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# Synthesis and properties of mononuclear tris(heteroleptic) osmium(II) complexes containing bidentate polypyridyl ligands†

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A general synthetic methodology has been elaborated for tris(bidentate ligand)osmium(II) complexes containing three different polypyridyl ligands. The tris(heteroleptic) complexes were characterized by NMR techniques, and the ligand dependence of their electrochemistry and electronic spectroscopy examined.

We recently published details of a general synthetic methodology for tris(heteroleptic)ruthenium(II) complexes of the type [Ru(pp)(pp′)(pp″)]$^{2+}$ (where pp, *etc.* are bidentate polypridyl ligands) based on the sequential addition of the pro-ligands to the oligomeric precursor [{Ru(CO)$_2$Cl$_2$}$_n$].[1,2] The consequent ability to deliberately control the ligand environment has been exploited in spectral,[3] photophysical[2,4] and electrochemical[2] characteristics of the ruthenium(II) species. Furthermore, the methodology has also been utilized in the synthesis of ligand-bridged dinuclear[5,6] and higher nucleate[7] complexes, and stereochemical aspects of the scheme have been investigated.[6,8]

The osmium(II) centre is of fundamental importance in the study of d$^6$ polypyridyl complexes, and while earlier studies using bis(heteroleptic) species have dealt with the influence of the ligand environment on the characteristics of the metal centre,[9–14] the wider variations provided by tris(heteroleptic) complexes have not been available.

The present work details a general procedure for such species, which has close analogies with that used for the ruthenium counterparts,[1,2] and provides access to an extensive array of osmium complexes, [Os(pp)(pp′)(pp″)]$^{2+}$. Preliminary studies of the physical characteristics of such species are reported.

## Results and Discussion

### Synthesis

In developing a synthetic methodology for the tris(heteroleptic) osmium(II) complexes a number of strategies were investigated, all necessarily involving an intermediate species of type [Os(pp)(pp′)X$_2$]$^{n+}$. For example, the possibility of forming the precursor [Os(pp)(pp′)Cl$_2$] by reaction of [Os(pp)Cl$_4$][15] with a second diimine (pp′) was attempted: however, under forcing conditions (microwave oven using high-boiling solvents such as ethylene glycol or *N*-methylpyrrolidone)[16] the major products were bis(heteroleptic) species, *e.g.* [Os(pp)(pp′)$_2$]$^{2+}$.

As an alternative approach, [Os(pp)(CO)$_2$Cl$_2$] was sought as a possible precursor for the synthesis of [Os(pp)(pp′)(CO)$_2$]$^{2+}$, which in turn could be transformed into the tris(heteroleptic) species. Schemes involving the carbonylation of [Os(bipy)Cl$_4$] (bipy = 2,2′-bipyridine) in 2-methoxyethanol under an elevated CO pressure (60 psig) at 80 °C,[15] an attempted carbonylation of the same substrate by formic acid–formaldehyde (40 : 3 v/v) and the reaction of OsCl$_3$·$x$H$_2$O with a 2.3-fold excess of bipy in 2-methoxyethanol solution under a CO atmosphere (60 psig)[17] all realised the target compound [Os(bipy)(CO)$_2$Cl$_2$] in a very low yield (<10%). In addition, Johannsen *et al.*[18] had reported the synthesis of *cis*-[Os(CO)$_2$Cl$_4$]$^{2-}$ (as the NEt$_4$$^+$ salt) from the reaction of hexahalogenoosmate(IV) complexes with unsaturated alcohols such as propen-2-ol (allyl alcohol). While this may have provided a pathway to [Os(pp)(CO)$_2$Cl$_2$], the yield was unsatisfactory and the method suffers the disadvantages of a long reaction time (7 d) and the toxicity of the alcohol.

Since none of these alternatives proved entirely satisfactory, we pursued a strategy similar to that for the ruthenium(II) species.[2] The first intermediate in that scheme was [Ru(pp)(CO)$_2$Cl$_2$], formed by reaction of pp with the oligomer [{Ru(CO)$_2$Cl$_2$}$_n$]: however, an alternative path was required in the present case as there appears no analogue of the ruthenium oligomer in osmium chemistry. Formic acid was treated under reflux with K$_2$[OsCl$_6$], and a polymeric compound of as yet uncertain composition isolated which reacted in the next step readily with a bidentate compound (pp) to produce [Os(pp)(CO)$_2$Cl$_2$]. It is assumed that K$_2$[OsCl$_6$] reacts (like RuCl$_3$[2]) as a decarbonylating reagent of formic acid: the formation of the polymer is favoured by the presence of formaldehyde in the reaction mixture. Over the course of the reaction (2.5 d) a change from red to green to orange and (finally) light yellow was observed. A solid material (**1**) was isolated in high yield: its IR spectrum exhibited CO stretching frequencies at 2114, 2053, 2015, 1968 and 1927 cm$^{-1}$, the number of absorptions being an indication of the presence of a polymeric structure although not the same as the ruthenium equivalent, [{Ru(CO)$_2$Cl$_2$}$_n$]. The exact formulation of this polymer is not known although microanalysis revealed near parity in the Cl : C atom ratio (*ca.* 6 : 5). Characterization was not rigorously pursued as the material proved satisfactory as a precursor for the subsequent reactions.

The synthetic strategy applied for the synthesis of tris(heteroleptic)osmium(II) complexes containing diimine ligands is summarized in Scheme 1. The polymer **1** reacted readily with a bidentate polypyridyl ligand [pp = bipy or 4,4′-dimethyl-2,2′-bipyridine (dmbipy)] to form a complex [Os(pp)(CO)$_2$Cl$_2$] **2**, with slight modifications in the procedure described for the ruthenium analogue.[2] As osmium(II) is in general more inert than ruthenium(II), ethanol was used as a solvent rather than methanol to reach higher reaction temperatures, in conjunction with microwave heating techniques to introduce some overheating effects to accelerate the reaction.[16] Complex **2** was isolated in good yield (typically around 70%), and absence of free pro-ligand was checked by thin-layer chromatography. The reaction showed no dependence on the choice of the pp. In the IR spectrum the CO stretching frequencies ($\tilde{\nu}_{CO}$) of [Os(pp)(CO)$_2$Cl$_2$] did not seem to show a predictable dependence on the nature of the ligand pp ($\tilde{\nu}_{CO}$ = 2037 and 1933 cm$^{-1}$ for dmbipy, and 2021 and 1942 cm$^{-1}$ for bipy). The $^1$H NMR data for two complexes [Os(pp)(CO)$_2$Cl$_2$] (pp = bipy or dmbipy) are given in the Experimental section: the spectra indicate the equivalence

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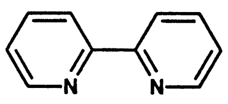
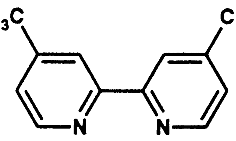
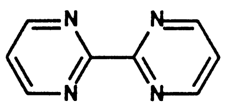
† *Non-SI unit employed:* psi ≈ 6895 Pa.



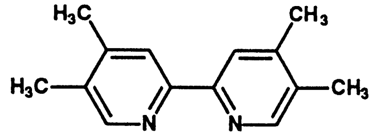
bipy = 2,2'-bipyridine



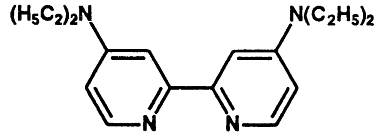
dmbipy = 4,4'-dimethyl-2,2'-bipyridine



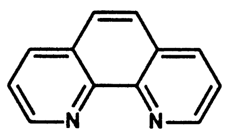
bpm = 2,2'-bipyrimidine



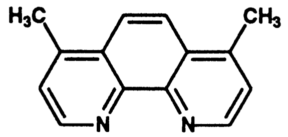
tmbipy = 4,4',5,5'-tetramethyl-2,2'-bipyridine



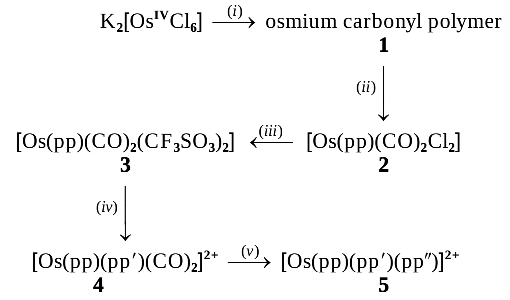
bdebipy = 4,4'- bis(diethylamino)-2,2'-bipyridine



phen = 1,10-phenanthroline



dmphen = 4,7-dimethyl-1,10-phenanthroline



**Scheme 1** Synthetic strategy for tris(heteroleptic) complexes. pp = bipy, dmbipy; pp′ = bipy, dmbipy, tmbipy, phen, dmphen; pp″ = bipy, dmphen, phen, bdebipy, bpm. (*i*) Formic acid-formaldehyde, 2–3 d; (*ii*) pp, ethanol, microwave oven, 30 min; (*iii*) $CF_3SO_3H$, 1,2-dichlorobenzene, 3 h; (*iv*) pp′, 2-methoxyethanol, 3 h; (*v*) pp″, $Et_3NO$, 2-methoxyethanol

of the two heterocyclic rings of the symmetrical ligand pp in the complex, consistent with either of two geometries: *viz. trans*-(Cl),*cis*(CO) or *cis*(Cl),*trans*(CO). As previously reported for the ruthenium(II) analogue,[2] the carbonyl ligands would be expected to adopt a *cis* relationship due to competition for π back bonding from the metal d orbitals, so the stereochemistry *trans*(Cl),*cis*(CO) is assumed.

The addition of the second bidentate compound pp′ to the complex $[Os(pp)(CO)_2Cl_2]$ was achieved after the conversion of **2** into the bis(trifluoromethanesulfonato) species $[Os(pp)(CO)_2(CF_3SO_3)_2]$ **3**. Compound **2** and trifluoromethaneslfonic acid were allowed to react in 1,2-dichlorobenzene at 120 °C,[19] and **3** was obtained in yields of 78 (pp = bipy) and 94% (pp = dmbipy) after purification. The grey solid material showed two CO stretching bands (2076 and 1986 $cm^{-1}$ for pp = bipy and 2071 and 1993 $cm^{-1}$ for pp = dmbipy) in the IR spectrum. Infrared characteristics of co-ordinated trifluoromethanesulfonate were also observed:[20,21] $\tilde{\nu}_{SO}$ at 1346 and 1163 $cm^{-1}$ (pp = bipy) and 1330 and 1170 $cm^{-1}$ (pp = dmbipy) as well as $\tilde{\nu}_{CF}$ at 1236 and 1200 $cm^{-1}$ (pp = bipy) and 1237 and 1208 $cm^{-1}$ (pp = dmbipy). According to the $^1H$ NMR spectra, $[Os(pp)(CO)_2(CF_3SO_3)_2]$ possesses a *cis*(CO),*cis*($CF_3SO_3$) geometry, based on the inequivalence of the two pyridyl rings in the pp ligand.

The reaction of compound **3** with a second bidentate compound pp′ in 2-methoxyethanol (120 °C) led to $[Os(pp)(pp')(CO)_2]^{2+}$ **4** in yields of 40–60%. The purity was checked primarily by $^1H$ NMR spectroscopy, and from a combination of NMR and IR spectroscopic studies there was no suggestion of the formation of the *trans*(CO) isomer: for example, in the case of $[Os(bipy)(dmbipy)(CO)_2]^{2+}$, the $^1H$ NMR spectrum showed two magnetically non-equivalent singlet methyl resonances, with an additional 14 distinct signals in the aromatic region.

The decarbonylation of compound **4** with trimethylamine *N*-oxide in the presence of a third bidentate compound pp″ produced tris(heteroleptic)osmium(II) complexes **5**. Purification was achieved by cation-exchange chromatography (SP Sephadex C25 absorbent; 0.2 mol $dm^{-3}$ sodium chloride or 0.125 mol $dm^{-3}$ sodium toluene-*p*-sulfonate solution as eluent), and $[Os(pp)(pp')(pp'')]^{2+}$ species **5** were isolated in variable yields depending on the ligand pp and pp′. The yields obtained for the osmium(II) complexes (10–40%) were generally lower than those obtained for the ruthenium(II) analogues.[2]

The microanalyses of representative examples of the intermediate species, and of the tris(heteroleptic) target compounds, are provided in the Experimental section.

The tris(heteroleptic) complexes were examined and characterized by several physical methods.

## Electrospray mass spectroscopy

The ESMS measurements were undertaken on representative examples of the dicarbonyl (**4**) and tris(heteroleptic) species (**5**) to verify the characterization. For each of the complexes $[Os(dmbipy)(bipy)(CO)_2][PF_6]_2$ **4a**, $[Os(dmbipy)(dmphen)(CO)_2][PF_6]_2$ **4c** and $[Os(dmbipy)(bipy)(dmphen)][PF_6]_2$ **5a**, a *m/z* peak corresponding to the loss of one $PF_6^-$ anion was obtained. For the complex **4a** two signals at *m/z* = 433 and 405 were also observed, corresponding to the ions $[Os(dmbipy)(CO)_2H]^+$ and $[Os(bipy)(CO)_2H]^+$, respectively.

## NMR spectroscopy

Owing to the low symmetry ($C_1$) of the tris(heteroleptic) complexes, the $^1H$ NMR spectra can be relatively complicated.[2] However, in the cases where the three ligands are derivatives of the same basic ligand structure (*e.g.* bipy), the 'pseudo-symmetry' provided by the three parent bipy rings leads to a simplified spectrum because of the overlap of resonances,[2] whereas if pp′ or pp″ differ from a bipy-derived structure the spectrum shows a more complex pattern. The complex [Os(dm-

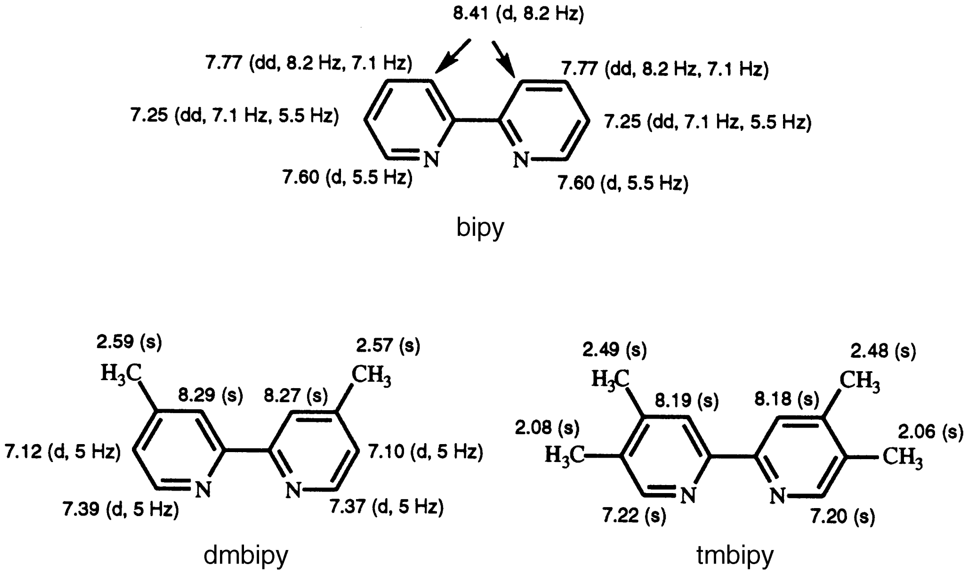


**Fig. 1** Chemical shifts and coupling constants of the ligands in the tris(heteroleptic) complex [Os(dmbipy)(bipy)(tmbipy)][PF$_6$]$_2$ **5c**

**Table 1** Electrochemical properties of the tris(heteroleptic)osmium(II) complexes

| Complex[a] | $E_{\frac{1}{2}}$[b]/V *vs.* SSCE<br>Oxidation | <br>Reduction | <br>$\Delta E_{\frac{1}{2}}$[c] |
|---|---|---|---|
| [Os(bipy)$_3$]$^{2+}$ | +0.81 | −1.29<br>−1.46<br>−1.79 | 2.10 |
| **5a** [Os(dmbipy)(bipy)(dmphen)]$^{2+}$ | +0.74 | −1.33<br>−1.55<br>−1.84 | 2.08 |
| **5b** [Os(dmbipy)(bipy)(phen)]$^{2+}$ | +0.79 | −1.29<br>−1.51<br>−1.82 | 2.08 |
| **5c** [Os(dmbipy)(bipy)(tmbipy)]$^{2+}$ | +0.70 | −1.34<br>−1.59<br>−1.93 | 2.05 |
| **5d** [Os(dmbipy)(bipy)(bpm)]$^{2+}$ | +0.92 | −0.99<br>−1.42<br>−1.70 | 1.91 |
| **5e** [Os(dmbipy)(bipy)(bdebipy)]$^{2+}$ | +0.46 | −1.40<br>−1.67 | 1.87 |

[a] As PF$_6^-$ salts. [b] Acetonitrile–0.1 mol dm$^{-3}$ NBu$^n_4$PF$_6$ solution; platinum-button working electrode; 298 K; scan rate 100 mV s$^{-1}$; Ag–Ag$^+$ reference electrode (quoted *vs.* SSCE as reference, which is 0.310 V cathodic of Ag–Ag$^+$). [c] $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}}(\mathrm{Os^{III/II}}) - E_{\frac{1}{2}}$(first ligand reduced).

bipy)(bipy)(tmbipy)][PF$_6$]$_2$ **5c** is taken as an example for discussion: while in principle there are 18 different environments for the aromatic protons, only 9 signals are observed because in each ligand the two constituent rings are similar and their resonances overlap. The aromatic protons associated with the dmbipy and tmbipy ligands are shifted to high field compared with those of 2,2′-bipyridine, as a consequence of a combination of inductive and anisotropic effects.[8] The assignments were achieved by decoupling and correlation spectroscopy (COSY) experiments. Fig. 1 shows the three ligands with their respective chemical shifts and coupling constants for the complex **5c**.

The separation of the magnetically non-equivalent methyl resonances for the tris(heteroleptic) complexes **5** is significantly smaller ($\Delta\delta \leqslant 0.02$ ppm) than that observed for the bis(heteroleptic) dicarbonyl compounds **4**. For the latter series, well separated singlet resonances are observed in the aliphatic region of the spectrum ($\Delta\delta \leqslant 0.37$ ppm). Such phenomena are based on differences in the π-acceptor characteristics and anisotropic effects of the CO and pp″ ligands, and have also been observed for the analogous ruthenium(II) complexes.[2,8]

## Electrochemical studies

Cyclic voltamograms of the tris(heteroleptic)osmium(II) complexes clearly show the metal-based oxidation and a series of reductions associated with the ligands. The ligand-based reductions occur in a stepwise manner to each ligand π* system, with the order of the reduction correlating with the ease of reduction of the unco-ordinated pro-ligands. The respective $E_{\frac{1}{2}}$ values for all tris(heteroleptic) complexes synthesized in this work are given in Table 1: in all cases, $\Delta E_p$ were in the range 70–90 mV, so that the couples are essentially reversible.

In the case of [Os(dmbipy)(bipy)(bdebipy)]$^{2+}$ **5e** only two of the three reductions were observed, presumably because the π* energy level of (bdebipy) is raised so that reduction is too cathodic to be accessible under the experimental conditions. For the same complex it is also noted that the Os$^{IV}$–Os$^{III}$ couple can be observed at $E_{\frac{1}{2}} \approx 1.24$ V, although the couple is only quasi-reversible ($\Delta E_p \approx 120$ mV).

There have been a number of recent proposals for the use of a ‘ligand electrochemical series’ in prediction of the oxidation and reduction potentials of metal complexes.[12,22] In the approach by Lever and co-workers[12] the fundamental electrochemical parameter [$E_L$(L)] for each ligand L is defined as one-sixth the potential for the Ru$^{III}$–Ru$^{II}$ couple for RuL$_6$ in acetonitrile solution. The metal-based couple of any complex is postulated[12a] to obey the relationship (1) where $S_M$ and $I_M$ are

$$E_{obs} = S_M \sum E_L(L) + I_M \tag{1}$$

constants for a particular metal. For the first ligand-based reduction process, there is a similar relationship[12b] (2). An

$$E_{red} = S_L \sum E_L(L) + I_L \tag{2}$$

implication of the use of the parameter $E_L$(L) in this way is that all ligands behave in the same way when attached to different metal centres, and also to the same metal centre in circumstances where the other ligands may be widely varied in terms of their σ-donor and π-donor/acceptor characteristics. While some studies have been done using osmium complexes, the availability of tris(heteroleptic) species makes possible a much broader testing of the hypothesis.

For the metal-based Os$^{III}$–Os$^{II}$ couples the values of $S_M$ and $I_M$ [equation (1)] have been reported as 1.01 and −0.40, respectively, in organic solvents such as acetonitrile.[12a] For the present series of complexes a plot of $E_{obs}$ *vs.* $\Sigma E_L$(L) is a straight line ($R = 0.99$) with $S_M = 1.03$ and $I_M = -0.50$ (Fig. 2). The discrep-

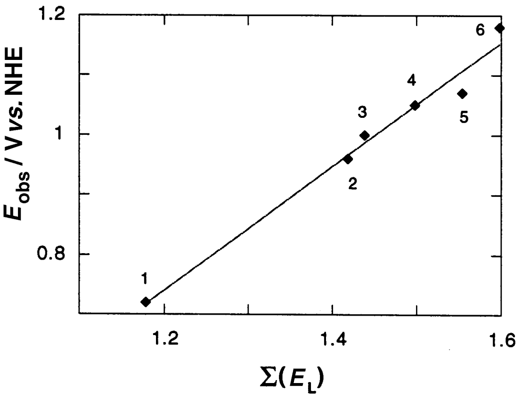


**Fig. 2** Plot of $E_{obs}$ (redox potential for $Os^{III}$–$Os^{II}$ couple) as a function of $\Sigma$ ($E_L$) (the sum of the 'electrochemical ligand parameters'). Complexes: 1, **5e**; 2, **5c**; 3, **5a**; 4, **5b**; 5, $[Os(bipy)_3]^{2+}$; 6, **5d**

ancy between this value of $I_M$ and that previously reported is interesting as the present value actually leads to an improved predictive use of equation (1) for calculating values of the redox potential for $Os^{III}$–$Os^{II}$ couples for many of the species listed in the original work.[12a] The contributions of the ligands to the overall potential appears to be additive, with no significant synergism between them.

For the ligand-based reduction processes, the values of $S_L$ and $I_L$ [equation (2)] of Os(pp) may be deduced from electrochemical data following the assumption of the assignment of the most reducible ligand. In previous studies the values for Os(bipy) ($S_L = 0.27$; $I_L = -1.38$)[12b] have been reported. For the present work, the bipy ligand can be assumed as the site of reduction for the complexes $[Os(bipy)_3]^{2+}$ and $[Os(dmbipy)(bipy)L]^{2+}$ (L = dmphen, tmbipy or bdebipy) and the plot is a straight line ($R = 0.994$) with $S_L = 0.29$ and $I_L = -1.33$. Again, these values lead to an improved use of equation (2) for calculating values of the redox potential for the first reduction of many of the osmium complexes listed in the original work.[12b]

## Electronic spectroscopy

The archetype of tris(bidentate ligand)osmium(II) complexes of the present type is $[Os(bipy)_3]^{2+}$. A broad and weak absorption band around 580 nm is assigned to arise from a spin-forbidden $^3$m.l.c.t. (metal-to-ligand charge-transfer) transition; $^1$m.l.c.t. ($d_\pi \longrightarrow \pi_1^*$) absorptions are located in the domain between 370 and 480 nm as well as in the UV range ($d_\pi \longrightarrow \pi_2^*$) and further absorptions in the UV range are associated with ligand-centred $\pi \longrightarrow \pi^*$ transitions.[23–26] The UV/VIS data for the tris(heteroleptic) species synthesized in this work are presented in the Experimental section, and representative spectra are shown in Fig. 3 for the series of complexes $[Os(dmbipy)(bipy)L]^{2+}$ (where L = bpm, tmbipy or bdebipy).

In earlier studies from our laboratory it was reported that the variation of the ligand environment in analogous ruthenium complexes allowed systematic control of the spectral and electrochemical characteristics of the complexes because of the ability to 'tune' the $d_\pi$ and $\pi^*$ energy levels.[3] The two approaches taken to the problem of shifting absorption to the red end of the spectrum were either to add electron-withdrawing groups to a polypyridyl ligand to lower $\pi^*$,[12,19,27,28] or to stabilize the 'hole' at $Ru^{III}$ in the m.l.c.t. state by introducing electron-donating ligands.[29,30] This strategy was useful in designing potential photosensitizers with broad-band absorption ('black absorbers'), complexes with desired redox characteristics,[3] and complexes with controllable photophysical properties, particularly with regard to lifetimes and photoinertness.

In Fig. 3 it can be observed that as the $\pi^*$ level of the ligand L in the series of complexes $[Os(dmbipy)(bipy)L]^{2+}$ is raised (*i.e.* bpm < tmbipy < bdebipy) there is a bathochromic shift in the m.l.c.t. absorptions. This is in fact opposite to the trend observed for similar series of ruthenium complexes.[2,3] The contrast is interesting. For both metal centres it is observed that as the ligand L becomes more readily reducible the $\pi^*$ level and the $d_\pi$ level are lowered. This is seen in electrochemical studies of the respective trends in the reduction and oxidation potentials of their complexes. Furthermore, the trend in reduction potentials is closely similar for the same ligands, regardless of the identity of the metal centre. The correlation between the $Os^{III}$–$Os^{II}$ potential and the energy of the lowest spin-allowed m.l.c.t. transition is shown in Fig. 4. In a manner consistent with previous observations,[11] we observe a shift of the lowest-lying $^1$m.l.c.t. bands towards higher energies as the $Os^{III}$–$Os^{II}$ couple is shifted to higher potentials, which is not consistent with the results for analogous ruthenium species. Since the directional trends of the dependence of the $\pi^*$ and $d_\pi$ energy levels on the identity of ligands correspond for the two metal centres, it would appear that the ligands have a more significant effect on the $d_\pi$ levels in the case of Os, leading to the observed reversal of the energy of the $d_\pi \longrightarrow \pi^*$ transition as the $\pi^*$ level varies. Accordingly, from the present data the $d_\pi$ levels appear to determine the absorption in the visible domain of the spectra. Such a result is consistent with the notion that the osmium centre has greater orbital extension, but a wider range of the tris(heteroleptic) complexes would need to be investigated to confirm these observations.

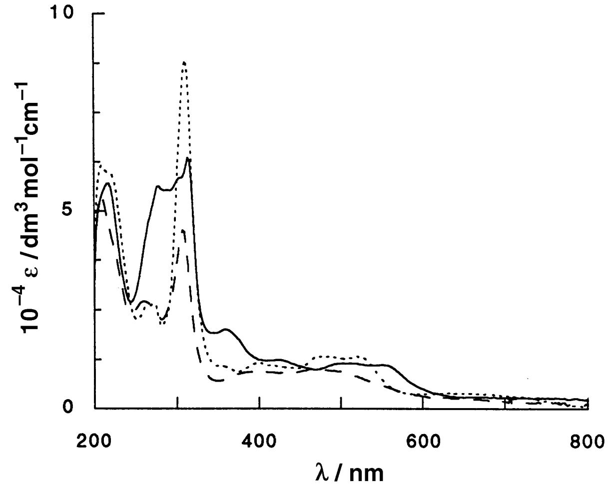


**Fig. 3** The UV/VIS absorption spectra of $[Os(dmbipy)(bipy)(bpm)][PF_6]_2$ (– – –), $[Os(dmbipy)(bipy)(bdebipy)][PF_6]_2$ (——) and $[Os(dmbipy)(bipy)(tmbipy)][PF_6]_2$ (······) in acetonitrile solution

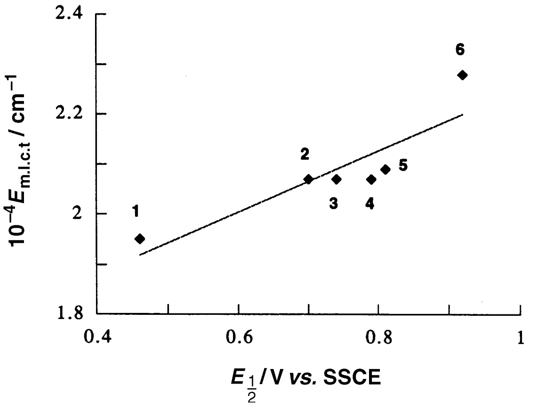


**Fig. 4** Charge-transfer band energies for the lowest-energy $^1$m.l.c.t. transition as a function of $E_{\frac{1}{2}}$ for the $Os^{III}$–$Os^{II}$ couple. Data are taken from Tables 2 and 3. Complexes as in Fig. 2

## Experimental

The UV/VIS spectra were recorded on a Cary 5E UV-visible-NIR spectrophotometer, NMR spectra on a Bruker AM3000 spectrometer, and infrared spectra on a Perkin-Elmer Series 1600 FTIR spectrometer. Electrochemical measurements were made in a dry-box (Ar) using a Bioanalytical Systems (BAS) 100A Electrochemical Analyzer. Unless otherwise indicated, cyclic voltammetry was carried out by using platinum working electrodes, and all potentials were measured relative to an Ag–AgNO$_3$ (0.01 mol dm$^{-3}$ in acetonitrile) reference electrode. Potentials are quoted relative to a saturated sodium chloride calomel electrode (SSCE, which is 310 mV cathodic of Ag–Ag$^+$), unless otherwise specified. Electrospray mass spectra were recorded using methods previously described.[31]

### Materials

The salt K$_2$[OsCl$_6$] (Strem), formic acid (BDH: AnalaR, 90%), FeCl$_2$·4H$_2$O (AJAX Chemicals) and 1,2-dimethoxyethanol (Fluka, puriss) were used without further purification. Trifluoromethanesulfonic acid (3 M) was distilled under vacuum before use. Trimethylamine *N*-oxide was obtained by vacuum sublimation of the hydrate (Fluka, purum) at 120 °C. The pro-ligands were used as supplied, or obtained from reported synthetic routes. Reagent solvents were used without further purification. For UV/VIS spectroscopy, HPLC-grade acetonitrile (Sigma-Aldrich) was used. The compound bdebipy was kindly donated by P. Besler (Université de Fribourg Suisse).

### Syntheses

**[{Os(CO)$_x$Cl$_y$}$_n$] 1.** Formaldehyde (5 cm$^3$) and K$_2$[OsCl$_6$] (1 g, 2.08 mmol) were added to a N$_2$-sparged solution of formic acid (90%, 50 cm$^3$). The solution was refluxed for 3 d: it changed from red-orange to brown-green within 1 h, to light green after 3 h, and ultimately to light yellow. It was allowed to cool to room temperature, then stored at 4 °C overnight. The solution was evaporated to dryness using an oil-bath (105 °C), the residue triturated with hexane and diethyl ether, and then dissolved in acetone to remove KCl. After filtration, the filtrate was evaporated to dryness, and the solid dried *in vacuo*. Yield: 840 mg; IR (Nujol): $\tilde{\nu}_{CO}$ = 2114, 2053, 2015, 1968 and 1927 cm$^{-1}$ (Found: C, 6.2; Cl, 21.9%).

***trans*(Cl)-[Os(pp)(CO)$_2$Cl$_2$] 2.** In a typical synthesis, [{Os(CO)$_x$Cl$_y$}$_n$] (200 mg) and dmbipy (115 mg, 0.620 mmol) were dissolved in 95% ethanol (40 cm$^3$), and the reaction mixture heated for 3 × 10 min intervals in a microwave oven (Sharp Carousel, medium power level). The volume of the solution was reduced to half, and the precipitated yellow solid was filtered off and washed with cold methanol. The procedure of volume reduction of the filtrate was repeated, with separation of further fractions. The excess of free pro-ligand was removed by adding a saturated methanolic solution of FeCl$_2$·4H$_2$O to the filtrate until no further red colouration was observed, followed by column chromatography (Sephadex LH20, methanol eluent). The combined light yellow, TLC-pure solid material was dried *in vacuo*. The absence of the ligand was confirmed by $^1$H NMR spectroscopy and TLC [silica gel absorbent, ethanol–water–sodium chloride (1 : 1 : 0.1 mol dm$^{-3}$) eluent].

[Os(dmbipy)(CO)$_2$Cl$_2$] **2a**: yield 70% (Found: C, 33.2; H, 2.2; N, 5.3. $C_{14}H_{12}Cl_2N_2O_2Os$ requires C, 33.5; H, 2.4; N, 5.6%); IR(Nujol) $\tilde{\nu}_{CO}$ = 2037 and 1933 cm$^{-1}$; $^1$H NMR (CDCl$_3$): δ 8.90 [d, 2 H, H$^6$, $J(H^5H^6) = 5.5$], 8.00 (s, 2 H, H$^3$), 7.42 [d, 2 H, H$^5$, $J(H^5H^6) = 5.5$ Hz] and 2.70 (s, 6 H, CH$_3$). [Os(bipy)(CO)$_2$Cl$_2$] **2b**: yield 60%; IR(Nujol) $\tilde{\nu}_{CO}$ = 2021 and 1942 cm$^{-1}$; $^1$H NMR (CD$_3$CN): δ 9.08 [d, 2 H, H$^6$, $J(H^5H^6) = 5.6$], 8.48 [d, 2 H, H$^3$, $J(H^3H^4) = 8.1$], 8.27 [dd, 2 H, H$^4$, $J(H^3H^4) = 8.1$, $J(H^4H^5) = 7.7$, $J(H^4H^6) = 1.2$] and 7.76 [dd, 2 H, H$^5$, $J(H^5H^6) = 5.6$, $J(H^4H^5) = 7.7$, $J(H^3H^5) = 1.2$ Hz] [Os(phen)(CO)$_2$Cl$_2$] **2c**: yield 70%; IR(Nujol) $\tilde{\nu}_{CO}$ = 2035 and 1978 cm$^{-1}$; $^1$H NMR (CDCl$_3$): δ 9.44 [d, 2 H, H$^2$, H$^9$, $J(H^2H^3) = J(H^9H^{10}) = 5.5$], 8.60 [d, 2 H, H$^4$, H$^7$, $J(H^3H^4) = J(H^7H^8) = 8.3$], 8.00 (s, 2 H, H$^{11}$, H$^{12}$) and 7.97 [dd, 2 H, H$^3$, H$^8$, $J(H^2H^3) = J(H^8H^9) = 5.5$, $J(H^7H^8) = J(H^3H^4) = 8.3$ Hz].

***cis*,*cis*-[Os(pp)(CO)$_2$(CF$_3$SO$_3$)$_2$] 3.** In a typical experiment, [Os(dmbipy)(CO)$_2$Cl$_2$] (100 mg, 0.199 mmol) was dissolved in 1,2-dichlorobenzene (50 cm$^3$), the solution sparged for 40 min with N$_2$, trifluoromethanesulfonic acid (0.5 cm$^3$) added, and the solution then heated for 3 h at 120 °C. After cooling to room temperature, the solution was stirred for 1 h at 0 °C. The complex was precipitated by addition of diethyl ether, the mixture being stored overnight in a freezer before filtration. The solid product was washed with cold water and diethyl ether, and dried at room temperature *in vacuo*.

[Os(dmbipy)(CO)$_2$(CF$_3$SO$_3$)$_2$] **3a**: yield 94%; IR(Nujol) 2071 and 1993 cm$^{-1}$ ($\tilde{\nu}_{CO}$), 1330 and 1170 ($\tilde{\nu}_{SO}$), 1237 and 1208 cm$^{-1}$ ($\tilde{\nu}_{CF}$); $^1$H NMR (CD$_3$CN): δ 8.79 [d, 1 H, H$^6$, $J(H^5H^6) = 6.0$], 8.65 [d, 1 H, H$^{6'}$, $J(H^{5'}H^{6'}) = 6.0$], 8.38 (s, 1 H, H$^{3'}$), 8.32 (s, 1 H, H$^3$), 7.77 [d, 1 H, H$^{5'}$, $J(H^{5'}H^{6'}) = 6.0$], 7.45 [d, 1 H, H$^5$, $J(H^5H^6) = 6.0$ Hz], 2.64 (s, 3 H, CH$_3$) and 2.62 (s, 3 H, CH$_3$). [Os(bipy)(CO)$_2$(CF$_3$SO$_3$)$_2$] **3b**: yield 78%; IR(Nujol) 2076 and 1986 ($\tilde{\nu}_{CO}$), 1346 and 1163 ($\tilde{\nu}_{SO}$), 1236 and 1200 cm$^{-1}$ ($\tilde{\nu}_{CF}$); $^1$H NMR (CD$_3$CN): δ 9.00 [d, 1 H, H$^6$, $J(H^5H^6) = 6.0$], 8.85 [d, 1 H, H$^{6'}$, $J(H^{5'}H^{6'}) = 6.0$], 8.55 [d, 1 H, H$^{3'}$, $J(H^{3'}H^{4'}) = 8.2$], 8.46 [d, 1 H, H$^3$, $J(H^3H^4) = 8.2$], 8.42 [dd, 1 H, H$^{4'}$, $J(H^{3'}H^{4'}) = 8.2$, $J(H^{4'}H^{5'}) = 7.7$, $J(H^{4'}H^{6'}) = 1.6$], 8.26 [dd, 1 H, H$^4$, $J(H^3H^4) = 8.2$, $J(H^4H^5) = 7.7$, $J(H^4H^6) = 1.6$], 7.98 [dd, 1 H, H$^{5'}$, $J(H^{4'}H^{5'}) = 7.7$, $J(H^{5'}H^{6'}) = 5.0$, $J(H^{3'}H^{5'}) = 1.6$], and 7.62 [dd, 1 H, H$^5$, $J(H^4H^5) = 7.7$, $J(H^5H^6) = 6.0$, $J(H^3H^5) = 1.6$ Hz]. [Os(phen)(CO)$_2$(CF$_3$SO$_3$)$_2$] **3c**: yield 73%; IR(Nujol) 2067 and 1998 ($\tilde{\nu}_{CO}$), 1336 and 1169 ($\tilde{\nu}_{SO}$), 1240 and 1208 cm$^{-1}$ ($\tilde{\nu}_{CF}$); $^1$H NMR (CD$_3$CN): δ 9.36 [d, 1 H, H$^2$, $J(H^2H^3) = 5.5$], 9.20 [d, 1 H, H$^9$, $J(H^8H^9) = 4.9$], 8.97 [d, 1 H, H$^7$, $J(H^7H^8) = 8.2$], 8.83 [d, 1 H, H$^4$, $J(H^3H^4) = 8.3$], 8.33–8.20 (2s, dd, 3 H, H$^5$, H$^6$, H$^8$) and 7.95 [dd, 1 H, H$^3$, $J(H^3H^4) = 8.3$, $J(H^2H^3) = 5.5$ Hz].

**[Os(pp)(pp′)(CO)$_2$][PF$_6$]$_2$ 4.** In a typical synthesis, [Os(dmbipy)(CO)$_2$(CF$_3$SO$_3$)$_2$] (50 mg, 0.068 mmol) and bipy (21.4 mg, 0.136 mmol) were dissolved in 2-methoxyethanol (20 cm$^3$) and the solution heated under reflux for 3 h. After evaporation to dryness, the brownish residue was dissolved in boiling water and the mixture filtered to remove the excess of pro-ligand. The complex was precipitated as the PF$_6^-$ salt by adding a saturated solution of KPF$_6$ to the filtrate. The light yellow solid was filtered off and washed with water and diethyl ether. The crude product was purified by column chromatography (Sephadex LH20 absorbent, methanol eluent). Recrystallization from acetonitrile–diethyl ether led to light yellow, feathery crystals.

[Os(dmbipy)(bipy)(CO)$_2$][PF$_6$]$_2$ **4a**: yield 58% (Found: C, 33.0; H, 2.25; N, 6.2. $C_{24}H_{20}F_{12}N_4O_2OsP_2$ requires C, 32.9; H, 2.30; N, 6.4%); IR(Nujol) $\tilde{\nu}_{CO}$ = 2078 and 2009 cm$^{-1}$; $^1$H NMR (CD$_3$CN): δ 9.26 [d, 1 H, H$^{6''}$, $J(H^{5''}H^{6''}) = 5.6$, $J(H^{4''}H^{6''}) = 1.2$], 9.06 [d, 1 H, H$^{6'}$, $J(H^{5'}H^{6'}) = 5.6$], 8.61 [d, 1 H, H$^{3''}$, $J(H^{3''}H^{4''}) = 8.1$], 8.52–8.43 [dd, d, s, 3 H, H$^{4''}$, H$^{3'}$, H$^{3'''}$], 8.33 (s, 1 H, H$^3$), 8.23 [dd, 1 H, H$^{4'''}$, $J(H^{3'''}H^{4'''}) = 8.1$, $J(H^{4'''}H^{5'''}) = 7.6$, $J(H^{4'''}H^{6'''}) = 1.6$], 7.90 [dd, 1 H, H$^{5''}$, $J(H^{4''}H^{5''}) = 7.6$, $J(H^{5''}H^{6''}) = 5.6$], 7.54 [dd, 1 H, H$^{5'''}$, $J(H^{4'''}H^{5'''}) = 7.6$, $J(H^{5'''}H^{6'''}) = 6.0$, $J(H^{3'''}H^{5'''}) = 1.6$], 7.38 [d, 1 H, H$^{6'''}$, $J(H^{5'''}H^{6'''}) = 5.6$], 7.34 [d, 1 H, H$^5$, $J(H^5H^6) = 6.0$], 7.22 [d, 1 H, H$^6$, $J(H^5H^6) = 6.0$ Hz], 2.75 (s, 3 H, CH$_3$′) and 2.50 (s, 3 H, CH$_3$). [Os(dmbipy)(dmbipy)(CO)$_2$][PF$_6$]$_2$ **4b**: yield 67% (Found: C, 37.1; H, 2.90; N, 5.8%. $C_{28}H_{28}F_{12}N_4O_2OsP_2$ requires C, 36.1; H, 3.05; N, 6.0%); IR(Nujol) $\tilde{\nu}_{CO}$ = 2070 and 2005 cm$^{-1}$; $^1$H NMR (CD$_3$CN): δ 9.04 [d, 1 H, H$^{6'}$, $J(H^{5'}H^{6'}) = 5.5$], 8.77 (s, 1 H, H$^{6'''}$), 8.43 (s, 1 H, H$^{3'}$), 8.31

(2s, 2 H, $H^3$, $H^{3'''}$), 8.22 (s, 1 H, $H^{3''}$), 7.70 [d, 1 H, $H^{5'}$, $J(H^{5'}H^{6'}) = 5.5$], 7.32 [d, 1 H, $H^5$, $J(H^5H^6) = 6.0$ Hz], 7.27 [d, 1 H, $H^6$, $J(H^5H^6) = 6.0$ Hz], 6.95 (s, 1 H, $H^{6''}$), 2.73 [s, 3 H, $CH_3(4')$], 2.60 [s, 3 H, $CH_3(4''')$], 2.50 [s, 3 H, $CH_3(4)$] 2.47 [s, 3 H, $CH_3(5''')$], 2.41 [s, 3 H, $CH_3(4'')$] and 2.04 [s, 3 H, $CH_3(5'')$]. [Os(dmbipy)(dmphen)(CO)$_2$][PF$_6$]$_2$ **4c**: yield 43%; IR(Nujol) $\tilde{\nu}_{CO} = 2083$ and 2015 cm$^{-1}$; $^1$H NMR (CD$_3$CN): δ 9.45 [d, 1 H, $H^{9''}$, $J(H^{8''}H^{9''}) = 6.0$], 9.15 [d, 1 H, $H^6$, $J(H^5H^6) = 6.0$], 8.47 (s, 2 H, $H^{3'}$), 8.45 (s, 1 H, $H^{12}$), 8.39 (s, 1 H, $H^{11}$), 8.31 (s, 1 H, $H^3$), 8.04 [d, 1 H, $H^{8''}$, $J(H^{8''}H^{9''}) = 6.0$], 7.75 [d, 1 H, $H^{5'}$, $J(H^{5'}H^{6'}) = 6.0$], 7.65 [d, 1 H, $H^{3''}$, $J(H^{2''}H^{3''}) = 5.5$], 7.58 [d, 1 H, $H^{2''}$, $J(H^{2''}H^{3''}) = 5.5$], 7.12 [d, 1 H, $H^5$, $J(H^5H^6) = 6.0$], 7.02 [d, 1 H, $H^6$, $J(H^5H^6) = 6.0$ Hz], 3.11 [s, 3 H, $CH_3(7'')$], 2.90 [s, 3 H, $CH_3(4')$], 2.75 [s, 3 H, $CH_3(4'')$] and 2.41 [s, 3 H, $CH_3(4)$]. [Os(dmbipy)(phen)(CO)$_2$][PF$_6$]$_2$ **4d**: yield 63% (Found: C, 34.8; H, 2.15; N, 6.1. $C_{26}H_{20}F_{12}N_4O_2OsP_2$ requires C, 34.7; H, 2.35; N, 6.2%); IR(Nujol) $\tilde{\nu}_{CO} = 2076$ and 2008 cm$^{-1}$; $^1$H NMR (CD$_3$CN): δ 9.62 [d, 1 H, $H^{9''}$, $J(H^{8''}H^{9''}) = 5.2$], 9.15 [d, 1 H, $H^6$, $J(H^5H^6) = 5.5$], 9.03 [d, 1 H, $H^{7''}$, $J(H^{7''}H^{8''}) = 8.2$], 8.79 [d, 1 H, $H^{4''}$, $J(H^{3''}H^{4''}) = 8.2$], 8.49 (s, 1 H, $H^3$), 8.40 (3s, d, dd, 5 H, $H^5$, $H^{5''}$, $H^{6''}$, $H^{3'}$, $H^{8''}$), 7.83 [dd, 1 H, $H^{3''}$, $^3J(H^{3''}H^{4''}) = 8.2$, $J(H^{2''}H^{3''}) = 5.0$], 7.75 [2d, 2 H, $H^{2''}$, $H^5$, $J(H^{2''}H^{3''}) = 5.0$, $J(H^5H^6) = 5.5$], 7.11 [d, 1 H, $H^{5'}$, $J(H^{5'}H^{6'}) = 5.1$], 7.05 [d, 1 H, $H^{6'}$, $J(H^{5'}H^{6'}) = 5.1$ Hz], 2.75 (s, 3 H, CH$_3$) and 2.41 (s, 3 H, CH$_3$).

**[Os(pp)(pp′)(pp″)][PF$_6$]$_2$ 5.** The compound [Os(dmbipy)(dmphen)(CO)$_2$][PF$_6$]$_2$ (20 mg, 0.022 mmol) and bipy (10.1 mg, 0.066 mmol) were dissolved in dry 2-methoxyethanol (6 cm$^3$), and a six-fold excess of trimethylamine *N*-oxide (9.9 mg, 0.132 mmol) was added. The almost colourless solution turned dark green within 10 min. It was heated at reflux for 3 h. After evaporation to dryness the residue was dissolved in hot water, and the solution filtered to eliminate the excess of pro-ligand. The filtrate was applied to a column of SP-Sephadex C25 cation exchanger, eluted with 0.2 mol dm$^{-3}$ NaCl, and the product precipitated by addition of a saturated aqueous solution of KPF$_6$ to the eluent containing the major band. The solid was collected on a low-porosity frit, and then washed with water (5 cm$^3$) and diethyl ether. Recrystallization of the green complex was achieved from acetonitrile–diethyl ether. Yield: 40%.

[Os(dmbipy)(bipy)(dmphen)][PF$_6$]$_2$ **5a**: yield 40% (Found: C, 41.0; H, 3.3; N, 7.6. $C_{36}H_{32}F_{12}N_6OsP_2$ requires C, 41.3; H, 3.1; N, 8.1%); $^1$H NMR (CD$_3$CN): δ 8.45 (dd, 2 H), 8.37–8.27 (m, 4 H), 7.88–7.65 (m, 5 H), 7.75–7.38 (m, 4 H), 7.30 (dd, 1 H), 7.22 (d, 1 H), 7.15 (d, 1 H), 7.06 (dd, 1 H), 6.94 (d, 1 H), 2.98 (s, 3 H, CH$_3$), 2.96 (s, 3 H, CH$_3$), 2.70 (s, 3 H, CH$_3$) and 2.45 (s, 3 H, CH$_3$); UV/VIS [acetonitrile, λ/nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$)] 206 (71 700), 232 (37 400), 266 (57 700), 290 (63 400), 370 (8780), 408 (12 300), 438 (15 900), 484 (15 500) and 546 (4900). [Os(dmbipy)(bipy)(phen)][PF$_6$]$_2$ **5b**: yield 26%; $^1$H NMR (CD$_3$CN): δ 8.48 (d, 1 H), 8.43 (d, 1 H), 8.40–8.28 (m, 4 H), 8.21 (s, 2 H), 7.98 (d, 2 H), 7.82 (dd, 1 H), 7.74 (dd, 2 H), 7.64 (m, 2 H), 7.54 (d, 1 H), 7.40 (d, 1 H), 7.33 (dd, 1 H), 7.20 (2d, 2 H), 7.07 (dd, 1 H), 6.95 (d, 1 H), 2.62 (s, 3 H, CH$_3$) and 2.52 (s, 3 H, CH$_3$); UV/VIS [acetonitrile, λ/nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$)] 202 (57 500), 268 (45 800), 290 (54 100), 364 (6780), 394 (8300), 434 (12 200), 484 (12 500) and 564 (3490). [Os(dmbipy)(bipy)(tmbipy)][PF$_6$]$_2$·H$_2$O **5c**: yield 32% (Found: C, 41.0; H, 3.3; N, 7.6. $C_{36}H_{38}F_{12}N_6OsP_2$ requires C, 41.1; H, 3.45; N, 8.0%); $^1$H NMR (CD$_3$CN): δ 8.42 [d, 1 H, $H^3$, $J(H^3H^4) = 8.2$], 8.41 [d, 1 H, $H^{3I}$, $J(H^{3I}H^{4I}) = 8.2$], 8.29 (s, 1 H, $H^{3II}$), 8.27 (s, 1 H, $H^{3III}$), 8.19 (s, 1 H, $H^{3IV}$), 8.18 (s, 1 H, $H^{3V}$), 7.78 [2dd, 2 H, $H^4$, $H^{4'}$, $J(H^3H^4) = J(H^{3I}H^{4I}) = 8.2$], 7.60 [d, 2 H, $H^6$, $H^{6I}$, $J(H^5H^6) = J(H^{5I}H^{6I}) = 5.5$], 7.38 [d, 2 H, $H^{6II}$, $H^{6III}$, $J(H^{5II}H^{6II}) = J(H^{5III}H^{6III}) = 5.5$], 7.27–7.19 [2d, 2s, $H^5$, $H^{5'}$, $H^{6IV}$, $H^{6V}$, $J(H^5H^6) = J(H^{5I}H^{6I}) = 5.5$], 7.11 [2d, 2 H, $H^{5II}$, $H^{5III}$, $J(H^{5II}H^{6II}) = J(H^{5III}H^{6III}) = 5.5$ Hz], 2.59 [s, 3 H, $CH_3(4^{II})$], 2.57 [s, 3 H, $CH_3(4^{III})$], 2.49 [s, 3 H, $CH_3(4^{IV})$], 2.48 [s, 3 H, $CH_3(4^{V})$], 2.07 [s, 3 H, $CH_3(5^{IV})$] and 2.05 [s, 3 H, $CH_3(5^{V})$]; UV/VIS [acetonitrile, λ/nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$)] 206 (59 800), 252 (26 100), 256 (26 800), 292 (88 600), 332 (10 900), 374 (11 700), 424 (10 800), 448 (13 300), 484 (13 600) and 600 (4430). [Os(dmbipy)(bipy)(bpm)][PF$_6$]$_2$·2Et$_2$O **5d**: yield 10% (Found: C, 40.1; H, 3.45; N, 9.5. $C_{38}H_{46}F_{12}N_8O_2OsP_2$ requires C, 40.5; H, 3.2; N, 9.9%); $^1$H NMR (CD$_3$CN): δ 8.98 (2d, 2 H), 8.81 (2d, 2 H), 8.67 (s, 2 H), 8.42 (2dd, 2 H), 8.,19 (d, 1 H), 8.10–7.92 (m, 5 H), 7.73 (d, 1 H), 7.64–7.46 (m, 4 H), 7.37 (d, 2 H) and 2.62 (s, 6 H, 2CH$_3$); UV/VIS [acetonitrile, λ/nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$)] 200 (52 700), 244 (27 200), 288 (45 100), 364 (9380), 438 (10 100) and 574 (3000). [Os(dmbipy)(bipy)(bdebipy)][PF$_6$]$_2$ **5e**: yield 33%; $^1$H NMR (CD$_3$CN): δ 8.38 (2d, 2 H), 8.30 (s, 1 H), 8.25 (s, 1 H), 7.85 (d, 1 H), 7.72–7.56 (m, 4 H), 7.39 (d, 1 H), 7.35–7.23 (m, 3 H), 7.18 (d, 1 H), 7.14 (dd, 1 H), 7.00 (d, 1 H), 6.83 (2d, 2 H), 6.45 (m, 2 H), 3.50 (4q, 8 H, CH$_2$ of Et$_2$N), 2.63 (s, 3 H, CH$_3$), 2.52 (s, 3 H, CH$_3$) and 1.15 (4t, 12 H, CH$_3$ of Et$_2$N); UV/VIS [acetonitrile, λ/nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$)]: 206 (57 000), 262 (56 300), 286 (58 500), 294 (63 500), 336 (20 100), 394 (12 400), 468 (11 600), 512 (11 200) and 620 (2920).

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