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# Mono- and dinuclear osmium *N*,*N*'-di- and tetraphenylbipyridyls and extended bipyridyls. Synthesis, structure and electrochemistry†

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The efficient synthesis of mono- and dinuclear Os(w) bipyridyl complexes is reported. These compounds show a two-step oxidation process leading to notable structural changes, which are reflected in their emission properties. During the second oxidation process a tetracation with a hydride-dihydrogen structure (instead of a trihydride) is formed. This results in a significant bathochromic shift of the emission band, accompanied by a moderate increase in intensity.

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#### Introduction

The interest in dinuclear and polynuclear metal-complexes in which the metal centers are linked by bridging bi- and tridentate ligands remains unabated. They are ideal structures to study electron transfer mechanisms,<sup>1</sup> provide the perfect ground to disentangle the origin of the factors affecting charge localization and, due to their electronic and magnetic properties, are also useful in the design of molecular electronic or photonic devices.<sup>2</sup> Properties in these systems are also related to the nature of the ligands and the spacers, in many cases biaryls, for which the influence of geometry and torsion angles<sup>3</sup> is of particular relevance in the design of electron transport-based devices.3,4 Furthermore, changes in the oxidation state of the metals often produce a substantial alteration of their photophysical properties, which has found application in different areas of chemistry, from materials to biochemistry.<sup>5</sup> All these reasons make the flexible access to new dinuclear and polynuclear metal-complexes a very attractive field of research.

<sup>†</sup>Electronic supplementary information (ESI) available: Full synthetic procedures, NMR spectra, electrochemical and computational details (in a.u., noncorrected zero-point vibrational energies included). CCDC 870543 and 870544. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32548a



of  $OsH_6(P^iPr_3)_2$  to build metallapolycycles by reaction with 2-phenylazines.<sup>7</sup> The reactions involve the activation of two or four C-H bonds, yielding compounds having five and eight fused cycles, respectively. This paper reports the synthesis, structural and electrochemical study of a series of mono- and binuclear Os(rv)-N,N'-di- and tetraphenyl bipyridyls with different conjugated and non-conjugated spacers. In addition, the dramatic influence of the redox processes on the structure

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of the complexes and their emission properties are also discussed.

#### **Results and discussion**

N,N'-Di- and tetraphenyl bipyridines 2-4 were prepared starting from 4-bromo-2-phenylpyridine (1) as depicted in Scheme 1. Nickel-catalyzed homocoupling of 1 using the mild conditions reported by Iyoda and col.<sup>8</sup> (NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/Zn/Et<sub>4</sub>NI, in tetrahydrofuran at 50 °C) afforded 2,2'-diphenyl-4,4'-bipyridine (2), which was isolated in 43% yield. The phenyl and anthranyl derivatives 3 and 4 were obtained by Suzuki coupling between 1 and 1,4-phenylboronic acid and anthracene-9,10diboronic acid bis(pinacol) ester in 82% and 35% yields, respectively. In turn, 2-phenyl-4-(2-(2-phenylpyridin-4-yl)ethynyl)pyridine (5) was prepared by means of two successive Sonogashira couplings (Scheme 2). Thus, the reaction of 1 with trimethylsilyl acetylene in the presence of  $Pd(PPh_3)_4$  led to 4-ethynyl-2-phenylpyridine (6), which after a second coupling with 1 under similar conditions afforded 5 in 68% yield. Finally, 2,2',6,6'-tetraphenyl-4,4'-bipyridine (8) was prepared in 36% yield by nickel-homocoupling of 4-chloro-2,6-diphenylpyridine (7), using the reaction conditions described for 2 (Scheme 2).



## Osmium(*w*)-polyhydride complexes containing *N*,*N*'-di- and tetraphenyl bipyridines

The hexahydride complex  $OsH_6(P^iPr_3)_2$  (9) activates an *ortho*-C-H bond of the phenyl substituent of 2-phenylpyridine, in agreement with the tendency shown by this compound to activate  $C(sp^2)$ -H bonds.<sup>6,7</sup> Thus, the treatment of toluene solutions of 9 with 1.0 equiv. of 2-phenylpyridine, for 18 h, under



reflux afforded the trihydride derivative **10**, which was isolated as a yellow solid in 77% yield according to Scheme 3.

Under the same conditions, the treatment of 9 with 1.0 equiv. of the diphenylbipyridine 2 led to a 2:1 mixture of the mononuclear compound 11, related to 10, and the bimetallic species 12 resulting from the C-H bond activation of both phenyl substituents by different metal centers. When the reaction between 9 and 2 was performed in a 1:3 molar ratio, the mononuclear complex 11 was selectively formed. However, the treatment of 9 with 0.3 equiv. of 2 produced the quantitative transformation of the bipyridine into the bimetallic derivative 12. Complexes 11 and 12 were isolated as dark red solids in 50% and 91% yields with regard to the respective limiting reagents. The presence of phenylidene and anthracenylidene spacers between the pyridyl groups has no significant influence on the reactivity of the bipyridines. Thus, similarly to 2, the addition of 0.3 equiv. of 3 and 4 to the toluene solutions of 9 gave the bimetallic derivatives 13 and 14 after 6 h and 15 h, respectively, under reflux. Both 13 and 14 were isolated as dark red solids in almost quantitative yield with regard to the bipyridines.

Complexes **10–14** were characterized by elemental analysis, IR and <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. Complexes **11** and **12** were further characterized by X-ray diffraction analysis. Fig. 2 and 3 show views of their molecular geometries. The structure of **11** (Fig. 2) proves the selective *ortho*-C-H bond activation of one of the phenyl substituents of the bipyridine to afford an osmatricycle core, which is planar (maximum deviation 0.121(3) Å for C(23)). The geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the phosphine ligands occupying axial positions (P(1)– Os–P(2) = 162.44(3)°). The metal coordination sphere is completed by the C(29) and N(1) atoms of the metalated bipyridine, which acts with a C(29)–Os–N(1) bite angle of 76.48(11)°,



Scheme 3 Synthesis of complexes 10–14.

and the hydride ligands. The Os–C(29) distance of 2.102(3) Å is similar to the Os–C bond lengths reported for osmafurans,<sup>6c,9</sup> osmapyrroles,<sup>10</sup> and related compounds,<sup>6i,11</sup> while the Os–N(1) distance of 2.155(3) Å compares well with the Os–N bond lengths found in lower  $\pi$ -electron osmacyclic nitrogen-containing compounds.<sup>10,11</sup> In agreement with a significant  $\pi$ -electron delocalization in the five-membered ring, the C(19)–C(24) distance of 1.466(4) Å is about 0.02 Å shorter than the C(21)– C(30) separation of 1.494(4) Å between the osmatricycle core and the pyridylphenyl substituent and the C(32)–C(35) separation of 1.487(4) Å between the pyridinic ring and the phenyl group of the latter. The pyridinic ring is almost planar with the metallatricycle core, the dihedral angle between the planes is 9.49(2)° whereas the dihedral angle between the pyridinic ring and its phenyl substituent is 32.03(1)°.

The structure of **12** (Fig. 3) proves the C–H bond activation of both phenyl substituents of the bipyridine, by different



**Fig. 2** Molecular diagram of complex **11**. Selected bond lengths (Å) and angles (°): Os–P(1) = 2.3412(9), Os–P(2) = 2.3503(9), Os–N(1) = 2.155(3), Os–C(29) = 2.102(3), C(19)–C(24) = 1.466(4), C(21)–C(30) = 1.494(4), C(32)–C(35) = 1.487(4); P(1)–Os–P(2) = 162.44(3), C(29)–Os–N(1) = 76.48(11).



Fig. 3 Molecular diagram of complex 12. Selected bond lengths (Å) and angles (°): Os-P(1) = 2.3304(15), Os-P(2) = 2.3355(15), Os-N = 2.135(4), Os-C(6) = 2.098(5); P(1)-Os-P(2) = 164.29(5), N-Os-C(6) = C6 OS N 75.60(17).

metal centers. The molecule can be described as a symmetrical dimer formed by two  $OsH_3(P^iPr_3)_2$  moieties, which are joined by a bridging diorthometallated 2,2'-diphenyl-4,4-bipyridine ligand. The geometry around the osmium atoms is as that of **11**; *i.e.*, a distorted pentagonal bipyramid with the phosphines occupying axial positions (P–Os–P = 164.29(5)°). The metal coordination spheres are completed by the donor atoms of the metallated bipyridine (C–Os–N = 75.60(17)°) and the hydride ligands. The Os–C and Os–N bond lengths of 2.098(5) Å and 2.135(4) Å, respectively, agree well with those of **11**.

To gain more insight into the structure and bonding situation of complexes 11 and 12, density functional theory (DFT) calculations<sup>12</sup> were carried out on model complex 12M, where the bulky isopropyl groups were replaced by hydrogen atoms. As can be readily seen in Fig. 4a, the most remarkable difference between the B3LYP/def2-SVP computed and the experimental structures is the non-planarity of the bipyridyl ligand in the gas-phase (computed torsion angle of 34.7°). We have also re-optimized the gas-phase geometry of 12M at the M06L/ def2-SVP<sup>13</sup> to take into account possible dispersion effects, but again a non-planar structure (torsion angle of 30.9°) was observed.<sup>14</sup> Although the discrepancy could be attributed to the use of the simple model in the calculations, this situation is similar to that of biphenyls having H atoms in all four ortho positions, which are especially susceptible to crystal-packing effects and adopt a planar geometry in the solid state but are twisted in the gas phase.3f-h In fact, the dihedral angle between the two phenyl rings is determined by competition between  $\pi$ -conjugation and steric repulsions; the former favours a coplanar configuration, while the latter prefers a non-planar form.<sup>15</sup>

Our calculations also suggest a significant degree of  $\pi$ -delocalization within the planar (C–C–C–N angle of 0.5°) five-membered osmacycle. This can be viewed in the computed Wiberg-bond orders of the C-C and C-N bonds which are intermediate between single and double bonds (ranging from 1.10 to 1.33) and points to a participation of the occupied  $d_{\pi}$ orbitals of the osmium center in the  $\pi$ -system of the ring. The computed HOMO and HOMO – 1 molecular orbitals (Fig. 4b) nicely confirm this hypothesis as well as the second-order perturbation theory of the Natural Bond Orbital (NBO) method, which clearly shows two-electron delocalizations from occupied  $d_{\pi}$  (Os) atomic orbitals to  $\pi^*(C6=C11)$  and  $\pi^*(N=C)$ molecular orbitals (associated second-order energies of  $\Delta E^{(2)}$  = -8.3 and -4.3 kcal mol<sup>-1</sup>, respectively). Moreover, the computed nuclear independent chemical shift (NICS)<sup>16</sup> value at the [3,+1] ring critical point of the electron density<sup>17</sup> is slightly negative (-1.03 ppm), thus indicating that the involvement of the metal fragment in the  $\pi$ -system of the ring makes it slightly aromatic.18

The <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **10–14** in toluene-d<sub>8</sub> are consistent with the structures shown in Fig. 2 and 3. As expected for three inequivalent hydride ligands, the <sup>1</sup>H NMR spectra at 203 K contain three hydride resonances at about -6, -11, and -12 ppm. These resonances are temperature dependent. Fig. 5 shows the high field region of the spectra of **14** as a function of the temperature. The resonances



**Fig. 4** (a) B3LYP/def2-SVP fully optimized geometry of compound **12M** showing the computed torsional angle (in degrees). (b) Molecular orbitals of complex **12M** (isosurface value of 0.035 au).



Fig. 5 High field of the  ${}^{1}H{}^{31}P{}$  NMR spectra (400 MHz, toluene-d<sub>8</sub>) of complex 14 as a function of temperature.

Complex	Temperature (K)	Coupling constant (Hz)
10	203	36.5
	213	44.4
11	193	48.3
	203	65.8
	213	86.1
13	203	42.4
	213	54.4
14	193	22.8
	203	32.2
	213	38.8
	223	45.8
15	203	30
	213	41
16	203	26.1
	213	29.2

at about -6 and -11 ppm coalesce between 235 K and 253 K. whereas a single hydride signal at about -10 ppm is observed at a temperature higher than 363 K. This is consistent with the operation of two thermally activated site exchange processes, in agreement with the behaviour of related OsH3-derivatives.<sup>6,19</sup> The exchange mechanism implies Os-H stretching, H-H shortening, and subsequent rotation of the resulting dihydrogen ligand. Since the activation barrier of both exchanges is similar, about 10 and 11 kcal mol<sup>-1</sup>, the transition states containing the dihydrogen ligand trans disposed to the nitrogen or carbon atoms of the metallated bipyridines are similarly favoured. The hydrogen atoms of 10, 11, 13, and 14 corresponding to the resonances at about -6 and -11 ppm undergo quantum exchange coupling<sup>20</sup> in addition to the thermally activated site exchange. Thus, the  $J_{H-H}$  values decrease with the temperature (Table 1). In agreement with the presence in these compounds of equivalent phosphines, their <sup>31</sup>P{<sup>1</sup>H} NMR spectra show a singlet at about 21 ppm, which is temperature invariant from 298 K to 203 K. In the  ${}^{13}C{}^{1}H{}$ NMR spectra at room temperature, the most noticeable resonance is that due to the metallated carbon atoms of the bipyridines that is observed at about 188 ppm as a triplet with a C-P coupling constant of about 6 Hz. The ethynylene spacer is not an inert group under the reaction conditions, in contrast to phenylidene and anthracenylidene, since the hexahydride precursor promotes its reduction into ethylidene. Thus, the treatment under reflux of toluene solutions of 9 with 3.0 equiv. of 5 gave after 10 min the mononuclear complex 15 (Scheme 4), as a result of the C-H bond activation of a phenyl substituent and the hydrogenation of the C-C triple bond of the organic molecule. As expected, the addition of 0.5 equiv. of 5 to the toluene solutions of 9 yielded the dinuclear species 16 after 4 h, under reflux. The latter is a consequence of the C-H activation of both phenyl substituents, by different metal centers, and the hydrogenation of the spacer. Complexes 15 and 16 were isolated as dark green solids in 16% (15) and 63%  $(16)^{21}$  yield with regard to 9 and 5, respectively.





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The  ${}^{1}H$ ,  ${}^{31}P{}^{1}H$  and  ${}^{13}C{}^{1}H$  NMR spectra of 15 and 16 in toluene-d<sub>8</sub> agree well with those of **10-14** and support the hydrogenation of the ethynylene spacer. In agreement with the presence of the resulting ethylidene group, both <sup>1</sup>H NMR spectra contain at 2.47 ppm the signal due to the CH<sub>2</sub>hydrogen atoms, which appear with the complex form for 15 and as a singlet for 16. Similar to 10-14, in the high field region of the spectra, at 203 K the hydride ligands display three resonances at -6.51, -11.21 and -12.16 (15) and -6.49, -11.20 and -12.12 (16) ppm, whereas at around 363 K only one hydride signal at about -10 ppm is observed. Also in these cases, the resonances at about -6 and -11 ppm undergo quantum exchange coupling in addition to the thermally activated site exchange. The activation barrier for the position exchanges is between 10 and 12 kcal mol<sup>-1</sup>. The  ${}^{31}P{}^{1}H$ NMR spectra at 298 K show a singlet at about 20 ppm. In the  $^{13}C{^{1}H}$  NMR spectra, the CH<sub>2</sub> resonances of the spacer appear at 35.4 and 35.6 (15) and 35.8 (16) ppm, whereas the signal due to the metalated carbon atoms is observed at 187.7 ppm for both compounds.

Complex 9 activates an ortho-C-H bond of both phenyl substituents of 2,6-diphenylpyridine. Treatment of toluene solutions of this d<sup>2</sup>-hexahydride complex with 1.0 equiv. of the organic molecule for 15 h, under reflux, afforded the dihydride derivative 17, which was isolated as a dark orange solid in 64% yield according to Scheme 5. Under the same conditions the treatment of 9 with 1.0 equiv. of 2,2',6,6'-tetraphenyl-4,4'-bipyridine (8) gave a 1:1 mixture of the mononuclear species 18, related to 17, and the bimetallic derivative 19. The latter results from the C-H bond activation of the four phenyl substituents by two different metal centers. Each osmium atom metallates both phenyl groups of a pyridinic unit. When 9 was treated with 3.0 equiv. of 8, its quantitative transformation into 18 occurred. However, the latter could not be separated from the excess of 8 due to the similar solubility of both compounds in the usual organic solvents. The addition of 0.2 equiv. of 8 to 9 selectively led to the bimetallic species 19, which was isolated as a dark red solid in 88% yield with regard to 8.

The <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **17–19** in toluene-d<sub>8</sub>, at room temperature, strongly support the structures proposed for these compounds in Scheme 5. In the

<sup>1</sup>H NMR spectra, the equivalent hydride ligands display at about -8 ppm a triplet with a H–P coupling constant of about 16 Hz. As expected for equivalent phosphines, the <sup>31</sup>P{<sup>1</sup>H} NMR spectra contain a singlet at about 0 ppm. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectra, the resonance due to the metallated carbon atoms of the pyridinic organic moiety appears at about 178 ppm as a triplet with a C–P coupling constant of about 7 Hz.



Scheme 5 Reactions of hexahydride 9 with 2,6-diphenylpyridine and 8.

#### **Electrochemical study**

Cyclic Voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV) experiments were carried out in order to study the electrochemical properties of the complexes **11–13**, **18** and **19**. 2,2',6,6'-Tetraphenyl-4,4'-bipyridine (**8**) was used as a model for the electrochemical behaviour of the coordinated bipyridine ligands. In the voltammograms of **8** only an irreversible reduction process is observed at  $E_p = -1.8$  V (Fig. 6). Therefore, no oxidation processes associated with the ligands are expected in the complexes.

The electrochemical study of the mononuclear complexes **11** and **18** shows two quasi-reversible processes at about 0 and 1 V (Table 2), which agree with the values found in the literature for the Os(rv)-Os(v) and Os(v)-Os(vI) processes, respectively.<sup>22</sup> Fig. 7 shows the CV and OSWV of **18**.

The electrochemistry of the bimetallic complexes **12**, **13** and **19** was also studied. In the three cases two quasi-reversible waves at about 0 and 1 V were observed (Table 2). No splitting of the waves due to electronic communication between the metal centers was found. It is worth to mention that all monometallic and bimetallic complexes behave similarly.

The spectroelectrochemical study of bimetallic complexes 12, 13 and 19 was subsequently performed. Electrochemical oxidations of these complexes did not exhibit bands that could be assigned to intervalence charge transfer (IVCT) processes. In all cases, it was found an increase of the band around 280 nm (probably associated with a ligand  $\pi$ - $\pi$ \* band) and the vanishing of the charge-transfer band around 450 nm as a consequence of the oxidation of the metal center. Spectroscopic data are detailed in Table 3 and UV-vis spectra are shown in ESI.<sup>†</sup> In contrast to the mononuclear complex 11, changes in the emission spectra of the binuclear complexes 12, 13 and 19 were found upon oxidation. In the three cases the transformation from Os(v) to Os(v) at 0.05 V vs. Fc<sup>+</sup>/Fc produced small changes in the emission spectra of the complexes ( $\lambda_{exc}$  = 280 nm). When the excitation wavelength is chosen to match the charge-transfer band that is present near  $\lambda = 450$  nm, no luminescence was detected. It is worth mentioning that the absorbance of the sample at a concentration of  $c = 2 \times 10^{-6}$  M is of near  $1 \times 10^{-3}$  and self-absorption processes do not affect

 Table 2
 Electrochemical data (V vs. Fc<sup>+</sup>/Fc)

Complex	1st wave potential <sup>a</sup>	and wave potential	
Complex	1st wave potential	211d wave potential	
11	0.0	0.97	
12	-0.02	0.94	
13	0.00	0.99	
18	-0.03	0.95	
19	-0.02	0.95	

<sup>*a*</sup> Half-wave potentials in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>CN (1:1) ( $c = 5 \times 10^{-4}$  M).



Fig. 6 CV (a) and OSWV (b) of 8 ( $c = 5 \times 10^{-4}$  M) in dichloromethane–acetonitrile (1:1) with 0.1 M of tetrabutylammonium hexafluorphosphate as a supporting electrolyte.



**Fig. 7** CV (a) and OSWV (b) of mononuclear complex **18** ( $c = 5 \times 10^{-4}$  M) in dichloromethane–acetonitrile (1 : 1) with 0.1 M of TBAHP as supporting electrolyte. The small irreversible wave that appears at around 0.80 V could be due to an irreversible oxidation of an impurity present in the sample.

 Table 3
 UV-vis-NIR spectra data of the studied complexes

Complex	$\lambda/\mathrm{nm}\left(\varepsilon \times 10^{-3}/\mathrm{M}^{-1}~\mathrm{cm}^{-1}\right)$	Isosbestic points
12	267 (17.83), 483 (6.94), 544 (sh)	_
12 <sup>2+</sup>	252 (30.87), 449 (2.57)	270, 315, 618
13	283 (7.30), 448 (1.85), 519 (sh)	
13 <sup>2+</sup>	260 (28.96), 388 (sh)	575
19	285 (7.07), 454 (2.73), 529 (sh)	_
19 <sup>2+</sup>	253 (26.77), 393 (sh)	590

the emission of the sample. The analysis of the excitation spectra (see ESI<sup>†</sup>) also supports that the emission is originated in a ligand-centered transition. The slight increase of the luminescence intensity may be due to the increase in the molar absorptivity of the sample. However, when a potential of 1.10 V is applied to oxidize the metal centers of the complexes from Os(v) to Os(vi), a bathochromic shift of the band is observed, accompanied by a moderate but significant increase in the luminescence intensity (Fig. 8).

Quantum yields of the different species are summarized in Table 4. The quantum yield of organic molecule 2 is higher than those of the organometallic species. For the bimetallic complexes the oxidation from Os(v) to Os(vI) produces a significant bathochromic shift from about 360 nm to 405 nm and an increase of the emission.

To calculate the number of electrons that are involved in each process, chrono-coulombimetry experiments on complexes 19 and 12 were performed (Fig. 9). When a voltage of 0.05 V vs.  $Fc^+/Fc$  pair is applied in the electrochemical cell (c = $2.5 \times 10^{-4}$  M; V = 10 mL; n =  $2.5 \times 10^{-6}$  mol) a current of 0.427 C is obtained for 19 and a charge of 0.496 C for 12, which noticeably coincides with the theoretical charge for a two-electron process (q = 0.482 C, note that the charge of the background is around 1%). We also carried out an oxidation applying a potential of E = -0.2 V vs. Fc to take into account the contribution of the first irreversible process to the total current. For complex 19 a charge of 0.062 C was found, while a value of 0.095 C was obtained in the case of 12. Therefore, even when the charge of the first process is subtracted to the charge of the oxidation at 0.05 V, these values clearly indicate the oxidation of two electrons for the first reversible wave. The large background currents, around 150% of the current originated from the oxidation of the metal centers, found when the oxidations were carried out at 1.10 V  $\nu$ s. Fc (above the potential of the second electrochemical reversible wave) make the calculations of the number of electrons of this oxidation process less accurate. However, a charge near to 0.5 C, when the background charge is subtracted, points again to a bi-electronic process.

The geometries of the corresponding oxidized species 12M<sup>2+</sup> and 12M<sup>4+</sup> were also optimized by means of computational methods. The two electron oxidation process on 12M leads to the open-shell singlet biradical 12M2+ where the unpaired electrons are mainly located at the osmium atoms (computed spin densities of 0.56 e and -0.56 e, respectively, see Fig. 10). As expected, a significant structural change is observed upon oxidation. In fact, the hydride ligand transoid to the metallated nitrogen atom and the central one approach each other as a consequence of the oxidation of the metal center. Thus, whereas a H…H bond length of 1.666 Å was computed for 12M, a shorter bond length (1.338 Å) is found for  $12M^{2+}$ . This shortening is even more remarkable in the  $12M^{4+}$ species formed as a consequence of the second 2-electron oxidation process. As can be readily seen in Fig. 10, the computed H…H bond length for the latter complex was 0.899 Å, a value typical for dihydrogen species.<sup>24</sup> The increase in the corresponding H···H bond order upon oxidation (0.09 < 0.17 < 0.48)clearly shows the structural change from a trihydride complex to a hydride-dihydrogen compound. In addition, the planarity of the five-membered osmacycle is also affected upon oxidation (Os-C-C-C dihedral angle ranging from 0.0° to 7.1° and to  $-19.0^{\circ}$  from 12M to  $12M^{2+}$  and to  $12M^{4+}$ , respectively). As a result, an increase in the NICS values computed at the [3,+1] ring critical point of the electron density was also observed (-1.03 < +2.76 < +3.35 ppm, respectively). Thus, both oxidized species are noticeably less aromatic than the parent planar complex 12M. From these data, it becomes obvious that the oxidation process leads to dramatic changes in the structure of the complexes which are reflected in their electronic structures and their emission properties.

Similar structural changes were found in the two-step oxidation of mononuclear complex 11M, a model complex of



Fig. 8 Emission spectra of 11 (a), 12 (b), 13 (c), 19 (d). Blue: Os(v); red: Os(v); green:  $Os(v_1)$ ,  $c = 2 \times 10^{-6}$  M, dichloromethane–acetonitrile 1 : 1.

Table 4 Emission quantum yields in the different oxidation states

Compound	$\lambda_{ m emi}$	$\phi_{ m F}{}^a$
2	377	0.140
11	367	0.005
11 <sup>+</sup>	470	0.006
11 <sup>2+</sup>	470	0.005
12	366	0.005
$12^{2+}$	365	0.013
12 <sup>4+</sup>	407, (sh 465)	0.030
13	363	0.020
13 <sup>2+</sup>	363	0.026
13 <sup>4+</sup>	404	0.074
19	363	0.020
19 <sup>2+</sup>	363	0.025
19 <sup>4+</sup>	405	0.110

<sup>*a*</sup> Quantum yields were calculated using anthracene as the standard.<sup>23</sup>

**11** where the isopropyl groups were replaced by methyl groups. As seen in Fig. 11, the ground state structure of **11M** resembles that of binuclear complex **12M**, *i.e.* a trihydride complex (computed H···H bond length of 1.668 Å), with a planar and aromatic five-membered osmacycle (Os–C–C–C angle of 0.5° and NICS of -1.06 ppm). As expected, the one-electron oxidation leads to the radical-cation **11M**<sup>++</sup>, where the unpaired electron is mainly located at the osmium atom (computed spin density of 0.64e), which exhibits a shorter H···H bond length (1.452 Å) and a less planar, and less aromatic, five-membered osmacycle (Os–C–C–C angle of  $-6.9^{\circ}$  and NICS of +3.40 ppm).

#### Conclusions

 $d^4$ -Mono and dinuclear Os-*N*,*N'*-di- and tetraphenylbipyridyls and extended bipyridyls have been synthesised by the

reaction of  $OsH_6(P^iPr_3)_2$  and the appropriate di- or tetraphenylbipyridines in high yields. The structures of some representative mono- and binuclear compounds have been determined by X-ray diffraction analysis and in the gas phase by DFT-calculations. The spectroelectrochemical study of bimetallic complexes 12-14 having different spacers showed significant changes in the emission spectra upon oxidation. While the transformation from Os(rv) to Os(v) produced small changes in the emission spectra of the complexes, the oxidation from Os(v) to Os(vi) provokes a notable bathochromic shift of the emission band, accompanied by a moderate but significant increase in intensity. DFT calculations carried out in the dication and tetracation model species 11M and 12M showed important structural modifications during the sequential oxidation. Thus, the final tetracation, formally an Os(vi) species, has a hydride-dihydrogen structure (instead of a trihydride) and it should be better considered an Os(w) species. Similar structural changes were found in the oxidation process of the mononuclear complexes which were also reflected in their photophysical properties.

#### **Experimental section**

General information, synthetic procedures, electrochemical and computational details are included in ESI.<sup>†</sup> 4-Bromo-2-phenylpyridine (1),<sup>25</sup> 4-chloro-2,6-diphenylpyridine (7)<sup>26</sup> and  $OsH_6(P^iPr_3)_2$  (9)<sup>27</sup> were prepared as previously described.

Procedures for the preparation of mono- and dinuclear complexes **11** and **12** are representative.

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Fig. 9 Chronocoulombimetric curves of the complexes **12** (a) and **19** (b) at E = 0.05 V vs. Fc<sup>+</sup>/Fc.



Fig. 10 B3LYP/def2-SVP fully optimized geometries of complexes 12M<sup>2+</sup> and 12M<sup>4+</sup>. Values in brackets indicate the computed spin densities.

## Reaction of $OsH_6(P^iPr_3)_2$ with 2,2'-diphenyl-4,4'-bipyridine (2): synthesis of complex 11

3 equiv. of 2,2'-diphenyl-4,4'-bipyridine (2) (71 mg, 0.23 mmol) was added to a solution of  $OsH_6(P^iPr_3)_2$  (9) (40 mg, 0.077 mmol) in toluene (5 mL) and heated under reflux for 0.5 hours, changing the color from pale yellow to dark red. The resulting solution was dried in vacuo. Methanol was added to afford a dark red solid which was washed with further portions of methanol and dried in vacuo. Yield: 32 mg (50%). Anal. calcd for C40H61N2OsP2: C, 58.44; H, 7.48; N, 3.41. Found: C, 58.10; H, 7.21; N, 3.51. IR (neat compound, cm<sup>-1</sup>):  $\nu$ (Os-H) 2128 (w), 1980 (w);  $\nu$ (C=N)  $\nu$ (C=C) 1592 (m), 1459 (m). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K):  $\delta$  9.80 (d,  $J_{H-H}$  = 6, 1H, CH-arom), 8.76 (d, J<sub>H-H</sub> = 7.2, 1H, CH-arom), 8.62 (d, J<sub>H-H</sub> = 4.9, 1H, CH-arom), 8.12 (d,  $J_{H-H}$  = 7.3, 2H, CH-arom), 8.03 (s, 1H, CH-arom), 7.93 (d,  $J_{H-H}$  = 7.2, 1H, CH-arom), 7.74 (s, 1H, CH-arom), 7.28 (t, J<sub>H-H</sub> = 7.3, 2H, CH-arom), 7.25 (t, J<sub>H-H</sub> = 7.3, 1H, CH-arom), 7.17 (t, J<sub>H-H</sub> = 7.2, 1H, CH-arom), 7.12



Fig. 11 B3LYP/def2-SVP fully optimized geometries of complexes 11M and  $11M^{\star\star}$ 

(t,  $J_{\text{H-H}} = 7.2$ , 1H, CH-arom), 6.87 (d,  $J_{\text{H-H}} = 4.9$ , 1H, CH-arom), 6.49 (d,  $J_{\text{H-H}} = 6$ , 1H, CH-arom), 1.91 (m, 6H, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.01 (dvt,  $J_{\text{H-H}} = 6.5$ , N = 12, 18H, PCH(CH<sub>3</sub>)<sub>2</sub>), 0.98 (dvt,  $J_{\text{H-H}} = 6.5$ , N = 12, 18H, PCH(CH<sub>3</sub>)<sub>2</sub>), -8.36 (br, 2H, OsH), -11.65 (br, 1H, OsH). <sup>1</sup>H NMR (300 MHz, C<sub>7</sub>D<sub>8</sub>, 193 K, high field region):  $\delta$  -6.40 (d,  $J_{\text{H-H}} = 48.3$ , 1H, Os-H), -10.87 (d,  $J_{\text{H-H}} = 48.3$ , 1H, Os-H), -11.82 (s, 1H, Os-H). <sup>13</sup>C{<sup>1</sup>H} NMR (75.48 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K):  $\delta$  188.4 (t,  $J_{\text{P-C}} = 6.6$ , Os-C), 168.5 (s,  $C_{\text{ipso}}$ ), 159.4 (s, CH-arom), 158.6 (s,  $C_{\text{ipso}}$ ), 150.8, 147.2 (both s, CH-arom), 146.0, 144.3, 142.5, 139.7 (all s,  $C_{\text{ipso}}$ ), 129.4, 129.0, 128.4, 127.5, 125.5, 119.6, 118.9, 117.9, 117.6, 115.7 (all s, CH-arom), 27.7 (vt, N = 24, PCH(CH<sub>3</sub>)<sub>2</sub>), 20.2, 19.9 (both s, PCH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K):  $\delta$  20.7 (s).

## Reaction of $OsH_6(P^iPr_3)_2$ with 2,2'-diphenyl-4,4'-bipyridine (2): synthesis of complex 12

2,2'-Diphenyl-4,4'-bipyridine (29 mg, 0.10 mmol) was added to a solution of  $OsH_6(P^iPr_3)_2$  (9) (150 mg, 0.29 mmol) in toluene (8 mL) and heated under reflux for 24 hours, changing the color from pale vellow to dark red. The resulting solution was dried in vacuo. Methanol was added to afford a dark red solid which was washed with further portions of methanol and dried in vacuo. Yield: 117.6 mg (91%). Anal. calcd for C<sub>58</sub>H<sub>106</sub>N<sub>2</sub>Os<sub>2</sub>P<sub>4</sub>: C, 52.15; H, 8.00; N, 2.10. Found: C, 51.8; H, 8.29; N, 1.62. IR (neat compound, cm<sup>-1</sup>):  $\nu$ (Os-H) 2098 (w), 1961 (w);  $\nu$ (C=N)  $\nu$ (C=C) 1578 (m), 1456 (m). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 293 K):  $\delta$  9.77 (d,  $J_{H-H}$  = 6.0, 2H, CH-arom), 8.75 (d, J<sub>H-H</sub> = 7.2, 2H, CH-arom), 8.21 (d, J<sub>H-H</sub> = 1.4, 2H, CHarom), 7.82 (d, J<sub>H-H</sub> = 7.2, 2H, CH-arom), 7.16 (t, J<sub>H-H</sub> = 7.2, 2H, CH-arom), 7.09 (t, J<sub>H-H</sub> = 7.2, 2H, CH-arom), 6.64 (dd, J<sub>H-H</sub> = 6.0,  $J_{H-H}$  = 1.4, 2H, CH-arom), 1.87 (m, 12H, PCH(CH<sub>3</sub>)<sub>2</sub>), 0.98 (dvt,  $J_{H-H}$  = 6.6, N = 13.3, 36H, PCH(CH<sub>3</sub>)<sub>2</sub>), 0.95 (dvt,  $J_{H-H}$ = 6.8, N = 13, 36H, PCH(CH<sub>3</sub>)<sub>2</sub>), -8.38 (br, 4H, OsH), -11.66 (br, 2H, OsH). <sup>1</sup>H NMR (300 MHz, C<sub>7</sub>D<sub>8</sub>, 213 K, high field region):  $\delta$  -6.43 (d,  $J_{H-H}$  = 49.8, 2H, Os-H), -10.96 (d,  $J_{H-H}$  = 49.8, 2H, Os-H), -11.85 (br, 2H, Os-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.63 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K):  $\delta$  188.3 (t,  $J_{P-C}$  = 6.5, Os-C), 168.3, 144.3, 141.3 (all s, C<sub>ipso</sub>), 159.3, 147.1, 128.3, 125.6, 118.8, 117.3, 114.8 (all s, CH-arom), 27.5 (vt, N = 24.0,  $PCH(CH_3)_2$ ), 20.1, 19.9 (both s, PCH( $CH_3$ )<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161.99 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K): δ 20.8 (s).

#### Structural analysis of complexes 11 and 12

Crystals suitable for X-ray diffraction were obtained by slow diffusion of methanol into solutions of the complexes in toluene. X-ray data were collected on a Bruker Smart APEX diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation,  $\lambda = 0.71073$  Å) operating at 50 kV and 30 (11) or 40 (12) mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s covering  $0.3^{\circ}$  in  $\omega$ . Data were corrected for absorption by using a multiscan method applied with the SADABS program.<sup>28</sup> The structures were solved by the Patterson (Os atoms of 11 and 12) method and conventional Fourier techniques and refined by full-matrix least squares on  $F^2$  with SHELXL97.29 Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely using a restricted riding model. Hydride ligands were observed in the difference Fourier maps but refined with the restrained Os-H bond length (1.59(1) Å, CSD). For both structures the highest electronic residuals were observed in the close proximity of the Os centers and make no chemical sense. CCDC-870543 (11) and 870544 (12) contain the supplementary crystallographic data for this paper.

 $C_{40}H_{60}N_2OSP_2$ ,  $M_W$  821.04, dark red, needle (0.20 × 0.05 × 0.05), triclinic, space group  $P\bar{1}$ , *a*: 8.5681(6) Å, *b*: 14.7204(10) Å, *c*: 15.3568(11) Å, *a*: 80.2450(10)°,  $\beta$ : 76.4900(10)°,  $\gamma$ : 80.7930 (10)°, V = 1841.4(2) Å<sup>3</sup>, Z = 2,  $D_{calc}$ : 1.481 g cm<sup>-3</sup>, F(000): 840, T = 100(2) K,  $\mu$  3.580 mm<sup>-1</sup>. 20 686 measured reflections (2 $\theta$ : 3–57°,  $\omega$  scans 0.3°), 7671 unique ( $R_{int} = 0.0407$ ); minimum/ maximum transmission factors 0.596/0.768. Final agreement factors were  $R^1 = 0.0278$  (6571 observed reflections,  $I > 2\sigma(I)$ ) and w $R^2 = 0.0453$ ; data/restraints/parameters 7671/3/428; GoF = 0.897. Largest peak and hole 1.111 and -1.342 e Å<sup>-3</sup>.

#### Crystal data for 12

C<sub>58</sub>H<sub>104</sub>N<sub>2</sub>Os<sub>2</sub>P<sub>4</sub>·2(C<sub>7</sub>H<sub>8</sub>), *M*<sub>W</sub> 1517.98, violet, prism (0.10 × 0.08 × 0.03), monoclinic, space group *P*2(1)/*c*, *a*: 17.258(4) Å, *b*: 8.775(2) Å, *c*: 23.919(6) Å, *a*: 90.00°, *β*: 103.864(5)°, *γ*: 90.00°, *V* = 3516.5(15) Å<sup>3</sup>, *Z* = 2, *D*<sub>calc</sub>: 1.434 g cm<sup>-3</sup>, *F*(000): 1556, *T* = 100(2) K, µ 3.741 mm<sup>-1</sup>. 43 143 measured reflections (2*θ*: 3–58°, *ω* scans 0.3°), 8774 unique (*R*<sub>int</sub> = 0.0867); minimum/ maximum transmission factors 0.655/0.825. Final agreement factors were *R*<sup>1</sup> = 0.0425 (5956 observed reflections, *I* > 2*σ*(*I*)) and w*R*<sup>2</sup> = 0.0701; data/restraints/parameters 8774/3/384; GoF = 0.852. Largest peak and hole 1.909 and –1.260 e Å<sup>-3</sup>.

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