl ether and dried *in vacuo*. The compound analysed as $[RuBr_2(bpy)(Me_2SO)_2]$. Yield 0.16 g (70%).

(b) A reaction similar to (v)(a) above was carried out by taking $[RuBr_2(Me_2SO)_3]$ and 2,2′-bipyridine in the molar ratio 1:2, and refluxing on a water-bath for 2 h. An orange coloured compound was obtained upon precipitation from the concentrated (~2 cm^3) solution with diethyl ether. It was isolated as in (v)(a) above. It analysed as $[Ru(bpy)_2Br_2]$. Yield 0.15 g (65%).

(vi) With o-phenylenediamine (PDA)

To a solution of [$RuBr_2(Me_2SO)_3$] (0.2 g) in methanol (10 cm^3), a solution of *o*-phenylenediamine (0.044 g) in methanol (10 cm^3) (molar ratio 1:1), was added. The reaction mixture was stirred at room temperature for 30 min. A light brown compound separated out, which was centrifuged, washed with methanol and dried *in vacuo*. The compound analysed as [$RuBr_2(PDA)(Me_2SO)_2$]. Yield 0.14 g (66%).

(vii) With carbon disulphide

To a solution of [$RuBr_2(Me_2SO)_3$] (0.2 g) in methanol (10 cm^3), carbon disulphide (5 cm^3) was added. The reaction mixture was refluxed on a water-bath at 60 °C for 5 h. A black compound separated out. More compound was obtained upon concentration of the mother liquor. The compound was washed with methanol and dried *in vacuo*. It analysed as [$RuBr_2(CS)(Me_2SO)_2$]. Yield 0.12 g (65%).

(viii) With carbon disulphide and triphenylphosphine

To a solution of [$RuBr_2(Me_2SO)_3$] (0.2 g) in methanol (10 cm^3), carbon disulphide (5 cm^3) and a solution of triphenylphosphine (0.21 g) in methanol (5 cm^3) (molar ratio 1:2) was added. The reaction mixture was refluxed at 60 °C on a water-bath for 3 h. A red crystalline compound separated out. It was centrifuged, washed with methanol and dried *in vacuo*. It analysed as [$RuBr_2(CS)(PPh_3)_3$]. Yield 0.26 g (59%).

(ix) With carbon disulphide and triphenylarsine

A reaction similar to (viii) above, was carried out using triphenylarsine instead of triphenylphosphine for 4 h, when a dark brown compound separated out. It was centrifuged, washed with methanol, then with ether and dried *in vacuo*. The compound analysed as [$RuBr_2(AsPh_3)_2(CS)(Me_2SO)$]. Yield 0.21 g (52%).

(x) With oxalic acid

(a) To a solution of [$RuBr_2(Me_2SO)_3$] (0.25 g) in ethanol (10 cm^3), a solution of oxalic acid (0.25 g) in ethanol (5 cm^3) (molar ratio 1:4) was added. The solution was stirred at room temperature for 3 h. A light yellow compound separated out, which was washed with ethanol and dried *in vacuo*. It analysed as [$RuBr(C_2O_4H)(Me_2SO)_2$]. Yield 0.12 g (56%).

(b) A reaction similar to (x)(a) above was carried out by refluxing the mixture on a water-bath for 30 min. The solution was cooled, when a yellow compound same as the above was obtained.

Catalytic oxidation of triphenylphosphine

A solution of [$RuBr_2(Me_2SO)_3$] (0.1 g) and triphenylphosphine (0.5 g) (molar ratio 1:10) in n-butanol (30 cm^3) was refluxed to boiling on an oil-bath for 4 h, while oxygen was bubbled through the solution, slowly. The solution was cooled and concentrated at reduced pressure, when a small quantity of brown compound separated out, which was removed. The solvent was removed from the mother liquor when a white compound was obtained, which was washed with diethyl ether several times. It analysed as $OPPh_3$ (m.p. 155 °C).

Results and discussion

Reactions of [$RuBr_2(Me_2SO)_3$] with some monodentate and bidentate ligands have been carried out at room temperature and at refluxing conditions of the solvent (methanol or ethanol). The products obtained have either partial or complete substitution of the coordinated Me_2SO groups.

Reactions of [$RuBr_2(Me_2SO)_3$]

With phosphorus and arsenic donor ligands

Reactions of [$RuBr_2(Me_2SO)_3$] with triphenylphosphine at room temperature or at the refluxing condition of methanol resulted in complete substitution of the Me_2SO groups leading to the formation of [$RuBr_2(PPh_3)_4$] and [$RuBr_2(OPPh_3)_3$], respectively. At the refluxing conditions of methanol, PPh_3 gets oxidised to $OPPh_3$. [$RuBr_3(Me_2SO)_3$] is found to be a good catalyst for the oxidation of PPh_3 to $OPPh_3$ (*vide infra*). The IR and ^1H NMR spectra of [$RuBr_2(PPh_3)_4$] and [$RuBr_2(OPPh_3)_3$] show the absence of any Me_2SO group. The IR spectrum of [$RuBr_2(OPPh_3)_3$] shows a strong absorption band at 1180 cm^{-1}, which could be assigned to $\nu(P=O)$ of $OPPh_3$ [17]. In ^1H NMR spectra of PPh_3 and $OPPh_3$ containing complexes, only one strong signal around $\delta 7.3$ was observed which is due to aromatic protons of PPh_3 or $OPPh_3$ (see Table 2).

The reaction of [$RuBr_2(Me_2SO)_3$] with $AsPh_3$ at room temperature led to the formation of a partially substituted product, viz. [$RuBr_2(AsPh_3)_2(Me_2SO)_2$]. The IR spectrum of the compound shows strong bands at 1103 and 1075 cm^{-1}. Normally a strong band at 1075 cm^{-1} is observed in the case of $AsPh_3$ containing complexes. Thus, the band at 1103 cm^{-1} could be assigned to $\nu(S=O)$ (S-bonded) of the Me_2SO group. A band of medium intensity at 444 cm^{-1} could be assigned to $\nu(Ru\text{–}S)$. All characteristic bands of $AsPh_3$ are also present. The ^1H NMR spectrum of the compound in $CDCl_3$ shows signals at $\delta 3.43$ and $\delta 7.3$. The former signal could be attributed to the methyl protons of S-bonded Me_2SO

TABLE 2. ^{1}H NMR and IR spectral data of ruthenium(II) complexes

Compounds	δ (ppm)	IR absorption (cm^{-1})
$[RuBr_2(OPPh_3)_3]$	7.3[a]	1180s
$[RuBr_2(AsPh_3)_2(Me_2SO)_2]$	3.43, 7.3[a]	1103s, 1075s, 444m
$[RuBr_2(CS)(AsPh_3)_2(Me_2SO)]$	3.4, 7.3[a]	1265s, 1112s, 1100s
$[RuBr_2(CS)(PPh_3)_3]$	7.3[a]	1265s
$[RuBr_2(CS)(Me_2SO)_2]$	3.37[b]	1250m, 1085s
$[RuBr(C_2O_4H)(Me_2SO)_2]$	3.25[b]	1623s, 1407m, 1104s, 433m
$[RuBr_2(py)_2(Me_2SO)_2]$	3.44s, 7.2t, 7.75t, 9.12d[a]	1080s, 1060s
$[RuBr_2(bpy)(Me_2SO)_2]$	3.3s, 7.66m, 8.12m, 8.66m, 9.82m[b]	1080s, 1060s
$[RuBr_2(phen)(Me_2SO)_2]$	3.7s, (7.6–8)m, 8.03s, 8.5d, 10.1d[c]	1075s, 1060s, 425m
$[RuBr_2(PDA)(Me_2SO)_2]$	7.3, 6.12s, 3.36s[b]	1080s, 420m
trans-$[RuBr_2(py)_4]$	7.06t, 7.63t, 8.73d[a]	
trans-$[RuBr_2(bpy)_2]$	7.7m, 8.18t, 8.95d[b]	
trans-$[RuBr_2(phen)_2]$	7.67q, 8.07d, 8.28s, 8.65d[c]	

Abbreviations: s: strong in IR, singlet in NMR; m: medium in IR, multiplet in NMR; d: doublet; t: triplet; q: quartet. [a]In $CDCl_3$. [b]In $(CD_3)_2SO$. [c]In CD_3CN.

groups [11], whereas the latter one is due to the aromatic protons of $AsPh_3$.

With carbon disulphide in the presence of PPh_3 or $AsPh_3$

Reaction of $[RuBr_2(Me_2SO)_3]$ with CS_2 in the presence of PPh_3 resulted in the complete substitution of Me_2SO by PPh_3 and incorporation of a thiocarbonyl group, leading to the formation of $[RuBr_2(CS)(PPh_3)_3]$. The similar reaction with $AsPh_3$, however, resulted in the partial substitution of Me_2SO groups and $[RuBr_2(CS)(AsPh_3)_2(Me_2SO)]$ was obtained. The IR spectra of both complexes show a strong band around 1265 cm^{-1} which could be assigned to ν(C=S) of the thiocarbonyl group [18]. All the bands due to PPh_3 or $AsPh_3$ are also present. Strong bands at 1100 and 1112 cm^{-1} are also observed in $[RuBr_2(CS)(AsPh_3)_2(Me_2SO)]$, which could be assigned to ν(S=O) of the S-bonded Me_2SO group. ^{1}H NMR spectra of both the compounds show a strong signal at δ7.3 characteristic of aromatic protons due to PPh_3 or $AsPh_3$. A signal at δ3.4 is observed in the case of $[RuBr_2(CS)(AsPh_3)_2(Me_2SO)]$ which may be assigned to the methyl protons or the S-bonded Me_2SO group. The ratio of proton area under the signal at δ3.4 and under the signal at δ7.3 is 1:5, which confirms the composition of the complex. In case of $[RuBr_2(CS)(PPh_3)_3]$, no proton signal was observed in the range δ2–4, confirming the absence of any Me_2SO group in the complex.

With carbon disulphide

Reaction of $[RuBr_2(Me_2SO)_3]$ with CS_2 resulted in the formation of $[RuBr_2(CS)(Me_2SO)_2]$, where only one Me_2SO group has been replaced by the thiocarbonyl group. Among the other bands due to Me_2SO, the IR shows bands at 1085 and 425 cm^{-1} which could be assigned to ν(S=O) and ν(Ru–S) of the S-bonded Me_2SO groups. In the IR, a strong band at 1250 cm^{-1} is also observed, which could be assigned to ν(C=S). A ^{1}H NMR spectrum of the complex in $(CD_3)_2SO$ shows a sharp singlet at δ3.37, characteristic of methyl protons of S-bonded Me_2SO groups. Normally the coordination of thiocarbonyl group is stabilised by the presence of π-acid ligands like PPh_3 [18]. Probably, this is one of the first examples where thiocarbonyl is coordinated to the metal ion along with a σ-donor ligand like Me_2SO.

With oxygen donor ligands

The reaction of $[RuBr_2(Me_2SO)_3]$ with oxalic acid results in the formation of $[RuBr(C_2O_4H)(Me_2SO)_2]$. The IR spectrum of the compound shows absorption at 1623 and 1407 cm^{-1} which could be assigned to ν_{asym}(CO) and ν_{sym}(CO), respectively of the oxalato group [17]. Further bands at 1104 and 433 cm^{-1} are also observed, which could be assigned to ν(S=O) and ν(Ru–S) respectively of S-bonded Me_2SO groups. The ^{1}H NMR spectrum of the compound in $(CD_3)_2SO$ shows one sharp singlet at δ3.25 which could be assigned to the methyl protons of S-bonded Me_2SO groups [11]. The ^{1}H NMR spectrum of the compound in D_2O shows a singlet at δ2.7 which may be assigned to proton signals of uncoordinated Me_2SO groups. It is likely that in D_2O, the complex dissociates leading to the exchange of the coordinated Me_2SO groups with water, and thereby free Me_2SO is observed in the aqueous solution.

With nitrogen donor ligands

Reactions of $[RuBr_2(Me_2SO)_3]$ with nitrogen donor ligands like pyridine, 1,10-phenanthroline, 2,2′-bipyridine and *o*-phenylenediamine at room temperature resulted in the formation of partially substituted products, viz. [RuBr$_2$(py)$_2$(Me$_2$SO)$_2$] or [RuBr$_2$(L-L)(Me$_2$SO)$_2$] (L-L = bpy, phen or PDA). The molar conductances of these compounds in acetonitrile at room temperature were found to be 5–10 Ω^{-1} cm^2 mol^{-1} which indicate the covalent nature of the bromide. Two strong absorption bands in the region 1080–1060 cm^{-1} (see Table 2) were observed for these complexes which could be assigned to ν(S=O) of S-bonded Me$_2$SO groups. A band of medium intensity at 425 cm^{-1} in the case of [RuBr$_2$(phen)(Me$_2$SO)$_2$] and at 420 cm^{-1} in the case of [RuBr$_2$(PDA)(Me$_2$SO)$_2$] could be assigned to ν(Ru–S). Reactions of [RuBr$_2$(Me$_2$SO)$_3$] with py, bpy and phen, carried out by refluxing in methanol resulted in the complete substitution of Me$_2$SO molecules by the ligands. The compounds thus obtained, analysed as [RuBr$_2$(py)$_4$] or [RuBr$_2$(L-L)$_2$] (L-L = phen or bpy). The IR spectra of these compounds showed no characteristic absorption in the region where ν(SO) for S-bonded or O-bonded Me$_2$SO should be observed.

The presence of S-bonded Me$_2$SO molecules in the case of partially substituted compounds and the absence of any Me$_2$SO molecules in the case of completely substituted compounds, was further confirmed with the help of ^{1}H NMR spectra. The ^{1}H NMR spectrum of [RuBr$_2$(py)$_4$] in CDCl$_3$ showed a doublet at δ8.74 and two triplets at δ7.63 and δ7.06 and no signal was observed in the region δ2–4. The absence of any signal in the region δ2–4 confirms the absence of any Me$_2$SO molecule. The presence of two triplets and one doublet in the region δ7–9 is due to the pyridine molecules in *trans*-[RuBr$_2$(py)$_4$] [19]. The ^{1}H NMR spectrum of [RuBr$_2$(py)$_2$(Me$_2$SO)$_2$] in CDCl$_3$ showed a sharp singlet at δ3.44, two triplets at δ7.2 and δ7.75, and one doublet at δ9.12. The singlet at δ3.44 could be assigned to the methyl protons of S-bonded Me$_2$SO molecules. The pattern of the signals in the region δ7.20–9.12 is characteristic of pyridine molecules coordinated in the *trans* positions [19]. Further, only one sharp signal at δ3.44 is indicative that the two Me$_2$SO molecules are in equivalent environments, which is possible only if a *trans* structure for [RuBr$_2$(py)$_2$(Me$_2$SO)$_2$] is envisaged. The ratio of the areas of the signals due to the protons of the pyridine and Me$_2$SO is 5:6, thereby confirming the presence of an equal number of pyridine and Me$_2$SO molecules in the complex.

The ^{1}H NMR spectrum of [Ru(bpy)$_2$Br$_2$] in (CD$_3$)$_2$SO showed a doublet at δ8.95, a triplet at δ8.18 and a multiplet (an asymmetrical quintet) at δ7.70 and no signals in the region δ2–4. Signals in the region δ7.5–9.0 are characteristic of aromatic protons of 2,2′-bipyridine. The structure proposed for [Ru(bpy)$_2$Br$_2$], on the basis of ^{1}H NMR, is a *trans* one. For the *trans* isomer, the four pyridine rings of the two bipyridine molecules have equivalent environments, whereas for the *cis* isomer, the pyridines of each ligand are inequivalent, but each is equivalent to one pyridine ring of the other bipyridine. Thus the aromatic region in the spectrum of the *trans* isomer should contain four multiplets, while that of the *cis* isomers should consist of signals from eight distinguishable hydrogens [20]. The spectrum of [Ru(bpy)$_2$Br$_2$] has one doublet, one triplet and one asymmetrical quintet (may be due to the combination of a doublet and a triplet). The ^{1}H NMR spectrum of [Ru(phen)$_2$Br$_2$] in CD$_3$CN showed a doublet at δ8.65 and a quartet at δ8.28, a doublet at δ8.07 and a quartet at δ7.67. The presence of four sets of signals in the aromatic region for 1,10-phenanthroline is expected only for a *trans* isomer similar to that of *trans*-[Ru(bpy)$_2$Br$_2$] discussed before. Hence a *trans* geometry for [Ru(phen)$_2$Br$_2$] is also proposed.

The ^{1}H NMR spectrum of [Ru(bpy)(Me$_2$SO)$_2$Br$_2$] in (CD$_3$)$_2$SO, showed a sharp singlet at δ3.30 and multiplets at δ7.66, δ8.12, δ8.66 and δ9.82. The signal at δ3.30 could be assigned to the methyl protons of S-bonded Me$_2$SO molecules. The spectrum in the aromatic region is not well resolved. However, the signals in the region δ7.5–10, could be assigned to the protons of 2,2′bipyridine. The ratio of the area under the signals in the aromatic region to the area of the signal at δ3.30 is 2:3, corresponding to 8 protons due to one bipyridine molecule:12 protons due to two Me$_2$SO molecules in the complex. The ^{1}H NMR spectrum of [Ru(phen)(Me$_2$SO)$_2$Br$_2$] in CD$_3$CN, showed a sharp singlet at δ3.7, a singlet at δ8.03, a doublet at δ8.50, another doublet at δ10.1, and few weak signals in the region δ7.6–8. The singlet at δ3.7 could be assigned due to the methyl protons of S-bonded Me$_2$SO molecules and all the signals in the aromatic region (between δ7.6–10.1) due to the protons of 1,10-phenanthroline. Further, the ratio of the areas under the signal at δ3.7 and the signals in the aromatic region confirm the composition of the complex as [Ru(phen)(Me$_2$SO)$_2$Br$_2$].

The ^{1}H NMR spectrum of [RuBr$_2$(PDA)(Me$_2$SO)$_2$] in (CD$_3$)$_2$SO shows a symmetrical octet centering at δ7.3, one singlet at δ6.12 and a sharp singlet at δ3.36. The symmetrical octet centering at δ7.3 is characteristic of symmetrically *o*-disubstituted benzenes [21]. The singlet at δ6.12 may be due to the four protons attached to the two nitrogen atoms of the amino group. In case, where *o*-amino groups are not bonded, the aromatic amino protons are expected in the range δ3.6–4.7 [21]. However, due to the coordination of the nitrogen atoms to the metal, electron density around the nitrogen is reduced, thereby decreasing the shielding of the protons at the nitrogen atoms and leading to a signal at a lower field, i.e. at a higher δ value (δ6.12). The ratio of the proton area under the signal at δ6.12 and under the signals around δ7.3 is 1:1, which confirms that the number of amino protons and aromatic protons is the same, i.e. four in each case. The signal at δ3.36 is due to the methyl protons of S-bonded Me_2SO groups [10]. The ratio of the proton area under δ3.36 and δ6.12 is 3:1 confirming the presence of twelve protons of two Me_2SO groups. The presence of a singlet for two Me_2SO groups at δ3.36 is indicative of the six methyl protons on each Me_2SO in equivalent environments. Hence a structure with two Me_2SO groups in the *trans* positions, the two amino groups of PDA in the *cis* positions and the two bromide ions in the *cis* positions is most probable.

Magnetic susceptibility and electronic absorption spectra

All the complexes described in this work are diamagnetic the same as their precursor, viz. $[RuBr_2(Me_2SO)_3]$. Diamagnetic behaviour conforms to the low-spin, d^6 configuration of Ru(II). The electronic absorption spectrum of $[RuBr_2(PDA)(Me_2SO)_2]$ shows two bands at 690 ($\epsilon = 68$) and 370 ($\epsilon = 280$) nm. Due to the low ϵ value, these bands may be thought of as due to spin allowed d–d transitions, viz. $^1A_{1g}$ to $^1T_{1g}$ or $^1T_{2g}$ [22]. The electronic absorption spectra of most other Ru(II) complexes (Table 3) show one or two absorption bands in the UV–Vis region having ϵ 10^3 or more, which may not be of the d–d type, but due to the charge transfer from Ru(II) to the ligands [22].

TABLE 3. Electronic absorption spectra of ruthenium(II) complexes

Compound	λ_{max} (nm) (ϵ)
$[RuBr_2(AsPh_3)_2(Me_2SO)_2]^b$	525sh
	382 (1460)
$[RuBr_2(CS)(PPh_3)_3]^b$	527 (1910)
	425 (2110)
$[RuBr_2(PDA)(Me_2SO)_2]^a$	690 (68)
	370 (280)
$[RuBr_2(AsPh_3)_2(CS)(Me_2SO)]^b$	276 (11,720)
$[RuBr_2(OPPh_3)_3]^b$	267 (12,800)
$[RuBr_2(CS)(Me_2SO)_2]^c$	390 (2530)
	297 (4640)
$[RuBr_2(phen)(Me_2SO)_2]^b$	432 (3430)
	272 (9650)
$[RuBr_2(bpy)(Me_2SO)_2]^a$	469 (2730)
	348 (3370)
	284 (8240)

[a]In acetonitrile. [b]In chloroform. [c]In dimethyl sulfoxide.

Catalytic activity of $[RuBr_2(Me_2SO)_3]$

When PPh_3 was oxidised by oxygen gas at the refluxing condition of n-butanol in the presence of $[RuBr_2(Me_2SO)_3]$, $OPPh_3$ was obtained in 90% yield. The reactions were carried out by taking different molar ratio of catalyst:PPh_3 (1:5 to 1:20), and in all cases about 80–90% of $OPPh_3$ was obtained. However, if the reactions were carried out in ethanol at refluxing conditions, the complex did not act as a catalyst and instead $[RuBr_2(OPPh_3)_3]$ was obtained. The IR spectrum of $OPPh_3$ showed a strong band at 1190 cm^{-1}, characteristic of $\nu(P{=}O)$ [17]. The metal complex isolated after the oxidation of PPh_3 seems to have a composition $[RuBr_2(CO)(PPh_3)_2(Me_2SO)]$*. This indicates that the reactive species acting as catalyst may be one which contains only one Me_2SO molecule viz. solvated $[RuBr_2(Me_2SO)]$. Two PPh_3 molecules and O_2 may get bonded to the Ru(II) ion leading to a state where two molecules of $OPPh_3$ could be formed. The mechanism of catalytic oxidation could be similar to that described by Graham *et al.* [24] or Takao *et al.* [25].

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*Confirmed by IR and ^1H NMR spectra. IR shows absorptions at 1928vs (ν(CO), 1180s (ν(SO) S-bonded Me_2SO) and 1090s (ν(SO) S-bonded Me_2SO and due to PPh_3) cm^{-1}. In presence of the metal complex n-butanol gets oxidised to the corresponding aldehyde and a CO group may be extracted from the aldehyde leading to the formation of a carbonyl complex [23]. ^1H NMR shows signals at δ7.42 and δ3.45 due to aromatic protons of the PPh_3 groups and due to methyl protons of the S-bonded Me_2SO group, respectively.

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