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# Synthesis and characterization of mono and dinuclear Ru(II) complexes with hexadentate ligands having $N_2P_4$ and $N_2As_4$ donor atoms

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## Abstract

The reactions of $RuCl_2(DMSO)_4$ (**1**) and $RuCl_2(PPh_3)_3$ (**2**) with the ligands $\alpha$, $\alpha'$-bis(bis(2-(diphenylphosphino)ethyl)amino)ethane (BDPE), $\alpha$, $\alpha'$-bis(bis(2-(diphenylarsino)ethyl)amino)ethane (BDAE) and $\alpha$, $\alpha'$-bis(bis(2-(diphenylphosphino)-*m*-xylene (BDPX) were carried out with 2:1 or 1:1 metal ligand molar ratios in different conditions. In the reaction of **1** with L (L = BDPE, BDPX) with a 2:1 molar ratio a mixture of two dinuclear octahedral complexes of the compositions $[Ru_2L(DMSO)_4Cl_2]Cl_2$ and $[Ru_2L(DMSO)_2Cl_4]$ were obtained. These complexes were separated by column chromatography and characterized. With a 1:1 molar ratio of **1** and L, mononuclear complexes as the major product along with some quantities of dinuclear complexes were formed. These complexes were separated and characterized. The reaction of **2** with the ligands L (L = BDPE, BDAE, BDPX) with a 2:1 molar ratio in dichloromethane resulted in the formation of dinuclear complexes of composition $[Ru_2L(PPh_3)_2Cl_4]$. The reaction of **2** with BDPE and BDPX in ethanol with longer refluxing time resulted in the displacement of all the three $PPh_3$ groups of **2** with the formation of complexes of the composition $[Ru_2LCl_4]$. Electrochemical studies of these complexes were also carried out.

## Introduction

The synthesis of transition metal complexes of polydentate tertiary phosphine ligands and metal ions of lower oxidation state, especially with Co(I) [1], Fe(II) [2], Rh(I) [3–5] and Ru(II) [6–8] are the subject matter of many recent reports. Interest in this area is due to the reaction of these complexes with $H_2$ to form hydrides and their catalytic activity in the hydrogenation of unsaturated organic substrates. With a view to synthesizing polydentate phosphine complexes and to study their reactivity we have recently synthesized hexadentate ligands viz. $\alpha$, $\alpha'$-bis(bis(2-(diphenylphosphino)ethyl)amino)ethane (BDPE), $\alpha$, $\alpha'$-bis(bis(2-(diphenylarsino)ethyl)amino)ethane (BDAE) and $\alpha$, $\alpha'$-bis(bis(2-diphenylphosphino)ethyl)amino-*m*-xylene (BDPX) (see Schemes 1 and 2) which have two sets of terdentate moieties, $NP_2$ or $NAs_2$, separated by ethylene or *m*-xylyl bridge. The notable features of these ligands are: (i) the presence of both $\sigma$-donor (N) and $\pi$-acceptor (P/As) coordinating atoms may have a balancing effect on the electron density on the metal ion, an important factor in homogeneous catalysis; (ii) ability of these ligands to stabilize lower oxidation states with the capability of such complexes to undergo reversible redox processes during catalytic reaction; (iii) incorporation of chelating effect in preventing the dissociation of M–P/As bonds, thus limiting the number of available coordination sites for reactivity studies.

We wish to report in this paper the synthesis of mono and dinuclear Ru(II) complexes formed by the reaction of $RuCl_2(DMSO)_4$ or $RuCl_2(PPh_3)_3$ with the ligands BDPE, BDAE and BDPX. The complexes were characterized on the basis of elemental analysis, conductivity data, IR, electronic and $^1H$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectral data. Electrochemical studies are also reported.

## Experimental

### *Materials*

The ligands BDPE, BDAE and BDPX were prepared by the procedure recently developed in this laboratory [9]. $RuCl_2(DMSO)_4$ [10] and $RuCl_2(PPh_3)_3$ [11] were prepared by published procedures. All organic solvents used were of reagent grade and

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were purified and dried before use. All preparations were carried out in an atmosphere of nitrogen.

### *Physical measurements*

Elemental analyses were performed on a Carlo Erba elemental analyser model 1106. A digisum Electronics digital conductivity meter model D1-909 was used for conductivity measurement. Magnetic measurements were carried out with a PAR model 155 vibrating sample magnetometer. IR spectra were recorded on A Carlzeiss Specord M80 spectrometer, as KBr pellets or in Nujol mull. $^{1}H$, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Jeol FX-100 FT-NMR. For $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR 10 mm spinning tube with a capillary of deuterium oxide for the internal lock was used. The UV–Vis spectra were recorded on a Shimadzu UV-160 spectrometer. Electrochemical measurements were carried out with a PAR electrochemical instrument equipped with a precision X-Y recorder. For cyclic voltammograms a PAR 175 Universal programmer coupled with the PAR 174A analyser was used with glassy carbon working electrode. All potentials were measured against SCE at 25 °C and tetrabutylammonium-perchlorate was used as supporting electrolyte.

### *Synthesis of the complexes*

#### *$[Ru_2(BDPE)(DMSO)_4Cl_2]Cl_2$ (1) and $[Ru_2(BDPE)(DMSO)_2Cl_4]$ (2)*

$RuCl_2(DMSO)_4$ (0.484 g, 1 mmol) was taken in methanol (20 $cm^3$) and the ligand BDPE (0.454 g, 0.5 mmol) dissolved in dichloromethane (30 $cm^3$) was added dropwise with stirring; the reaction mixture was refluxed for 4 h. A yellow precipitate (complex **1**) which separated during reflux was isolated by filtration and recrystallized from chloroform–ethanol mixture (yield 0.35 g). After isolation of complex **1** the filtrate was dried by a rotary evaporator and the solid mass was dissolved in a minimum volume of chloroform, filtered, and the filtrate was passed through a silica gel column using $CHCl_3$–MeOH (9:1) solvent mixture. The first fraction of the eluent gave complex **2** (yield 0.16 g).

#### *$[Ru(BDPE)(DMSO)Cl]$ (3) and $[Ru_2(BDPE)(DMSO)_2Cl_4]$ (2)*

$RuCl_2(DMSO)_4$ and BDPE were reacted in a 1:1 mole ratio under similar conditions to those mentioned for **1** and **2** in dichloromethane. After 4 h of refluxing the volume of the yellow solution was reduced to *c.* 10 $cm^3$, ethanol (10 $cm^3$) was added dropwise and the reaction mixture was kept at room temperature overnight. The yellow precipitate which deposited was a mixture of two complexes (checked by TLC). These were separated by column chromatography using a 9:1 $CHCl_3$–MeOH solvent mixture. The first fraction of the eluent gave complex **2** (yield 0.14 g) and the second fraction yielded complex **3** (yield 0.16 g).

#### *$[Ru_2(BDAE)(DMSO)_4Cl_2]Cl_2$ (4)*

This compound was synthesized by the reaction of $RuCl_2(DMSO)_4$ and BDAE in a 2:1 mole ratio following the same procedure as described for **1**. The yellow compound which separated during reflux was isolated by filtration and recrystallized from $CHCl_3$–EtOH mixture (yield 0.32 g).

#### *$[Ru_2(BDPX)(DMSO)_4Cl_2]Cl_2$ (5) and $[Ru_2(BDPX)(DMSO)_2Cl_4]$ (6)*

The ligand BDPX (0.492 g, 0.5 mmol) and $RuCl_2(DMSO)_4$ (0.484 g, 1 mmol) were reacted under the same conditions as those described for **1** and **2**. No compound was precipitated during reflux. The solvent of the reaction mixture was reduced to *c.* 5 $cm^3$ by a rotary evaporator and passed through a column using 9:1 $CHCl_3$–EtOH solvent mixture. The first and second fraction of the eluents gave **5** (yield 0.3 g) and **6** (yield 0.22 g), respectively.

#### *$[Ru(BDPX)(DMSO)_2Cl_2]$ (7) and $[Ru_2(BDPX)(DMSO)_2Cl_4]$ (6)*

$RuCl_2(DMSO)_4$ (0.242 g, 0.5 mmol) and the ligand BDPX (0.492 g, 0.5 mmol) were refluxed in dichloromethane for 5 h. The volume of the solution was reduced to *c.* 5 $cm^3$ and added to n-hexane (25 $cm^3$) with stirring. The yellow precipitate which separated was a mixture of two complexes (checked by TLC) which were separated by column chromatography using benzene–methanol solvent mixture. The 9:1 benzene–methanol mixture gave complex **7** (yield 0.29 g) and the 4:1 solvent mixture gave **6** (yield 0.12 g).

#### *$[Ru_2(BDPE)(PPh_3)_2Cl_4]$ (8) and $[Ru_2(BDAE)(PPh_3)_2Cl_4]$ (9)*

$RuCl_2(PPh_3)_3$ (0.48 g, 0.5 mmol) was taken in dichloromethane (25 $cm^3$) and the ligand BDPE/BDAE (0.25 mmol) dissolved in dichloromethane was added dropwise and refluxed for 4 h. During reflux a yellow compound separated which was isolated by filtration washed with diethyl ether and dried *in vacuo* (yield 0.31 g for **7**; 0.3 g for **8**).

#### *$[Ru_2(BDPX)(PPh_3)_2Cl_4]$ (10)*

This compound was prepared by the same procedure as that described for **8** and **9** with the difference that no compound was separated during reflux. The solution was dried by rotary evaporator and the solid yellow mass was washed with diethyl ether, extracted with a minimum volume of chloroform and passed through a silica gel column using 9:1 $CHCl_3$–MeOH solvent mixture. The first fraction of the eluent gave **9** (yield, 0.26 g).

### *[$Ru_2$(BDPE)$Cl_4$] (11)*

$RuCl_2(PPh_3)_3$ (0.48 g, 0.5 mmol) and the ligand BDPE (0.227 g, 0.25 mmol) were refluxed in ethanol for 8 h. The solvent of the reaction mixture was removed by a rotary evaporator and the solid mass was washed with ether, extracted with a minimum volume of methanol and passed through a column using 4:1 MeOH–$CHCl_3$ mixture. The first fraction gave complex **11** (yield, 0.16 g).

### *[$Ru_2$(BDPX)$Cl_4$] (12) and [$Ru_2$(BDPX)$Cl_4$] (12a)*

The reaction of $RuCl_2(PPh_3)_3$ and the ligand BDPX under the conditions described for **10**, followed by passing through a column gave complexes **12** (yield 0.14 g) and **12a** (yield 0.10 g).

## Results and discussion

For the preparation of Ru(II) complexes two starting materials, viz. $RuCl_2(DMSO)_4$ and $RuCl_2(PPh_3)_3$, were taken and were reacted with the ligands BDPE, BDAE and BDPX in a 2:1 or 1:1 molar ratio of metal ion to ligand in different solvents.

The reaction of $RuCl_2(DMSO)_4$ with BDPE or BDPX ligands in a 2:1 molar ratio resulted in the formation of a mixture of two complexes (checked by TLC) which were separated by column chromatography. Analytical and conductivity data of these complexes suggest the compositions $[Ru_2L(DMSO)_4Cl_2]Cl_2$ and $[Ru_2L(DMSO)_2Cl_4]$ where L = BDPE (**1** and **2**) and BDPX (**5** and **6**). The same reactions carried out in a 1:1 molar ratio, resulted in a mixture of mononuclear (major) and dinuclear (minor) complexes which were separated by column chromatography. The compositions of these complexes are $[Ru_2(BDPE)(DMSO)_2Cl_4]$ (**2**), [Ru(BDPE)(DMSO)Cl]Cl (**3**), $[Ru_2(BDPX)(DMSO)_2Cl_4]$ (**6**) and $[Ru(BDPX)(DMSO)_2Cl_2]$ (**7**).

The reaction of $RuCl_2(DMSO)_4$ with the ligand BDAE in a 2:1 molar ratio gave a dinuclear complex of composition $[Ru_2(BDAE)(DMSO)_4Cl_2]Cl_2$ (**4**).

The reaction of $RuCl_2(PPh_3)_3$ with the ligands BDPE, BDAE and BDPX in a 2:1 molar ratio in dichloromethane resulted in the formation of $[Ru_2L(PPh_3)_2Cl_4)$ (where L = BDPE, BDAE and BDPX) **8–10**. The same reaction when conducted in ethanol with a longer refluxing time resulted in the displacement of all the three $PPh_3$ groups of $RuCl_2(PPh_3)_3$ with the formation of complexes of the composition $[Ru_2LCL_4]$ (L = BDPE, BDPX) **11–12a**. This reaction gave a single complex in the case of BDPE whereas for BDPX the reaction resulted in a mixture of two complexes **12** and **12a** which were separated by column chromatography.

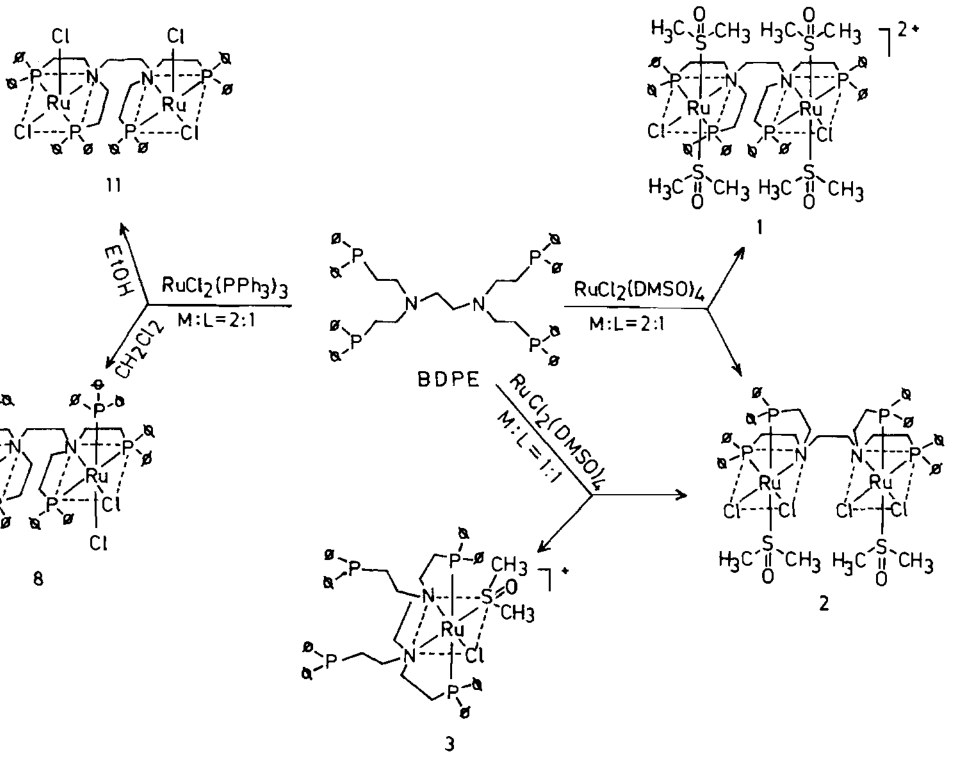
The reaction products obtained from BDPE and BDPX are shown in Schemes 1 and 2, respectively. Elemental analysis and conductivity data of the complexes are presented in Table 1. Selected IR bands and electronic spectral data are shown in Table 2. Tables 3 and 4 provide $^1H$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectral data.

Molar conductance measurements show that, except for **1** and **3–5**, all the other complexes are non-electrolyte; complexes **1**, **4** and **5** correspond to a 1:2 electrolyte and complex **3** is a 1:1 electrolyte. Magnetic measurements show that these complexes are diamagnetic.

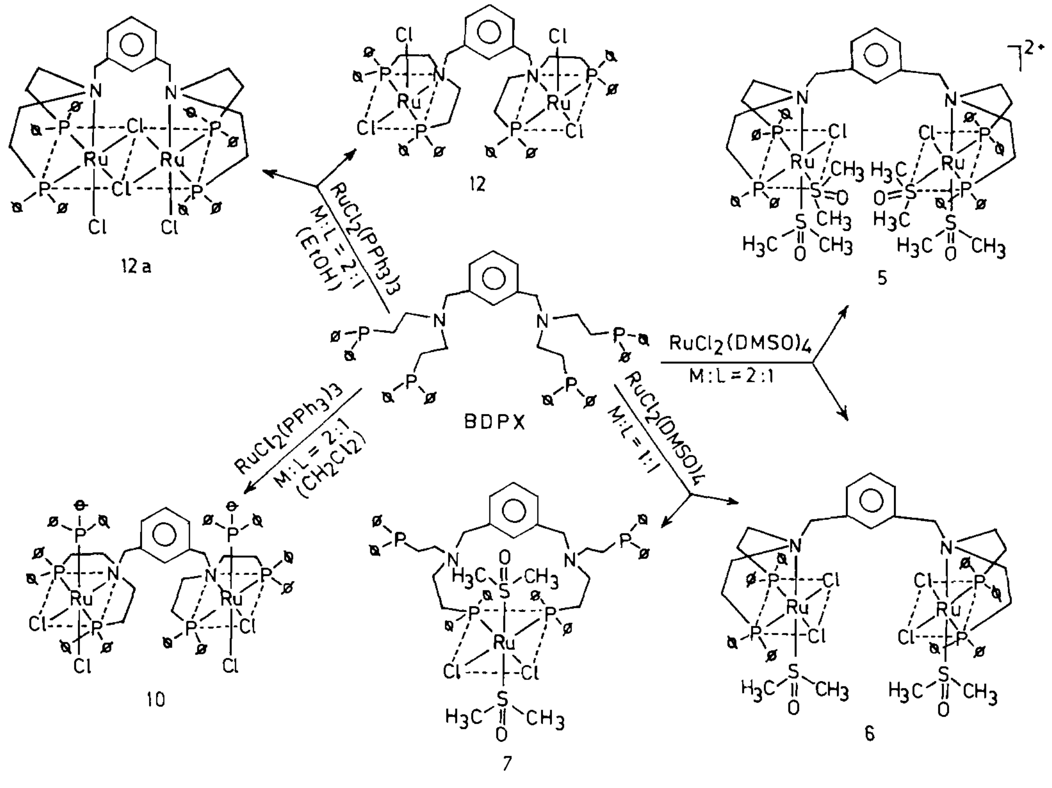
The IR spectra of the complexes exhibit a medium intensity band in the range 480–535 $cm^{-1}$, assigned to $\nu$(Ru–P/As) [12, 13], and a medium to weak intensity band in the range 305–330 $cm^{-1}$, assigned to $\nu$(Ru–Cl) [12, 13]. Complexes **1–7** with a coordinated DMSO molecule show a strong absorption frequency at $1095 \pm 5$ $cm^{-1}$ due to $\nu$(S=O) of the S-bonded DMSO molecule [10, 12, 13] and a medium intensity band at $443 \pm 3$ $cm^{-1}$ which is assigned to $\nu$(Ru–S) [10, 12, 13].

The $^1H$ and $^{13}C\{^1H\}$ NMR data of the ligands and their complexes are presented in Tables 3 and 4. An analysis of these data shows that for all dinuclear complexes the resonating signals for protons and carbon atoms of *x*-$CH_2$, *y*-$CH_2$ and *z*-$CH_2$ (see Table 3 for labelling) are significantly deshielded compared to those of the free ligands. In the case of $^1H$ the downfield shifts are in the ranges $\delta$ 0.42–0.66, $\delta$ 0.38–0.60 and $\delta$ 0.91–1.17 for *x*-$CH_2$, *y*-$CH_2$ and *z*-$CH_2$, respectively. Resonances for the carbon atoms of these groups in $^{13}C\{^1H\}$ are in the ranges $\delta$ 4.06–5.80, $\delta$ 2.27–4.56 and $\delta$ 3.88–6.47. The downfield shifts of $^1H$ and $^{13}C$ are due to coordination of phosphorus and nitrogen atoms of the ligand to the metal ion. The resonances due to the aromatic moiety appeared in the ranges $\delta$ 6.66–8.08 for $^1H$ and $\delta$ 126.73–141.20 for $^{13}C$.

For mononuclear complexes **3** and **7** the resonances due to *x*-$CH_2$ and *y*-$CH_2$ are splitted into two components due to the presence of both coordinated and free N–$CH_2$–$CH_2$–$PPh_2$ arms. The coordinated arms show significant downfield shifts but resonance signals due to free arms appeared at a position very close to those of the free ligand. In both the mononuclear complexes *z*-$CH_2$ appeared as a singlet but in complex **3** it shows notable downfield shifting indicating that the nitrogen atoms of the ligand are



Scheme 1.



Scheme 2.

TABLE 1. Analytical and conductivity data for Ru(II) complexes

| Complex | Found (%) | | | Calculated (%) | | | Conductivity in DMF $\Lambda_M$ ($\Omega^{-1}$ cm$^2$ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| | C | H | N | C | H | N | |
| $[Ru_2(BDPE)(DMSO)_4Cl_2]Cl_2$ (**1**) | 50.33 | 5.22 | 1.68 | 50.63 | 5.37 | 1.79 | 136[a] |
| $[Ru_2(BDPE)(DMSO)_2Cl_4]$ (**2**) | 52.46 | 5.02 | 1.86 | 52.84 | 5.11 | 1.99 | 8[b] |
| $[Ru(BDPE)(DMSO)Cl]Cl$ (**3**) | 61.92 | 5.76 | 2.31 | 62.17 | 5.70 | 2.41 | 82[c] |
| $[Ru_2(BDAE)(DMSO)_4Cl_2]Cl_2$ (**4**) | 45.38 | 4.71 | 1.49 | 45.51 | 4.83 | 1.61 | 144[a] |
| $[Ru_2(BDPX)(DMSO)_4Cl_2]Cl_2$ (**5**) | 52.81 | 5.20 | 1.56 | 52.68 | 5.36 | 1.71 | 138[a] |
| $[Ru_2(BDPX)(DMSO)_2Cl_4]$ (**6**) | 54.76 | 5.06 | 1.78 | 54.98 | 5.12 | 1.89 | 12[b] |
| $[Ru(BDPX)(DMSO)_2Cl_2]$ (**7**) | 62.32 | 5.67 | 2.02 | 62.19 | 5.79 | 2.13 | 7[b] |
| $[Ru_2(BDPE)(PPh_3)_2Cl_4]$ (**8**) | 63.17 | 5.18 | 1.43 | 63.49 | 5.07 | 1.58 | 9[b] |
| $[Ru_2(BDAE)(PPh_3)_2Cl_4]$ (**9**) | 57.58 | 4.50 | 1.31 | 57.76 | 4.61 | 1.43 | 8[b] |
| $[Ru_2(BDPX)(PPh_3)_2Cl_4]$ (**10**) | 64.46 | 4.96 | 1.40 | 64.77 | 5.07 | 1.51 | 10[b] |
| $[Ru_2(BDPE)Cl_4]$ (**11**) | 55.35 | 4.87 | 2.16 | 55.58 | 4.79 | 2.24 | 11[b] |
| $[Ru_2(BDPX)Cl_4]$ (**12**) | 57.64 | 4.68 | 2.20 | 57.82 | 4.82 | 2.11 | 8[b] |
| $[Ru_2(BDPX)Cl_4]$ (**12a**) | 57.69 | 4.92 | 2.04 | 57.82 | 4.82 | 2.11 | 10[b] |

[a] 1:2 Electrolyte. [b] Non-electrolyte. [c] 1:1 Electrolyte.

involved in coordination. Apart from the resonances due to ligand moiety complexes **4**–**7** exhibit a singlet in the range $\delta$ 2.87–3.13 in $^1H$ NMR and in the range $\delta$ 49.38–50.18 in $^{13}C\{^1H\}$ NMR, assigned to the $CH_3$ group of the coordinated DMSO molecule [12].

The $^{31}P\{^1H\}$ NMR spectral data are extremely useful for geometrical assignment. Complexes **1** and **5** with the same composition $[Ru_2L(DMSO)_4Cl_2]Cl_2$ (L = BDPE (**1**) and BDPX (**5**)) and obtained from similar reaction, show different types of $^{31}P\{^1H\}$ spectra. Complex **1** exhibits a singlet at $\delta$ 31.37 whereas complex **5** shows two doublets at $\delta$ 30.40 and $\delta$ 46.68 with $J$(P–P) = 19.55 Hz (Fig. 1). This data indicates the magnetic equivalence of all the four phosphorus atoms in complex **1**. Complex **5** has however two types of non-equivalent phosphorus atoms with a $J$(P–P) value of 19.55 Hz, indicating a *cis*-disposition [12–14]. These results can be explained on the basis of a dinuclear octahedral geometry for **1** in which DMSO molecules are in axial positions and NPPCl donor atoms are in the equatorial plane with *trans* disposition of phosphorus atoms, as shown in Scheme 1 (**1**). For complex **5** a dinuclear octahedral geometry in which a nitrogen atom and a DMSO molecule are in axial positions and two phosphorus atoms, chloride and a DMSO molecule are in the equatorial plane with *cis*-disposition of phosphorus atoms is suggested as shown in Scheme 2 (**5**). The doublet at $\delta$ 46.68 of **5** is assigned to phosphorus atoms *trans* to chloride [12, 13] and the doublet at $\delta$ 30.40 is due to phosphorus atoms *trans* to DMSO molecules.

This difference in coordination of **1** and **5** is due to the difference in the bridging groups ethylene and *m*-xylyl between the two NPP coordination sets of BDPE and BDPX, respectively. The separation between two coordination NPP sets in BDPE by an ethylene bridge ($-CH_2-CH_2-$) makes it difficult for nitrogen to coordinate through the axial position in a dinuclear system because of severe steric overcrowding whereas coordination of nitrogen through the equatorial plane causes a maximum separation and minimum overcrowding between two metal centres and thus forms stable complexes. In the case of BDPX the *m*-xylyl moiety makes sufficient separation between two coordination units and, therefore, the nitrogen atom can easily coordinate through the axial position. Molecular models of complexes **1** and **5** also support this fact.

A similar situation was observed in complexes **2** and **6** which have the same composition, $[Ru_2L(DMSO)_2Cl_4]$ (L = BDPE and BDPX). The $^{31}P\{^1H\}$ NMR of **2** shows two doublets at $\delta$ 30.72 and $\delta$ 46.71 with $J$(P–P) = 21.95 Hz whereas complex **6** exhibits a singlet at $\delta$ 46.50. These data indicate that complex **2** has two non-equivalent phosphorus atoms which are *cis* to each other whereas complex **6** has all the four phosphorus atoms equivalent. The $\delta$ value in the range 44–48 is usually found for the phosphorus atom of a $PPh_2$ group *trans* to chloride in Ru(II) complexes with the $NP_2$ donor set of the ligand [12–14]. These data, therefore, suggest a dinuclear octahedral geometry for **2** in which one phosphorus atom is in an axial position, *trans* to DMSO molecule, and another phosphorus atom is in the equatorial plane *trans* to chloride, as shown in Scheme 2 (**2**). For complex **6** an octahedral dinuclear geometry in which two phosphorus atoms are in the equatorial plane, mutually *cis* to each other and *trans* to chloride, with nitrogen and DMSO molecule in axial positions is suggested (Scheme 2 (**6**)).

TABLE 2. Selected IR bands and electronic spectral data for Ru(II) complexes

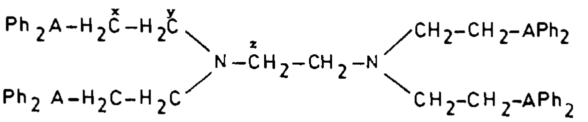
| Complex | IR data ($cm^{-1}$)[a] | | | | Electronic spectral data | |
|---|---|---|---|---|---|---|
| | $\nu$(Ru–P/As) | $\nu$(Ru–Cl) | $\nu$(S=O) | $\nu$(Ru–S) | Solvent | $\lambda_{max}$ (nm) ($\epsilon$($M^{-1}$ $cm^{-1}$)) |
| $[Ru_2(BDPE)(DMSO)_4Cl_2]Cl_2$ (**1**) | 518s | 320w | 1095s | 440m | $CH_2Cl_2$ | 443(525), 390(900), 336(1500), 304(2600), 260(13400) |
| $[Ru_2(BDPE)(DMSO)_2Cl_4]$ (**2**) | 516m, 525m | 310w, 318w | 1095s | 442m | $CH_2Cl_2$ | 456(430), 398(845), 344(1520), 300(2850), 260(16400) |
| $[Ru(BDPE)(DMSO)Cl]Cl$ (**3**) | 512s | 320w | 1098s | 445m | $CH_2Cl_2$ | 448(160), 398(350), 340(560), 303(2050), 258(12800) |
| $[Ru_2(BDAE)(DMSO)_4Cl_2]Cl_2$ (**4**) | 480s | 305m | 1090s | 440m | $CHCl_3$ | 450(640), 390(1040), 344(1200), 295(2280), 260(23260) |
| $[Ru_2(BDPX)(DMSO)_4Cl_2]Cl_2$ (**5**) | 510m, 525m | 310m | 1100s<br>1090s | 445m<br>436m | $CH_2Cl_2$ | 458(330), 402(700), 340(1880), 297(2900), 260(13725) |
| $[Ru_2(BDPX)(DMSO)_2Cl_4]$ (**6**) | 520s | 312m | 1092s | 440m | $CH_2Cl_2$ | 470(305), 392(600), 345(1420), 305(2830), 260(14400) |
| $[Ru(BDPX)(DMSO)_2Cl_2]$ (**7**) | 520s | 310m | 1095s | 442m | $CH_2Cl_2$ | 454(145), 397(240), 342(1245), 302(2400), 258(16350) |
| $[Ru_2(BDPE)(PPh_3)_2Cl_4]$ (**8**) | 515s, 535s | 310m, 320w | | | $CHCl_3$ | 476(445), 395(820), 342(1200), 300(2330), 260(12500) |
| $[Ru_2(BDAE)(PPh_3)_2Cl_4]$ (**9**) | 475s, 532m | 310m, 328m | | | $CHCl_3$ | 490(620), 390(925), 342(1180), 292(2080), 260(21550) |
| $[Ru_2(BDPX)(PPh_3)_2Cl_4]$ (**10**) | 512s, 532s | 310m, 320m | | | $CHCl_3$ | 470(705), 395(950), 345(1350), 295(3050), 258(14750) |
| $[Ru_2(BDPE)Cl_4]$ (**11**) | 512s | 312m, 330m | | | $CH_2Cl_2$ | 622(180), 502(355), 375(650), 348(1280), 302(2320), 260(12600) |
| $[Ru_2(BDPX)Cl_4]$ (**12**) | 515s | 310m, 330m | | | $CHCl_3$ | 630(210), 510(340), 376(700), 355(1350), 300(2640), 258(14920) |
| $[Ru_2(BDPX)Cl_4]$ (**12a**) | 502s | 290w, 328m | | | $CHCl_3$ | 450(650), 376(1580), 295(2760), 258(18570) |

s = strong, m = medium, w = weak. [a]As KBr pellets or in nujol mull (lower region).

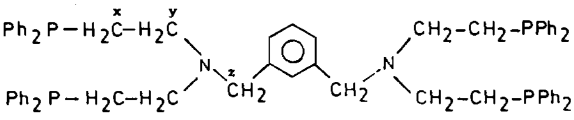
TABLE 3. ${}^{1}$H NMR Spectral data for the ligands and their Ru(II) complexes[a]

| Compound | Chemical shift (δ)[b] | | | | |
|---|---|---|---|---|---|
| | $x$-$CH_2$[c] | $y$-$CH_2$ | $z$-$CH_2$ | Ph | $CH_3$ of DMSO |
| BDPE | 1.88m | 2.22m | 2.37s | 7.16 | |
| BDAE | 1.94t | 2.26t | 2.44s | 7.28 | |
| BDPX | 2.09m | 2.56m | 3.52s | 7.14, 7.27 | |
| $[Ru_2(BDPE)(DMSO)_4Cl_2]Cl_2$ (1) | 2.54m | 2.74m | 3.34s | 6.90–7.97 | 2.93s |
| $[Ru_2(BDPE)(DMSO)_2Cl_4]$ (2) | 2.51m | 2.76m | 3.36s | 6.89–8.02 | 2.87s |
| $[Ru(BDPE)(DMSO)Cl]Cl$ (3) | 2.51m, 2.07m | 2.76m, 2.36m | 3.47s | 6.97–8.08 | 2.96s |
| $[Ru_2(BDAE)(DMSO)_4Cl_2]Cl_2$ (4) | 2.58m | 2.74m | 3.35s | 6.93–7.97 | 2.98s |
| $[Ru_2(BDPX)(DMSO)_4Cl_2]Cl_2$ (5) | 2.58m | 3.12m | 4.60s | 6.87–8.04 | 2.93s, 3.10s |
| $[Ru_2(BDPX)(DMSO)_2Cl_4]$ (6) | 2.69m | 3.16m | 4.62s | 6.99–7.88 | 3.13s |
| $[Ru(BDPX)(DMSO)_2Cl_2]$ (7) | 2.46m, 2.14m | 2.83m, 2.66m | 3.63s | 7.00–7.97 | 3.01s |
| $[Ru_2(BDPE)(PPh_3)_2Cl_4]$ (8) | 2.52m | 2.78m | 3.42m | 6.84–7.81 | |
| $[Ru_2(BDAE)(PPh_3)_2Cl_4]$ (9) | 2.40m | 2.77m | 3.43s | 6.66–7.76 | |
| $[Ru_2(BDPX)(PPh_3)_2Cl_4]$ (10) | 2.54m | 2.97m | 4.61s | 6.66–8.02 | |
| $[Ru_2(BDPE)Cl_4]$ (11) | 2.53m | 2.75m | 3.54s | 6.74–7.67 | |
| $[Ru_2(BDPX)Cl_4]$ (12) | 2.51m | 2.94m | 4.58s | 7.18–7.64 | |
| $[Ru_2(BDPX)Cl_4]$ (12a) | 2.56m | 3.05m | 4.65s | 6.96–7.72 | |

s = singlet, t = triplet, m = multiplet. [a]All spectra were recorded in $CDCl_3$. [b]Relative to tetramethylsilane. [c]See below for labelling.



A=P, (BDPE)
A=As,(BDAE)



(BDPX)

TABLE 4. ${}^{13}C\{{}^{1}H\}$ and ${}^{31}P\{{}^{1}H\}$ NMR spectral data for the ligands and their Ru(II) complexes[a]

| Compound | ${}^{13}C\{{}^{1}H\}$ NMR data, chemical shift (δ)[b] | | | | | ${}^{31}P\{{}^{1}H\}$ NMR data | |
|---|---|---|---|---|---|---|---|
| | $x$-$CH_2$[d] | $y$-$CH_2$ | $z$-$CH_2$ | Ph | $CH_3$ of DMSO | Chemical shift (δ)[c] | $J$(P–P) (Hz) |
| BDPE | 25.57d[e] | 50.33d[f] | 52.06s | 128.85–138.89 | | −19.01s | |
| BDAE | 25.54s | 50.57s | 52.21s | 128.56–141.08 | | | |
| BDPX | 25.92d[g] | 49.98d[h] | 58.58s | 127.98–139.14 | | −20.89s | |
| 1 | 30.12s | 53.67s | 58.89s | 127.90–135.74 | 49.38s | 31.37s | |
| 2 | 30.13s, 30.67s | 53.72s | 58.89s | 127.86–135.79 | 49.43s | 30.72d, 46.71d | 21.95 |
| 3 | 30.86s, 26.43d | 53.24s, 51.16d | 53.84s | 127.85–135.94 | 49.63s | 32.94s, −19.74s | |
| 4 | 29.83s | 53.27s | 58.34s | 128.43–137.25 | 50.05s | | |
| 5 | 30.62s, 30.10s | 54.36s | 62.46s | 127.17–139.06 | 49.87s, 51.54s | 30.40d, 46.68d | 19.55 |
| 6 | 30.52s | 54.54s | 62.69s | 127.89–139.16 | 50.07s | 46.50s | |
| 7 | 30.56s, 26.03d | 51.56s, 50.46d | 58.63s | 127.33–139.44 | 50.18s | 46.32s, −19.68s | |
| 8 | 30.88s | 53.05s | 58.79s | 126.68–141.20 | | 24.86d, 48.86t | 26.86 |
| 9 | 31.02s | 53.98s | 58.68s | 126.77–140.71 | | 49.32s | |
| 10 | 31.72s | 53.14s | 62.47s | 126.73–140.86 | | 25.16d, 47.29t | 26.85 |
| 11 | 29.70s | 52.76s | 58.38s | 128.48–135.01 | | 29.31s | |
| 12 | 29.98s | 52.25s | 62.50s | 128.56–134.66 | | 30.70s | |
| 12a | 30.56s | 52.87s | 62.90s | 128.52–135.73 | | 59.28s | |

s = singlet, d = doublet, t = triplet. [a]Spectra were recorded in $CHCl_3$. [b]Relative to tetramethylsilance. [c]Relative to 85% $H_3PO_4$. [d]See Table 3 for labelling. [e]$J$(P–P) = 13.43 Hz. [f]$J$(C–P) = 23.20 Hz. [g]$J$(C–P) = 12.2 Hz. [h]$J$(C–P) = 23.20 Hz.

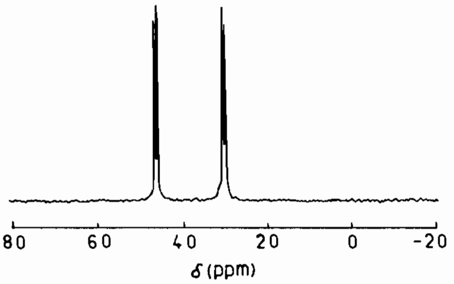


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $[Ru_2(BDPX)(DMSO)_4Cl_2]Cl_2$ in $CHCl_3$.

The mononuclear complexes **3** and **7** formed by BDPE and BDPX, however, have different compositions, [Ru(BDPE)(DMSO)Cl]Cl (**3**) and $[Ru(BDPX)(DMSO)_2Cl_2]$ (**7**). The $^{31}P\{^1H\}$ NMR of **3** exhibits two resonances at δ 32.94 and δ −19.74 and for **7** the same appeared at δ 46.32 and δ −19.68. These data indicate the presence of both coordinated and free $PPh_2$ groups in these complexes and the coordinated $PPh_2$ groups are equivalent in each complex. The δ value for bonded $PPh_2$ in **3** (32.94) is close to that found for complex **1** and is assigned to phosphorus atoms which are mutually *trans* to each other. For complex **7** the δ value of 46.32 compares very well with that expected for a phosphorus atom *trans* to chloride. These data are consistent with the proposed mononuclear octahedral geometry for complexes **3** and **7**, as shown in Schemes 1 (**3**) and 2 (**7**), respectively.

For complex **4** with the composition $[Ru_2(BDAE)(DMSO)_4Cl_2]Cl_2$, similar to complex **1**, a dinuclear octahedral geometry with DMSO molecules in axial positions as suggested for **1** is proposed. This is based on the $^1H$ and $^{13}C\{^1H\}$ NMR data. The $^1H$ NMR spectrum shows a singlet at δ 2.98 and $^{13}C\{^1H\}$ NMR exhibits a singlet at δ 50.05 for the $CH_3$ group of coordinated DMSO molecules. The appearance of a singlet in both the spectra indicates that all four DMSO molecules are equivalent, a fact consistent with the proposed structure. The IR spectrum of the complexes shows a single strong sharp band for ν(S=O) at 1090 $cm^{-1}$ [10, 12, 13] and a medium intensity band at 440 $cm^{-1}$ for ν(Ru–S) supporting the coordination of DMSO molecules in equivalent positions.

Complexes **8**–**10** have the composition $[Ru_2L(PPh_3)_2Cl_2]Cl_2$ (L = BDPE, BDAE and BDPX). The $^{31}P\{^1H\}$ NMR spectra of **8** and **10** are similar and exhibit a doublet and a triplet at δ 24.86 and δ 48.86 with a J(P–P) value of 26.86 Hz for **8** and at δ 25.16 and δ 47.29 with a J(P–P) value of 26.85 Hz for **10** (Fig. 2). Complex **9** shows a singlet at δ 49.32. The triplets of **8** (δ 46.86) and **10** (δ 47.29) and the singlet of **9** (δ 49.32) are assigned to the phosphorus atom of the coordinated $PPh_3$ group and the δ values indicate the $PPh_3$ group is coordinated in a position *trans* to chloride. The doublets observed for complexes **8** and **10** are due to phosphorus atoms of $PPh_2$ groups. The splitting pattern is of the $AB_2$ type and the coupling constants J(P–P) of 26.86 and 26.85 Hz are characteristic of *cis* coupling. These results are, therefore, consistent with a dinuclear octahedral geometry in which a $PPh_3$ group and a chloride are in axial positions and nitrogen, two phosphorus atoms and a chloride forms the equatorial plane with *trans* disposition of phosphorus atoms, as shown in Schemes 1 (8) and 2 (10).

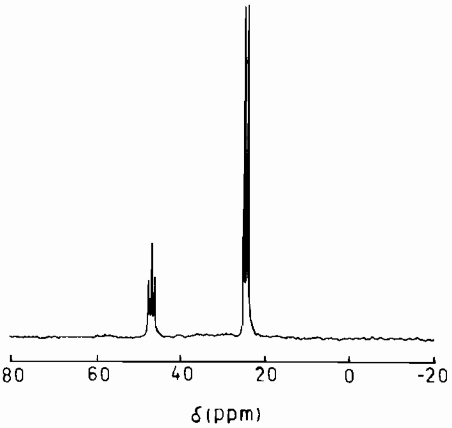


Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of $[Ru_2(BDPX)(PPh_3)_2Cl_4]$ in $CHCl_3$.

The $^{31}P\{^1H\}$ NMR spectra of the complexes $[Ru_2(BDPE)Cl_4]$ (**11**) and $[Ru_2(BDPX)Cl_2]$ (**12**) exhibit a singlet at δ 29.31 and δ 30.70, respectively, indicating the equivalence of the phosphorus atoms in each case. The δ values of 29.31 and 30.70 are very close to those found for **1**, **3**, **8** and **10** where phosphorus atoms are *trans* to each other. From these data a dinuclear pentacoordinate Ru(II) with square pyramidal geometry is proposed, as shown in Schemes 1 (11) and 2 (12) (electronic spectral data, discussed below, also support a square pyramidal geometry). Such a geometry for Ru(II) with $PPh_3$ and chloride ligands is also reported by other groups [15] and also from this laboratory [16].

Complex **12a** which has the same composition as that of **12**, $[Ru_2(BDPX)Cl_4]$, shows a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ 59.28, with a significantly higher δ value compared to those found for complexes **11** and **12**. This compound was obtained for the ligand BDPX but not for BDPE. The possible geometry of this complex is shown in Scheme 2 (12a) where two chlorides bridge between two Ru(II) ions, and the nitrogen atom of the ligand and one chloride are in axial positions. The higher δ value can be attributed to the fact that the bond strength between the metal ion and bridged chloride is weaker than that between the metal ion and non-bridged chloride (terminal), as a result of this the *trans* Ru–P bond becomes stronger (due to *trans* effect) and results in a higher downfield shift (higher $\delta$ value) of the phosphorus resonance.

The electronic spectral data (presented in Table 2) for complexes **1–10** and **12a** are similar. The two absorptions in the regions 443–490 and 390–402 nm are due to d–d transitions which closely resemble those found for other tertiary phosphine and chloride ligands in the octahedral complexes of Ru(II) with spin-paired $(t_{2g})^6$ ground state configuration [12, 14, 17]. Complexes **11** and **12** show three absorptions at 622, 502 and 375 nm for **11** and 630, 510 and 376 nm for **12**. These data shows strong similarities with those reported for other five coordinate Ru(II) complexes such as $RuCl_2(PPh_3)_3$ [18] and $[RuX(dcpe)_2](BPh_4)$ (X = Cl, Br, I) [6] where a square pyramidal geometry is suggested; for the complex $RuCl_2(PPh_3)_3$ the geometry was also determined by a single crystal X-ray study [19]. Apart from the above-mentioned absorptions all complexes exhibit three additional bands in the 340–345, 295–305 and 258–260 nm regions which may be due to LMCT and charge transfer involving P or As lone pairs and the phenyl rings.

### *Electrochemical study*

The cyclic voltammetry of complexes **1–12** was studied in the potential range of 0 to + 1.6 V (versus SCE) in dichloromethane at 25 °C. Figures 3, 4 and 5 display the cyclic voltammograms of the mononuclear complex $[Ru(BDPX)(DMSO)_2Cl_2]$ (**7**), the dinuclear complexes $[Ru_2(BDAE)(DMSO)_4Cl_2]Cl_2$ (**4**) and $[Ru_2(BDPE)(PPh_3)_2Cl_4]$ (**8**), respectively. The electrochemical data are presented in Table 5.

The mononuclear complexes **3** and **7** show a reversible redox couple at +0.53 and +0.56 V, respectively. These results are very close to the reported values found for Ru(II) with tertiary phosphine ligands [20] and are assigned to the Ru(II)/Ru(III) couple. The electrochemical response of the dinuclear complexes is similar and exhibits two reversible one electron redox couples in the ranges +0.54 to +0.65 V and +0.68 to +0.87 V. These observations can be attributed to the sequential one electron transfer process:

$$\mathrm{Ru(II){-}Ru(II)} \underset{+e}{\overset{-e}{\rightleftharpoons}} \mathrm{Ru(III){-}Ru(II)}$$

$$\underset{+e}{\overset{-e}{\rightleftharpoons}} \mathrm{Ru(III){-}Ru(III)}$$

Similar observations have also been noted for a number of dinuclear Ru(III) complexes [21] and are often used to calculate the stability of the mixed valence species, expressed in terms of the comproportionation constant, $K_{com}$.

$$K_{com} = \exp(nF\Delta E/RT)$$

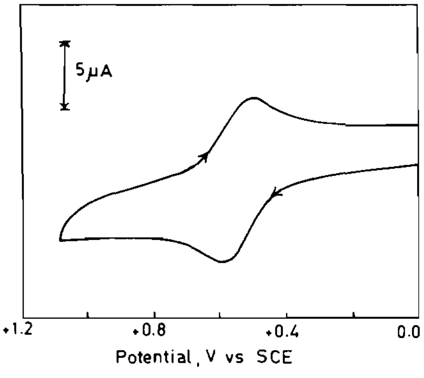


Fig. 3. Cyclic voltammogram of $[Ru(BDPX)(DMSO)_2Cl_2]$, $3\times10^{-3}$ M solution in $CH_2Cl_2$ at 25 °C.

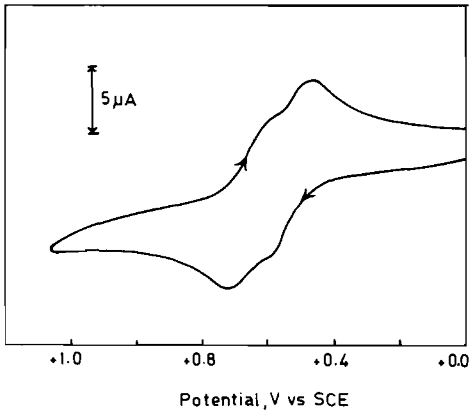


Fig. 4. Cyclic voltammogram of $[Ru_2(BDAE)(DMSO)_4Cl_2]Cl_2$, $3\times10^{-3}$ M solution in $CH_2Cl_2$ at 25 °C.

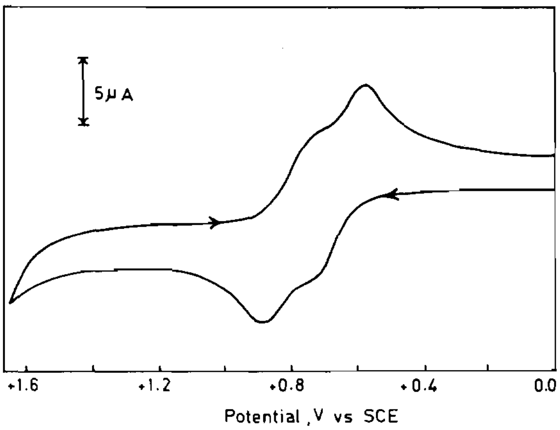


Fig. 5. Cyclic voltammogram of $[Ru_2(BDPE)(PPh_3)_2Cl_4]$, $3.5\times10^{-3}$ M solution in $CH_2Cl_2$ at 25 °C.

TABLE 5. Comparison of cyclic voltammetry data of Ru(II) complexes in $CH_2Cl_2$

| Complex | $E_{1/2}{}^{a}$ (V) | | $K_{com}{}^{b}$ |
|---|---|---|---|
| | Ru(II)–Ru(II)/Ru(III)–Ru(II) | Ru(III)–Ru(II)/Ru(III)–Ru(III) | |
| $[Ru_2(BDPE)(DMSO)_4Cl_2]Cl_2$ (**1**) | 0.62 | 0.81 | $1.69\times10^3$ |
| $[Ru_2(BDPE)(DMSO)_2Cl_4]$ (**2**) | 0.60 | 0.82 | $5.28\times10^3$ |
| $[Ru(BDPE)(DMSO)Cl]Cl$ (**3**) | $0.53^c$ | | |
| $[Ru_2(BDAE)(DMSO)_4Cl_2]Cl_2$ (**4**) | 0.54 | 0.68 | $2.34\times10^2$ |
| $[Ru_2(BDPX)(DMSO)_4Cl_2]Cl_2$ (**5**) | 0.63 | 0.84 | $3.58\times10^3$ |
| $[Ru_2(BDPX)(DMSO)_2Cl_4]$ (**6**) | 0.61 | 0.84 | $7.79\times10^3$ |
| $[Ru(BDPX)(DMSO)_2Cl_2]$ (**7**) | $0.56^c$ | | |
| $[Ru_2(BDPE)(PPh_3)_2Cl_4]$ (**8**) | 0.65 | 0.81 | $5.10\times10^2$ |
| $[Ru_2(BDAE)(PPh_3)_2Cl_4]$ (**9**) | 0.57 | 0.85 | $5.47\times10^4$ |
| $[Ru_2(BDPX)(PPh_3)_2Cl_4]$ (**10**) | 0.58 | 0.87 | $8.07\times10^4$ |
| $[Ru_2(BDPE)Cl_4]$ (**11**) | 0.62 | 0.76 | $2.34\times10^2$ |
| $[Ru_2(BDPX)Cl_4]$ (**12**) | 0.57 | 0.78 | $3.58\times10^3$ |

$^aE_{1/2}=0.5\ (E_{pa}+E_{pc})$ and potentials are referenced to standard calomel electrode (SCE). $^b$See text for calculation. $^cE_{1/2}$ for Ru(II)/Ru(III) couple.

where $\Delta E$ is the difference between the two potentials in volts. The $K_{com}$ values for the dinuclear complexes were calculated and are presented in Table 5.

The notable point in this study is that the oxidation and reduction couples are reversible and do not change with repeated scan for a long time. This is probably due to the presence of $\sigma$-donor and $\pi$-acceptor coordinating atoms in the ligands, a combination of effects capable of controlling electron density on the metal ion.

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