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Synthesis and redox properties of trinuclear ruthenium and osmium complexes containing 2,2′-biimidazolate as bridging ligand

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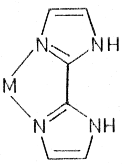
Abstract

A series of trinuclear complexes of ruthenium and osmium containing the terminal ligands 2-(phenylazo)pyridine (pap), triphenyl phosphine (PPh_3) and the bridging ligand 2,2′-biimidazolate ($biim^{2-}$) have been synthesised. These are characterised by the analyses of their physicochemical data. Electron spray ionization mass spectrum of one representative compound has been reported which authenticates the formulation of the compound. Cyclic voltammetric studies on the above trinuclear complexes are reported. These undergo three successive metal centered one electron transfer processes. The half-wave potentials for the oxidation processes are dependent largely on the electrochemical parameters of the coordinating ligands. Partial oxidation of the trinuclear complexes led to unsymmetrical bridge cleavage reaction. In addition to the above metal oxidation processes the above complexes showed multiple ligand reduction responses at the negative of the Ag–AgCl reference.

Keywords: Ruthenium osmium biimidazolate; Trinuclear; Synthesis; Redox; 2-(Phenylazo)pyridine

1. Introduction

This work stems from our recent interest in the synthesis of multimetallic redox active complexes based on bidentate bridging ligands in the context of studies [1–5] of electron transfer processes and intermetal electronic interactions. Recently, we have reported [6] some homo- and hetero-binuclear ruthenium and osmium complexes which contained 2,2′-biimidazolate as bridge and 2-(phenylazo)pyridine (pap) as terminal ligand. It may be noted that 2,2′-biimidazole ($biimH_2$) can act as a bridge only on complete deprotonation (I and II). The pK_a values of $biimH_2$ are high [7] and for this reason, even coordinated M–$biimH_2$, in most cases, fails to act as a building unit for the construction of a dinuclear compound. However, we have now shown [6] that the presence of a strong π-acceptor ligand like pap can augment the acidity of coordinated $biimH_2$, as in $[(pap)_2Ru(biimH_2)]^{2+}$, by a considerable extent and in turn makes it a useful building unit for the synthesis of multinuclear systems.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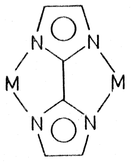
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Herein we report the synthesis and redox properties of some Ru/Os trinuclear complexes obtained from the reactions of $M(PPh_3)_3X_2$ (M = Ru, X = Cl and M = Os, X = Br) and $M(pap)_2(biim)$ (M = Ru, Os).

2. Experimental section

The starting complexes, $M(PPh_3)_3X_2$ and $[M(pap)_2biimH_2](ClO_4)_2$ (M = Ru, Os; X = Cl, Br) and 2,2′-biimidazole ($biimH_2$) were synthesized as reported earlier [6–10]. Solvents and chemicals used for syntheses were of analytical grade. Supporting electrolyte (tetraethyl

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ammonium perchlorate, TEAP) and solvents for electrochemical work were obtained as described previously [11].

2.1. Physical measurements

A Shimadzu UV 2100 UV–Vis Recording Spectrophotometer was used to record electronic spectra. IR spectra were recorded with a Perkin-Elmer 783 IR Spectrophotometer. A Perkin-Elmer 240C elemental analyser was used to collect microanalytical data (C,H,N). Electrochemical measurements were carried out under a dry nitrogen atmosphere on a PAR Model 370-4 Electrochemistry System as described earlier [12]. All potentials reported in this work are uncorrected for junction contribution. Electrical conductivities were measured by using a Systronics Direct Reading Conductivity Meter 304. ESMS measurements were carried out by using a sector type mass spectrometer (JEOL-D300) connected with a home made ESI interface as described earlier [13].

2.2. Determination of pK values

pH-metric titrations [6] were performed under dinitrogen atmosphere on 25 ml of a 4×10^{-3} M pollution of $[M(pap)_2(biimH_2)](ClO_4)_2$ (M=Ru, Os) in 1:1 water–dioxane mixture (ionic strength of the solution was maintained at 0.1 M with $NaClO_4$). The solutions were magnetically stirred and thermostated at 298 K. To the test solution was added enough of a carbonate-free [14] sodium hydroxide solution (0.814 N) to make it alkaline (pH~10). The solution was then titrated with standard perchloric acid (0.12 N). The burette for delivering perchloric acid was accurate to ±0.01 ml. For equilibrium reaction [(3) and (4)], relation (1) holds [15]. In the procedure adopted by us we have Eq. (2) defining $\tilde{n}$.

$$\tilde{n}/2 - \tilde{n}[H^+]^2 = 1 - \tilde{n}/2 - \tilde{n}[H^+]K_1 + K_1K_2 \quad (1)$$

$$\tilde{n} = [Na^+] - [ClO_4^-]/c \quad (2)$$

Here Na^+ and ClO_4^- originate from added sodium hydroxide and perchloric acid respectively, c is the total concentration of the complex and K_1, K_2 are the thermodynamic dissociation constants of the dibasic acid.

2.3. Syntheses of complexes

The monomeric complexes, $[M(pap)_2(biimH_2)](ClO_4)_2$, (M=Ru, Os) were used as building blocks for the syntheses of trinuclear species.

The mono protonated and completely deprotonated forms of the above building units were isolated separately by adjustment of pH. The violet complex, $[Ru(pap)_2(biimH)]^+$ was generated in solution by raising the pH of the aqueous acetonitrile solution containing its conjugate acid, $[Ru(pap)_2(biimH_2)]^{2+}$ to 5.5. This monocationic complex was isolated as its PF_6 salt in 90% yield. Single crystals of the above were obtained by slow diffusion of acetonitrile solution of the compound into toluene.

2.3.1. $[\{Ru(pap)_2biim\}_2Ru(PPh_3)_2](ClO_4)_2\cdot H_2O$

$[Ru(pap)_2(biimH_2)](ClO_4)_2$ (0.112 g, 0.14 mmol) was dissolved in 25 ml of dichloromethane and to it triethylamine (0.04 g, 0.4 mmol) was added. The colour of the solution changed from pink to blue–violet. To this solution $Ru(PPh_3)_3Cl_2$ (0.068 g, 0.07 mmol) was added and was stirred for 75 min at room temperature. A dark microcrystalline precipitate of the trimer was obtained on addition of hexane to the red–violet reaction mixture. The crude product was then purified on a silica-gel column using 4:1 (v/v) chloroform/acetonitrile mixture as eluant. The major red–violet band was collected. The compound thus obtained was finally crystallised from dichloromethane–diethylether. Yield: 55%. Anal. Calcd. for $C_{92}H_{76}N_{20}Cl_2O_9Ru_3$: C, 54.10; H, 3.72; N, 13.72. Found: C, 54.17; H, 3.86; N, 13.60%. $\Lambda_M = 260\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH_3CN).

2.3.2. $[\{Os(pap)_2biim\}_2Ru(PPh_3)_2](ClO_4)_2\cdot 2H_2O$

This compound was synthesised by a similar procedure as described above using $[Os(pap)_2(biimH_2)](ClO_4)_2\cdot 2H_2O$ instead of $[Ru(pap)_2(biimH_2)](ClO_4)_2$. Yield: 40%. Colour: brown–violet. Anal. Calcd. for $C_{92}H_{78}N_{20}Cl_2O_{10}Os_2Ru$: C, 49.36; H, 3.48; N, 12.51. Found: C, 49.41; H, 3.32; N, 12.48%. $\Lambda_M = 270\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH_3CN).

2.3.3. $[\{Ru(pap)_2biim\}_2Os(PPh_3)_2](ClO_4)_2\cdot 2H_2O$

This compound was similarly synthesised by using $[Ru(pap)_2(biimH_2)](ClO_4)_2$ and $Os(PPh_3)_3Br_2$ as the reagents and the mixture was refluxed on a water-bath. Yield: 42%. Colour: pink. Anal. Calcd. for $C_{92}H_{78}N_{20}Cl_2O_{10}Ru_2Os$: C, 51.41; H, 3.63; N, 13.03. Found: C, 51.61; H, 3.69; N, 12.61%. $\Lambda_M = 240\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH_3CN).

2.3.4. $[\{Os(pap)_2biim\}_2Os(PPh_3)_2](ClO_4)_2\cdot H_2O$

This compound was also synthesised similarly by refluxing a dichloromethane solution of $[Os(pap)_2(biimH_2)](ClO_4)_2\cdot 2H_2O$ with $Os(PPh_3)_3Br_2$. Yield: 35%. Colour: pinkish brown. Anal. Calcd. for $C_{92}H_{76}N_{20}Cl_2O_9Os_3$: C, 47.84; H, 3.29; N, 12.13. Found: C, 47.63; H, 3.41; N, 12.35%. $\Lambda_M = 270\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH_3CN).

3. Results and discussion

3.1. The starting compound

The mononuclear compound of the dianion, $biim^{2-}$, viz.

$[M(pap)_2(biim)]$ ($M=Ru^{II}$, Os^{II}) which may be conveniently generated [6] from their conjugate acids (Eqs. (3) and (4)) were used for the synthesis of multinuclear compounds.

$$\underset{\mathbf{1}}{[M(pap)_2(biimH_2)]^{2+}} \overset{K_1}{\rightleftharpoons} \underset{\mathbf{2}}{[M(pap)_2(biimH)]^{+}} + H^{+} \tag{3}$$

$M = Ru$, $pK_1 = 4.2\pm0.1$ and $M = Os$, $pK_1 = 3.8\pm0.1$

$$\underset{\mathbf{2}}{[M(pap)_2(biimH)]^{+}} \overset{K_2}{\rightleftharpoons} \underset{\mathbf{3}}{[M(pap)_2(biim)]} + H^{+} \tag{4}$$

$M = Ru$, $pK_2 = 8.0\pm0.1$ and $M = Os$, $pK_2 = 6.5\pm0.1$

Of the above two conjugate bases, the intermediate monoprotonated compound, $[Ru(pap)_2(biimH)]^+$ was isolated as its PF_6 salt. It formed very fine fibre like crystals [16] obtained by slow diffusion of acetonitrile solution into toluene. The $\nu_{N=N}$ appears at a low frequency in $[Ru(pap)_2(biim)]$ (1240 cm^{-1}) and that appears at 1250 and 1260 cm^{-1}, respectively, in monoprotonated and diprotonated compounds. Thus, deprotonation of coordinated $biimH_2$ augment the $d\pi$–$p\pi$ back donation between ruthenium (t_{2g}) and low lying π^*(azo) orbitals of pap.

*3.2. Reactions of $[M(pap)_2biim]$ (**3**) and $M(PPh_3)_3X_2$ – synthesis of trinuclear species*

The deprotonated mononuclear biimidazolate compounds, **3** ($M=Ru,Os$) react smoothly with $M(PPh_3)_3X_2$ [8–10] in 2:1 ratio to yield trimeric complexes (Eq. (5)) which were isolated as their perchlorate salts in moderate to high yields.

$$2[M(pap)_2biim] + M(PPh_3)_3X_2 \xrightarrow{CH_2Cl_2} [\{M(pap)_2biim\}_2M(PPh_3)_2]^{2+} + PPh_3 + \text{other products} \tag{5}$$

Final purification of the products were made by column chromatography on a silica-gel column using $CHCl_3$–CH_3CN as eluant.

3.3. Characterization

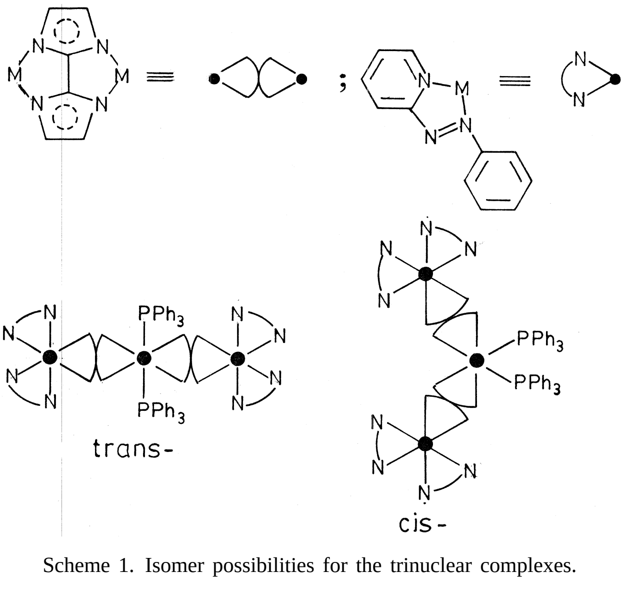
The compounds, isolated as above, were formulated based on their analytical data. ESMS data of a representative sample were used to authenticate the trimeric formulation of these compounds which is discussed later. These are 1:2 electrolytes in CH_3CN. Their IR spectra consist of characteristic absorptions for both pap and $biim^{2-}$ ligands. Some selected group frequencies are: (i) a doublet ($\nu_{N=N}$) [17] at 1270–1250 cm^{-1}, (ii) absorptions at 700 and 530 cm^{-1} characterizes [18] the presence of the $M(PPh_3)_2$ fragment, (iii) the presence of ionic ClO_4^- was confirmed by the two characteristic absorptions; a broad absorption at 1100 cm^{-1} and an intense sharp band at 620 cm^{-1}. Assuming that the *trans*, *cis*-geometry of the building unit $M(pap)_2(biim)$ is retained, there could be two geometric possibilities for the trimetallic compounds (Scheme 1).

We have not been able to establish the geometry of the isolated compound, however, we note here that a *cis*-Ru^{II}–$(PPh_3)_2$ moeity is more commonly obtained [19] than a *trans*-Ru^{II}–$(PPh_3)_2$ due to greater degree of π-interactions in the *cis*-configuration. The trinuclear complexes exhibited multiple transitions in the visible region (Table 1). Of which the bands in the region 510–545 nm may be assigned as metal-to-ligand charge transfer (MLCT) transitions. The analogous MLCT band for the mononuclear complexes $M(pap)_2(biim)$ appear in the range 515–530 nm. The molar absorption constants [20] of the trinuclear complexes are much larger than the corresponding monomers.

Fig. 1 displays positive ion ESI mass spectrum [13,21] of $[\{Ru(pap)_2biim\}_2Ru(PPh_3)_2](ClO_4)_2$ (molecular weight 2023.8). The multiply charged ions are generated from loss of negative counter ions, which is denoted by $[M–nX]^{z+}$, where M and X represent the molecule and ClO_4^-, respectively. The spectrum is dominated by the two intense peaks at m/z 912 and 782, respectively. Of which the response at 912 is assigned to $[M–2X]^{2+}$ while, that at 782 is due to $[M–2X–PPh_3]^{2+}$. A relatively small peak, due to $[M–X]^+$, at 1924 was also observable. The other responses may be due to new species formed by solvation, loss of the triphenyl phosphines etc. These we do not consider here.

3.4. Electrochemistry

The redox responses in both anodic and cathodic regions were determined for each trinuclear species using cyclic



Scheme 1. Isomer possibilities for the trinuclear complexes.

Table 1
The UV–Vis spectral data at 298 K

Compound	Absorption[a] λ_{max}/nm(ϵ/dm^3 mol^{-1} cm^{-1})
$[\{Ru(pap)_2biim\}_2Ru(PPh_3)_2](ClO_4)_2 \cdot H_2O$	680[b](3600), 540(18 600), 368[b](32 000), 320(48 350), 220(96 500)
$[\{Os(pap)_2biim\}_2Ru(PPh_3)_2](ClO_4)_2 \cdot 2H_2O$	675[b](3200), 511(14 500), 315(45 000), 220(96 000)
$[\{Ru(pap)_2biim\}_2Os(PPh_3)_2](ClO_4)_2 \cdot 2H_2O$	678[b](3000), 541(16 500), 367[b](28 000), 315(46 500), 220(94 100)
$[\{Os(pap)_2biim\}_2Os(PPh_3)_2](ClO_4)_2 \cdot H_2O$	710[b](2700), 515(13 600), 334[b](30 400), 312(48 200), 218(92 800)

[a] In CH_3CN.

[b] Shoulder.

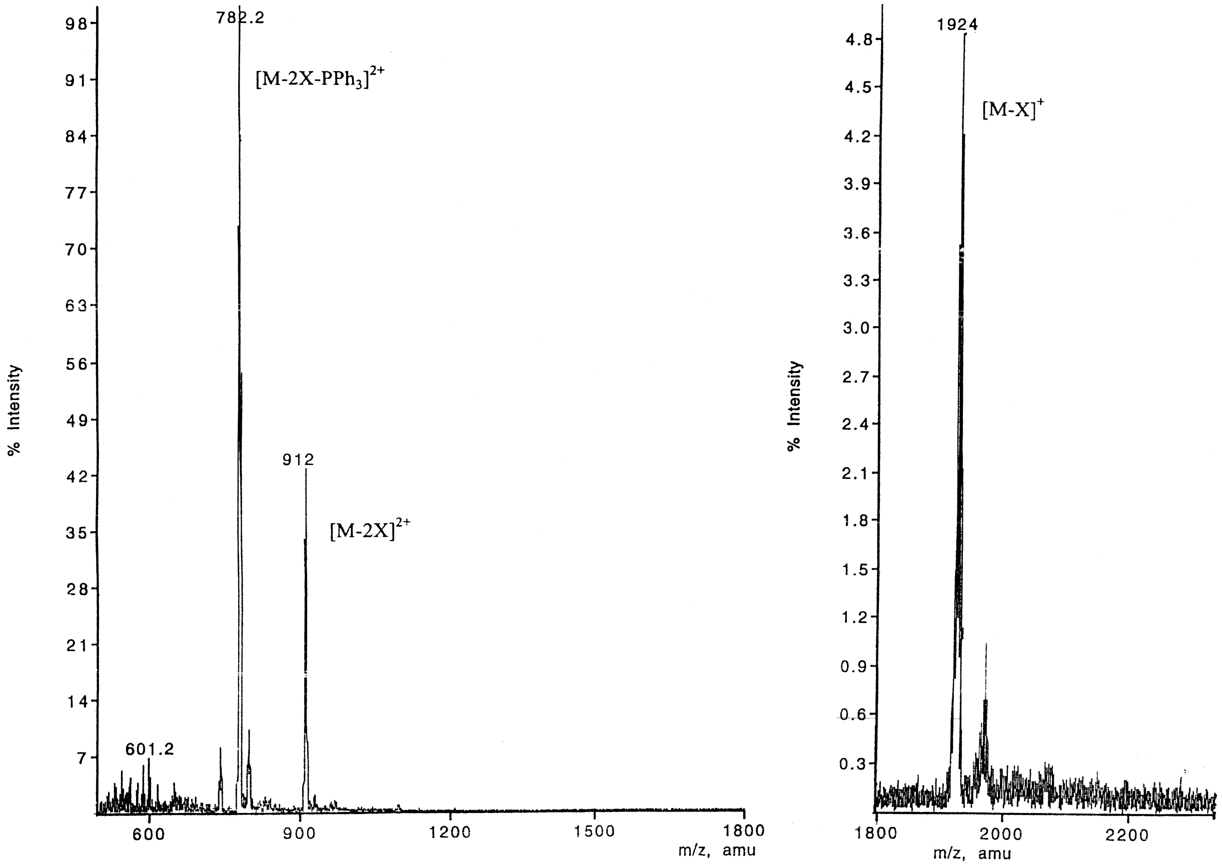


Fig. 1. Positive ion ESI mass spectrum of $[\{Ru(pap)_2biim\}_2Ru(PPh_3)_2](ClO_4)_2$.

voltammetric studies (CV). Electrochemical data are collected in Table 2 and a representative voltammogram is shown in Fig. 2. The value for the ferrocenium–ferrocene couple under our experimental condition is 0.44 V.

3.4.1. Oxidation processes

The mononuclear complexes $[M(pap)_2(biimH_2)]^{2+}$ undergo oxidation irreversibly [6] at 1.70 V (M = Ru) and 1.52 V (M = Os) in acetonitrile. This response shifts

Table 2
Cyclic voltammetric data[a]

Compound	Oxidation $E_{1/2}$/V	Reduction $-E_{1/2}$/V
$[\{Ru(pap)_2biim\}_2Ru(PPh_3)_2]^{2+}$	0.85, 1.15, 1.37[b]	0.37, 0.97, 1.78
$[\{Os(pap)_2biim\}_2Ru(PPh_3)_2]^{2+}$	0.89, 1.10, 1.35[b]	0.36, 0.95, 2.14[c]
$[\{Ru(pap)_2biim\}_2Os(PPh_3)_2]^{2+}$	0.55, 1.46[b]	0.34, 0.92, 1.71
$[\{Os(pap)_2biim\}_2Os(PPh_3)_2]^{2+}$	0.60, 1.05, 1.26[b]	0.32, 0.90, 1.75

[a] Experiments were carried out in CH_3CN at 298 K using 0.1 M NEt_4ClO_4 as supporting electrolyte. The reported data correspond to a scan rate of 50 mV s^{-1}.

[b] Irreversible response; the potential corresponds to E_{pa}.

[c] Irreversible response; the potential corresponds to E_{pc}.

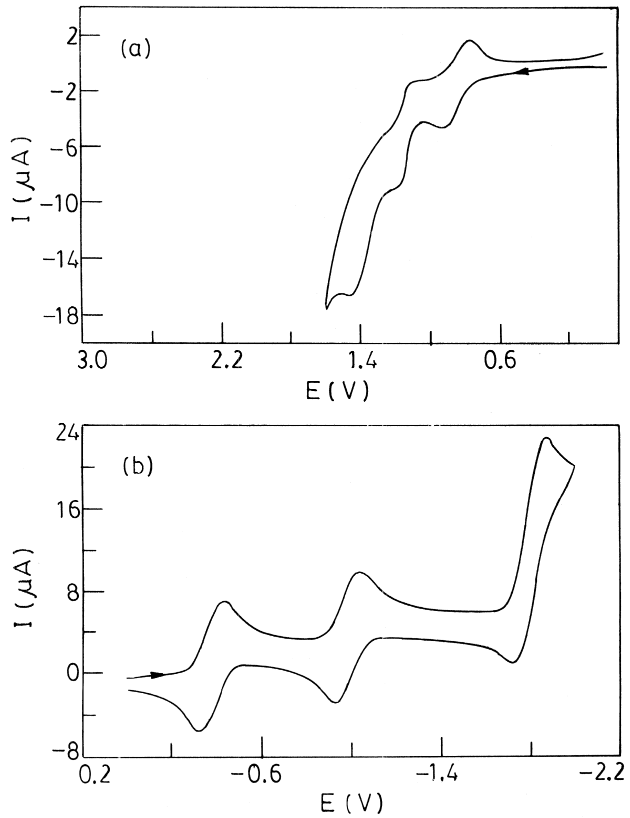


Fig. 2. Cyclic voltammograms of $[\{Ru(pap)_2biim\}_2Ru(PPh_3)_2](ClO_4)_2$ in CH_3CN: (a) anodic scan using Pt as working electrode and (b) cathodic scan using glassy-carbon as working electrode.

cathodically for the deprotonated complexes, viz. $[M(pap)_2(biimH)]^+$ and $[M(pap)_2(biim)]$. The low p*K* values for the above protonated complexes is believed to be responsible for the irreversible nature in an aprotic solvent. In the trimeric complexes, $[\{M(pap)_2biim\}_2M'(PPh_3)_2]^{2+}$, there are two types of metal ions viz. (i) terminal metal ion coordinated by two pap and one $biim^{2-}$ ligands and (ii) central metal ion coordinated by two PPh_3 and two $biim^{2-}$ ligands. Electrochemical parameters [22] of one pap ligand is almost similar to two PPh_3 ligands. Therefore, it is proposed that the central metal ion will be oxidised prior to the terminal ones. For the homo-trinuclear complex $[\{Ru(pap)_2biim\}_2Ru(PPh_3)_2]^{2+}$, three successive electrode oxidation couples are observed. The first oxidation potential of the above complex is systematically lower (0.85 V) than the anodic responses for the mononuclear complex. This is due to the stronger π-donor ability [23] of the dianion bridge $biim^{2-}$ than the neutral terminal $biimH_2$. The redox processes on the positive of the Ag–AgCl reference may be proposed as below (Eqs. (6)–(8)).

$$[(pap)_2\overset{II}{M}(biim)\overset{II}{M}'(PPh_3)_2(biim)\overset{II}{M}(pap)_2]^{2+} \rightleftharpoons$$

$$[(pap)_2\overset{II}{M}(biim)\overset{III}{M}'(PPh_3)_2(biim)\overset{II}{M}(pap)_2]^{3+} + e^- \qquad (6)$$

$$[(pap)_2\overset{II}{M}(biim)\overset{III}{M}'(PPh_3)_2(biim)\overset{II}{M}(pap)_2]^{3+} \rightleftharpoons$$

$$[(pap)_2\overset{III}{M}(biim)\overset{III}{M}'(PPh_3)_2(biim)\overset{II}{M}(pap)_2]^{4+} + e^- \qquad (7)$$

$$[(pap)_2\overset{III}{M}(biim)\overset{III}{M}'(PPh_3)_2(biim)\overset{II}{M}(pap)_2]^{4+} \rightarrow$$

$$[(pap)_2\overset{III}{M}(biim)\overset{III}{M}'(PPh_3)_2(biim)\overset{III}{M}(pap)_2]^{5+} + e^- \qquad (8)$$

In order to study the properties of the mixed-valence species, controlled-potential coulometry of $[\{Ru(pap)_2biim\}_2Ru(PPh_3)_2]^{2+}$ was performed at 0.95 V in acetonitrile. But, the spectrum of the electrolysed solution did not show any characteristic IT band. This suggests that the mixed-valence, Ru^{II}–Ru^{III}–Ru^{II}, trimer is stable only on the cyclic voltammetry time-scale, but is unstable on a longer time-scale and undergoes unsymmetrical bridge cleavage to form a mixture of unidentified products. A similar result was obtained from the spectral analysis of the partially oxidised trimer with Ce^{4+}.

3.4.2. Reduction processes

Free pap displays two quasireversible cyclic voltammetric responses [11] at −1.31 and −1.57 V. Therefore, multiple reduction waves were anticipated in the trinuclear complexes. All the trimeric complexes show almost identical voltammetric responses in the range 0 to −2.5 V at a glassy-carbon working electrode. This indicates that the ligand-based reductions are very little affected by the change of metal from ruthenium to osmium. Theoretically, eight-electron reductions are expected in a complex containing four pap ligands. However, in practice, four-electron reductions are observed amongst which one is a single step two-electron transfer. The two-electron nature of this reduction has been established by comparing its current height with that of the standard ferrocene/ferrocenium couple under identical experimental conditions. We believe that other reductions lie beyond the accessible potential range.

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