Mononuclear and Binuclear Tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine (tpphz) Ruthenium and Osmium Complexes

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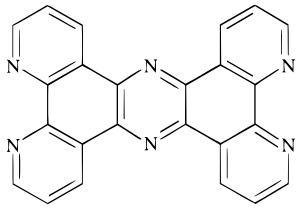
The monometallic complexes $[(bpy)_2Ru(tpphz)]^{2+}$ (**4**) and $[(bpy)_2Os(tpphz)]^{2+}$ (**5**), where tpphz is the poorly soluble fully aromatic tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine, have been obtained by reaction of 5,6-diamino-1,10-phenanthroline with $[(bpy)_2M(phendione)]^{2+}$ (M = Ru^{II} or Os^{II}). Reaction of **4** and **5** with metallic precursors yielded the homo- and heterobimetallic complexes $[(bpy)_2Ru(tpphz)Ru(NH_3)_4]^{4+}$ (**6**), $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ (**7**), $[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$ (**8**), and $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ (**9**). The mononuclear **4** and **5** aggregate in solution, probably by $\pi-\pi$ stacking of the tpphz part as shown from proton NMR. The complexes show one reversible metal-centered oxidation and several reversible (except **6**) reductions which add one electron on the tpphz ligand, one electron on one bpy of each metallic end, a second electron on one bpy of each metallic end, and then a second electron on the tpphz ligand. The complexes (except **8**) are luminescent in acetonitrile. Quenching of the luminescence by water has been attributed to proton quenching at the phenazine nitrogen atoms.

Introduction

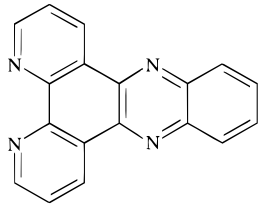
The increasing interest in dinuclear ruthenium and osmium compounds stems mainly in their intense metal to ligand charge transfer in conjunction with favorable photostability, which allows photoinitiated energy transfer and sensitization processes.[1] Multielectron-transfer systems that are photochemically and electrochemically active[2] with possible applications as two electron-transfer reagents in water splitting devices[3] or for the study of long distance electron or energy transfer have been described in the past few years.

We have directed our efforts to the synthesis and study of rigid and conjugated dimetallic systems, with known intermetallic distances allowing accurate determination of the rate constants of electron and energy transfer processes. Most of the systems studied up to now are linear molecules in which the two remote electrophore or chromophore sites are linked by extended bridging spacers such as alkenes,[4] alkynes,[5] or polyphenyls.[6] However the main drawback of such bridging spacers is the possible rotation around the σ-bonds, which decreases the long-distance electronic coupling between the terminal sites by loss of coplanearity of the π-electrons or aromatic parts.

As part of a larger project involving the study of long distance electron transfer through polyaromatic molecules, we have prepared the fully conjugated bridging ligand tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-h:2‴,3‴-*j*]phenazine (tpphz).[7] This ligand and



tpphz



dppz

its monometallic complexes are closely related to the currently much investigated dppz (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) complexes $[L_2M(dppz)]^{2+}$ (L = bpy, phen; M = Ru^{II}, Os^{II}) or $[(4\text{-Mepy})(CO)_3Re^{I}(dppz)]^{+}$. These compounds are used as molecular light switches for DNA[8] and micellar solutions[9] or for the study of fast electron transfer through DNA.[10] It has been shown that intercalation of the planar dppz ligand between the base pairs of DNA protected the dppz nitrogens from proton

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transfer quenching; similarly, the complex $[(tpy)RuO(dppz)]^{2+}$ was found to be a good DNA cleavage agent with high DNA affinity.[11]

We wish to report here the synthesis and characterization of the monometallic complexes $[(bpy)_2Ru(tpphz)]^{2+}$ and $[(bpy)_2Os(tpphz)]^{2+}$ and the dimetallic complexes $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$, $[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$, $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$, and $[(bpy)_2Ru(tpphz)Ru(NH_3)_4]^{4+}$.

Experimental Section

Materials. 5-Nitro-1,10-phenanthroline, 1,10-phenanthroline-5,6-dione (phendione),[12] $[Ru(bpy)_2Cl_2]\cdot 2H_2O$,[13] $[Os(bpy)_2Cl_2]\cdot 2H_2O$[14] and $[Ru(bpy)_2(phendione)](PF_6)_2$ (Ru(phendione)),[15] $[Ru(NH_3)_4(acetone)_2](PF_6)_2$[16] were prepared according to the literature. $[Os(bpy)_2(phendione)](PF_6)_2$ (Os(phendione)) was synthesized according to ref 15 and purified by chromatography (yield: 51%). NBu_4PF_6 was recrystallized several times from ethanol and dried for 24 h at 140 °C under vacuum. Very dry DMF for cyclic voltammetry was purified according to ref 17.

All other solvents and reagents used were at least reagent grade quality and were used without further purification.

Methods and Instrumentation. UV−vis−near IR spectra were taken on a Shimadzu UV-3100 spectrophotometer. FTIR spectra were obtained using a Perkin-Elmer 1725 instrument. 1D and 2D ^{1}H NMR spectra were recorded on Bruker WF-250 and Bruker AMX-400 spectrometers and processed with the program SwaN-MR.[18] Chemical shifts were measured with reference to the residual solvent signals. Electrochemical measurements were performed on an Electromat 2000 system. Cyclic voltammograms were obtained using a platinum working electrode, a platinum auxiliary electrode, and a saturated potassium chloride calomel reference electrode (Tacussel). Linear and differential pulsed voltammetry was done using a platinum rotating disk electrode. At the end of each experiment, ferrocene was added as an internal standard. The potentials were then automatically corrected for uncompensated cell resistance.[19] Mass spectra (CI and FAB) were recorded on a Nermag R10-R10 spectrometer. Luminescence experiments were performed in air-equilibrated acetonitrile or water solutions at room temperature. Steady-state luminescence was performed on an SLM AMINCO 500 C spectrofluorimeter and peak integrals were computed using the software package. Preliminary studies with DNA were performed in Tris buffer at pH 7.5 with Aldrich calf thymus DNA (type 1) using a procedure given in ref 8k.

Syntheses. Tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine (tpphz) (1). From Phendione and Ammonium Acetate. A mixture of 2.90 g (13.8 mmol) of 1,10-phenanthroline-5,6-dione, 15.0 g of ammonium acetate, and 0.30 g (1.72 mmol) of sodium hydrosulfite under argon was heated gently to 180 °C and maintained at this temperature for 2 h with occasional stirring. Upon cooling, 20 mL of water was added, and the precipitate was collected by filtration and washed well with water, methanol, and acetone. The product was triturated in refluxing ethanol (100 mL), hot filtered, washed with ethanol, and dried under vacuum. Yield: 1.26 g (47%).

From Phendione and 3. 1,10-Phenanthroline-5,6-diamine, **3** (100 mg, 0.476 mmol), was added to a boiling solution of phendione (100 mg, 0.476 mmol) in methanol (20 mL). After 1.5 h of reflux, a suspension formed; the solution was then hot filtered to recuperate a pale yellow powder subsequently washed with methanol and diethyl ether. Yield: 172 mg (94%). Anal. Calcd for $C_{24}H_{12}N_6$: C, 74.99; H, 3.15; N, 21.86. Found: C, 75.51; H, 3.07; N, 21.77. MS: MH^+ found 385, $C_{24}H_{13}N_6$ requires 385. ^{1}H NMR [$CDCl_3$/trifluoroacetic acid-*d*)], δ, ppm (multiplicity, number of protons, attribution, *J*, *J*′): 10.23 (dd, 4H, a, 8.3 Hz, 1.6 Hz), 9.49 (dd, 4H, c, 5.1 Hz, 1.4 Hz), 8.43 (dd, 4H, b, 8.3 Hz, 5.1 Hz).

5-Nitro-6-amino-1,10-phenanthroline (2). To a suspension of 4.0 g (17.8 mmol) of 5-nitro-1,10-phenanthroline and 8.0 g (118.9 mmol) of hydroxylamine hydrochloride in 100 mL of refluxing ethanol was added a solution of 9 g (160.4 mmol) of potassium hydroxide in 100 mL of ethanol dropwise over the course of 45 min. The reaction mixture was refluxed for a further 30 min, cooled, and poured into ice-cold water (300 mL). The precipitate was washed thoroughly with water, methanol, and chloroform and dried. Yield: 1.45 g (33%). Anal. Calcd for $C_{12}H_8N_4O_2$: C, 60.00; H, 3.36; N, 23.32. Found: C, 59.75; H, 3.40; N, 23.30. FTIR (KBr pellets): 3401, 3266, 3143, 1631, 1596, 1263 cm^{-1}. ^{1}H NMR [$(CD_3)_2SO$], δ, ppm: 9.3 (d, 1H, a, 4.3 Hz); 9.2 (d, 1H, c, 8.5 Hz); 8.9 (d, 1H, a′, 4.3 Hz); 8.83 (d, 1H, c′, 8.6 Hz); 8.7 (s, 2H, NH); 8.0 (dd, 1H, b, 8.7 Hz, 4.3 Hz); 7.8 (dd, 1H, b′, 8.6 Hz, 4.3 Hz).

5,6-Diamino-1,10-phenanthroline (3). To a mixture of 0.2 g (0.83 mmol) of 5-nitro-6-amino-1,10-phenanthroline and 0.1 g of palladium on activated carbon (10% Pd) in 200 mL of refluxing ethanol was added 1.0 mL (17.2 mmol) of hydrazine hydrate (55%) dropwise over 15 min. The reaction mixture was refluxed for a further 45 min, and filtered while hot. After concentration under vacuum, the yellow product was precipitated from the cold filtrate by the addition of petroleum ether (40−60 °C), filtered, washed well with petroleum ether (40−60 °C), and dried under vacuum. Yield: 140 mg (83%). Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.66; H, 4.79; N, 26.65. Found: C, 68.50; H, 4.49; N, 26.38; FTIR (KBr pellets): 3372, 3267, 1610, 1564 cm^{-1}. ^{1}H NMR [CD_3OD], δ, ppm: 8.93 (dd, 2H, c, 4.3 Hz, 1.6 Hz); 8.60 (dd, 2H, a, 8.5 Hz, 1.6 Hz); 7.58 (dd, 2H, b, 8.5 Hz, 4.3 Hz).

$[(bpy)_2Ru(tpphz)](PF_6)_2\cdot 5H_2O$ (4). An amount of 88.6 mg (0.42 mmol) of **3** dissolved in hot methanol (45 mL) was added to a boiling solution of Ru(phendione) (200 mg, 0.21 mmol) in acetonitrile (10 mL). The solution was then heated at 80 °C for 6 h and within 15 min after the addition of the ligand a color change from brown to red occured. After the mixture was cooled to room temperature, the formerly formed suspension was filtered off and well washed with acetonitrile. To the concentrated filtrate a saturated aqueous NH_4PF_6 solution was added to precipitate the complex. The pure red-orange product was filtered, washed with water, ethanol, and diethyl ether, and finally dried under vacuum. Yield: 230 mg (93%). It could be recrystallized from a mixture of acetonitrile/methanol/saturated NH_4PF_6 to yield 196 mg (80%) of brillant orange flakes. Anal. Calcd for $C_{44}H_{28}N_{10}RuP_2F_{12}\cdot 5H_2O$: C, 44.19; H, 3.37; N, 11.71. Found: C, 44.28; H, 2.88; N, 11.70. FAB-MS (3-nitrobenzylalcohol matrix): m/z = 943 $(M - PF_6)^+$, 798 $(M - 2PF_6)^+$.

$[(bpy)_2Os(tpphz)](PF_6)_2\cdot 4H_2O$ (5). The route for the preparation of Os(tpphz) was analogous to that described for **4** with 1 equiv of Os(phendione) for 1.5 equiv of phendiamine **3** and gave after precipitation a brown product in 90% yield. Anal. Calcd for

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$C_{44}H_{28}N_{10}OsP_2F_{12}\cdot 4H_2O$: C, 42.31; H, 2.91; N, 11.28 Found: C, 42.46; H, 2.86; N, 11.47. FAB-MS (3-nitrobenzylalcohol matrix): m/z =1735 $(M - PF_6)^+$, 1590 $(M - 2PF_6)^+$, 1445 $(M - 3PF_6)^+$.

$[(bpy)_2Ru(tpphz)Ru(NH_3)_4](PF_6)_4\cdot 4H_2O$ (6). A thoroughly deoxygenated suspension of 1 equiv of Ru(tpphz) in acetone was added to 1.2 equiv of $[Ru(NH_3)_4(acetone)_2](PF_6)_2$ contained in a deoxygenated flask. The initially orange solution of **4** turned immediately red-brown on contact with the tetraammineruthenium complex. The solution was stirred at room temperature for 30 min. After addition of a saturated aqueous NH_4PF_6 solution, the resulting brown precipitate was filtered off and washed with water and diethyl ether. The complex was then subjected to silica gel chromatography (acetonitrile, saturated aqueous potassium nitrate (7/2.5/0.5 v/v) as eluent) to give the desired complex in 68% yield. Anal. Calcd for $C_{44}H_{40}N_{14}Ru_2P_4F_{24}\cdot 4H_2O$: C, 32.64; H, 2.99; N, 12.11. Found: C, 32.53; H, 2.96; N, 11.76. FAB-MS (3-nitrobenzylalcohol matrix): m/z = 1403 $(M - PF_6)^+$, 1259 $(M - 2PF_6 + H)^+$.

$[(bpy)_2Ru(tpphz)Ru(bpy)_2](PF_6)_4\cdot 2H_2O$ (7). Route A. A mixture of 1.2 g (2.31 mmol) of $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ and 0.37 g (0.963 mmol) of tpphz in 70 mL ethanol/water (50/50) was refluxed for 24 h. Upon cooling, the reaction mixture was filtered and the solvent removed at 70 °C under vacuum. The residue was dissolved in 50 mL water, filtered, and the resulting solution added dropwise to a 50 mL aqueous solution of NH_4PF_6. The precipitate was filtered and recrystallized twice by the slow evaporation of acetone from a solution of acetone/water. Yield: 1.37 g (84%).

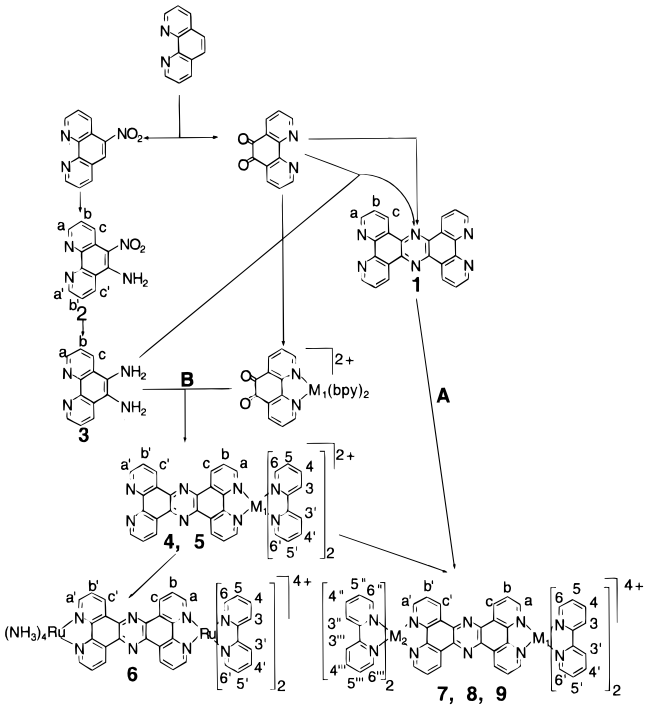
Route B. A solution of $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (16 mg, 0.031 mmol) and silver triflate (16 mg, 0.062 mmol) in DMF (5 mL) was stirred for 10 min at room temperature. After centrifugation to remove silver chloride and a wash of the vessels with 5 mL of DMF, **4** (30 mg, 0.025 mmol) dissolved in 5 mL of DMF was added to the collected blood-red solution. The reaction mixture was then deoxygenated before being heated at 120 °C for 2 h. The deep red solution was cooled to room temperature, filtered and stored overnight at 4 °C after addition of a saturated aqueous ammonium hexafluorophosphate solution until cloudiness appeared. The precipitated product was filtered off, washed with water, ethanol, and diethyl ether and finally dried under vacuum to yield 35.5 mg (76%) of a pure red powder.

Anal. Calcd for $C_{64}H_{44}N_{14}Ru_2P_4F_24\cdot 2H_2O$: C, 42.07; H, 2.65; N, 10.73. Found: C, 41.98; H, 2.73; N, 10.59. FAB-MS (3-nitrobenzylalcohol matrix): m/z = 1647 $(M - PF_6)^+$, 1502 $(M - 2PF_6)^+$.

$[(bpy)_2Os(tpphz)Os(bpy)_2](PF_6)_4\cdot 4H_2O$ (8). A solution of $[Os(bpy)_2Cl_2]\cdot 2H_2O$ (49 mg, 0.085 mmol) and 1 equiv of **5** (88 mg, 0.071 mmol) in ethylene glycol (20 mL) was thoroughly deoxygenated. The purple mixture was heated for 6 h at 150 °C under argon and quickly turned brown. The solution was cooled to room temperature followed by the addition of an equal volume of a saturated aqueous ammonium hexafluorophosphate solution under vigorous stirring. The brownish solid was collected and washed with water, small amounts of ethanol, and diethyl ether. Purification by chromatography on silica gel column was performed with a mixture of acetonitrile, water, saturated aqueous potassium nitrate and butan-1-ol (5.5/2.5/0.5/0.5 v/v) as eluent. The collected brown fractions were regrouped and concentrated in vacuo. Excess nitrate salt was filtered off by adding acetone to the brown solution, and the flask was washed with acetonitrile to dissolve the remaining complex. After subsequent concentration on the rotatory evaporator, an excess of NH_4PF_6 was added to precipitate the complex as a pure brown powder. Yield: 92 mg (53%). Anal. Calcd for $C_{64}H_{44}N_{14}Os_2P_4F_{24}\cdot 4H_2O$: C, 37.65; H, 2.57; N, 9.61. Found: C, 37.75; H, 2.50; N, 9.67. FAB-MS (3-nitrobenzylalcohol matrix): m/z = 1825 $(M - PF_6)^+$, 1680 $(M - 2PF_6)^+$, 1534 $(M - 3PF_6)^+$, 1390 $(M - 4PF_6)^+$.

$[(bpy)_2Ru(tpphz)Os(bpy)_2](PF_6)_4\cdot 8H_2O$ (9). This complex was prepared in an analogous manner to **8** except that the ruthenium monometallic complex **4** was used in place of the osmium monometallic complex **5**. The heterodinuclear complex was then purified by chromatography on silica gel column (acetonitrile, water, and saturated aqueous potassium nitrate (64:30:6.v/v) as eluent) and treated as above. Yield: 105 mg (61%). Anal. Calcd for $C_{64}H_{44}N_{14}OsRuP_4F_{24}\cdot 8H_2O$: C, 37.97; H, 2.99; N, 9.69. Found: C, 37.91; H, 2.84; N, 9.61. FAB-MS (3-nitrobenzylalcohol matrix): m/z = 1735 $(M - PF_6)^+$, 1590 $(M - 2PF_6)^+$, 1445 $(M - 3PF_6)^+$.

Scheme 1. Synthetic Routes for the Preparation of the Ligand and Complexes: **4**, M_1 = Ru; **5**, M_1 = Os; **7**, M_1 = M_2 = Ru; **8**, M_1 = M_2 = Os; and **9**, M_1 = Ru and M_2 = Os



Results and Discussion

Syntheses. The outline of the syntheses of the ligand and the complexes is presented in Scheme 1. The ligand tpphz **1** can be obtained in a single step by reaction of 1,10-Phenanthroline-5,6-dione (phendione) with ammonium acetate. **1** can also be prepared by condensation of phendione with 5,6-diamino-1,10-phenanthroline, **3**. The latter was prepared by amination of 5-nitro-1,10-phenanthroline with hydroxylamine in basic medium,[20] and the subsequent reduction of 5-nitro-6-amino-1,10-phenanthroline, **2**. Reaction of **1** with $[M(bpy)_2Cl_2]$ (route A) slowly produces the homodinuclear complex $[(bpy)_2M(tpphz)M(bpy)_2]^{4+}$. The low solubility of **1** in most solvents prevents efficient synthesis of the mononuclear complexes $[(bpy)_2M_1(tpphz)]^{2+}$ (M_1 = Ru, **4**, and M_2 = Os, **5**) since these mononuclear complexes are much more soluble than the free ligand. However, these complexes **4** and **5** can be easily obtained by condensation of 5,6-diamino-1,10-phenanthroline, **3**, with the precoordinated phendione in $[M_1(bpy)_2phendione]^{2+}$. It must be emphasized that, due to the deactivating effect of the tppz phenazine part, this condensation reaction is significantly slower (completed in 6 h) than that with *o*-phenylenediamine (15 min in boiling ethanol). This synthetic route allows the synthesis of monometallic complexes bearing very, or even fully, insoluble ligands without formation of dimetallic species. Reaction of **4** and **5** with "$Ru(NH_3)_4$" or "$M_2(bpy)_2$" yielded the complexes **6**, **7** (M_1 = M_2 = Ru), **8** (M_1 = Ru, M_2 = Os), and **9** (M_1 = M_2 = Os). All these complexes have been obtained as PF_6 salts and purified by chromatography. They have been characterized by elemental analysis, FAB mass spectrometry (see Experimental Section) and 1D and 2D ^1H NMR spectroscopy.

^1H NMR Spectra. The ^1H NMR spectra of these complexes have been assigned with the aid of COSY spectra in the aromatic

(20) For similar amination of heterocycles, see for example: (a) Savosin, I. V.; Shaburov, V. V. *Zh. Org. Khim.* **1990**, *26*, 1790. (b) Nasielski-Hinkens, R.; Benedek-Vamos, M.; Maetens, D.; Nasielski, J. *J. Organomet. Chem.* **1981**, *217*, 179.

Table 1. ^{1}H NMR Data for the Complexes **4**−**9**[a]

	4[b]	**5**[c]	**6**	**7**	**8**	**9**
a	9.82; 2H; dd 8.2, 1.7	9.60; 2H; dd 8.1, nr	10.03; 2H; dd 8.2, 1.2	10.23; 4H, dd 8.0, nr	9.76; 4H; dd 8.2, 1.2	10.02; 2H; dd 8.2, 1.3
b	7.96; 2H; dd 8.2, nr	7.83; 2H; dd 8.3, 5.5	8.66; 2H; dd 8.2, 5.4	8.27; 4H; dd 8.0, 5.7	7.94; 4H, dd 8.2, 5.5	8.06; 2H; dd 8.2; 5.5
c	8.92; 2H; dd 4.5, 1.7	8.49; 2H; nr nr	8.34; 2H; dd 5.4, 1.2	8.48; 4H; dd 5.7, nr	8.25, 4H; dd 5.5, 1.2	8.35; 2H; dd 5.4, 1.3
a′	9.69; 2H; dd 8.2, 1.3	9.14; 2H; dd 8.3, nr	8.79; 2H; dd 8.1, 1.1			9.80; 2H; dd 8.2, 1.1
b′	7.96, 2H; dd 8.2, nr	7.83; 2H; dd 8.3, 5.5	8.14; 2H; dd 8.1, 5.5			7.97; 2H; dd 8.2; 5.4
c′	8.30; 2H; dd 5.4, 1.3	8.24; 2H; dd 5.5, 1.1	8.61; 2H; dd 5.5, 1.1			8.28; 2H; dd 5.5, 1.1
3	8.61; 2H; d 8.6	8.62; 2H; d 8.1	8.64; 2H; d 8.0	9.05; 4H; d 8.7	8.59; 4H; d 9.4	8.84; 2H; d 7.7
4	8.18; 2H; t 8.2; 1.5	8.00;.2H; td 8.1, 1.1	8.20; 2H; td 8.0, 1.4	8.39; 4H; td 8.3, 1.1	7.98; 4H; td 8.2, 1.5	8.20; 2H; td 8.0, 1.4
5	7.53; 2H; ddd 6.6, 1.3, nr	7.47; 2H; ddd 6.7; 1.3, nr	7.55; 2H; ddd 6.6, 1.2, nr	7.72; 4H; ddd 6.6, nr	7.44; 4H; ddd 6.7, 1.3, nr	7.55; 2H; ddd 6.7, 1.2, nr
6	7.97; 2H; d 4.9	8.08; 2H; d 5.4	7.94; 2H; d 4.9	8.47; 4H; d 5.3	7.82; 4H; d 5.4	7.97; 2H; d 5.6
3′	8.58; 2H; d 9.2	8.57; 2H; d 8.3	8.60; 2H; d 8.4	9.01; 4H; d 8.7	8.55; 4H; d 9.4	8.60; 2H; d 8.3
4′	8.08; 2H; td 8.2, 1.5	7.89; 2H; td 7.8, 1.3	8.09; 2H; td 8.0, 1.5	8.27; 4H; td 7.6, 1.7	7.88; 4H; td 8.1, 0.8	8.09; 2H; td 7.3; nr
5′	7.34, 2H; ddd 6.6, 1.3, nr	7.30; 2H; ddd 6.7, nr	7.32; 2H; ddd 6.4, 1.2, nr	7.34; 4H; ddd 6.6, nr	7.20; 4h; ddd 6.7, 1.3, nr	7.32; 2H; ddd 6.7, 1.2, nr
6′	7.93; 2H;d 5.7	7.87; 2H; d 4.7	7.80; 2H; d 4.9	7.92; 4H; d 5.6	7.68; 4H; d 5.7	7.80; 2H; d 5.7
3″						8.62; 2H; d 7.3
4″						8.01; 2H; td 8.2, 1.2
5″						7.47; 2H; ddd 6.7, 1.2, nr
6″						7.84; 2H; d 5.8
3‴						8.58; 2H; d 8.0
4‴						7.93; 2H; td 8.1, nr
5‴						7.23; 2H; ddd 6.7, 1.2, nr
6‴						7.70; 2H; d 5.6

[a] Measured at 250 MHz in CD_3CN at 297 K. The atom labeling scheme is shown in Scheme 1. Respectively: chemical shift (ppm), number of protons, multiplicity, *J* (Hz), *J*′ (Hz). Multiplicity abbreviations: s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, td = triplet of doublets, nr = not clearly resolved (overlap or shoulder). [b] Concentration = 6.6×10^{-3} mol L^{-1}. [c] Concentration = 6.4×10^{-3}mol L^{-1}.

region. The results are presented in Table 1. Comparison of the chemical shifts shows that, for a given proton, the absorption moves downfield in the order: uncomplexed end, **5**, **8**, **4**, **9** ≈ **6**, **7**. This variation can be interpreted in terms of electronic effects, since very similar geometries around the metal atoms in the bipyridyl osmium and ruthenium complexes[21−23] preclude any important geometric effect. Complexation reduces the residual electron density on the ligands, which has a deshielding effect on the resonance field. This effect is more pronounced with $(bpy)_2Ru^{II}$(tpphz) moiety than with $(bpy)_2Os^{II}$(tpphz), since Ru^{II} has lower energy orbitals than Os^{II} and that smaller back-donation from Ru than for Os decreases the electron density on the ligands. Consequently, the residual electron density on the ligands is smaller in ruthenium complexes than in the osmium analogues. Comparison of $[(bpy)_2Ru(tpphz)Ru(NH_3)_4]^{4+}$ (**6**) and $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ (**9**) shows that the effect of $Ru(NH_3)_4$ on the ancillary ligands electron density is in the same range than that of $Os(bpy)_2$. This is also consistent with similar oxidation potentials for these moieties (*vide infra*).

Surprisingly enough, the ^{1}H spectra of the monuclear complexes **4** and **5** are very sensitive to concentration. This displacement can reach 0.6 ppm between extreme conditions. As an example, the Figure 1 shows two room temperature ^{1}H spectra of **4** at two different concentrations. The most affected protons are clearly the tpphz protons, which move downfield with increasing concentration, and the bpy protons H_6 which move upfield in the same conditions. These two H_6 protons are the two bpy protons located above the phenanthroline part of tpphz (Figure 2). For the other bpy protons, the chemical shifts are not concentration dependent. We have attributed this concentration effect to an aggregation of mononuclear species by stacking of the tpphz parts in solution. Consistent with this hypothesis, an increase of the temperature causes similar effects as dilution. This aggregation, which must be very rapid with respect to the NMR time scale, modifies the local electron density and/or the ring current effects in the vicinity of the tpphz

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(23) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.

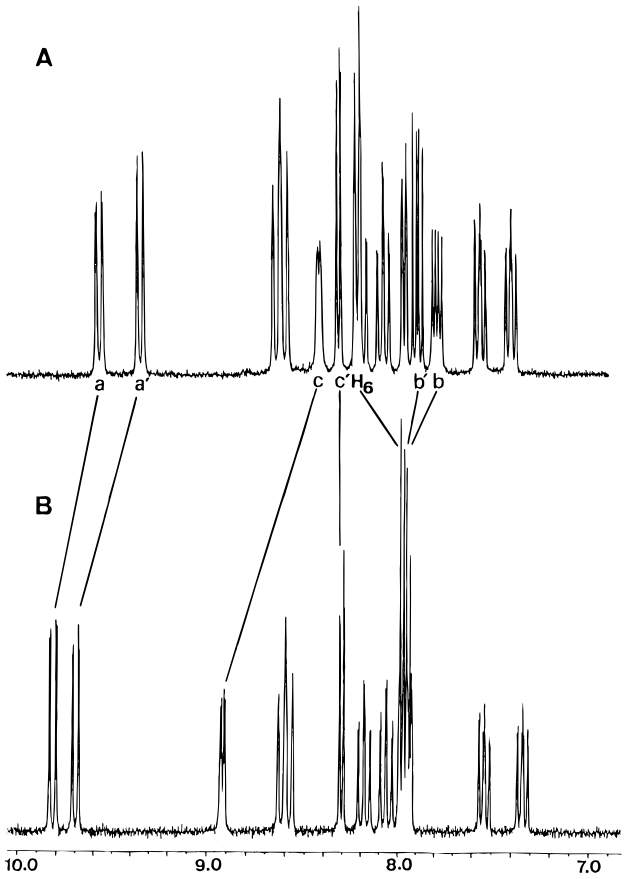

Figure 1. Proton NMR spectra (250 MHz, 298 K) of **4** in CD_3CN at different concentrations: (A) concentration 6.6×10^{-3} mol L^{-1}; (B) concentration 2.0×10^{-3} mol L^{-1}.

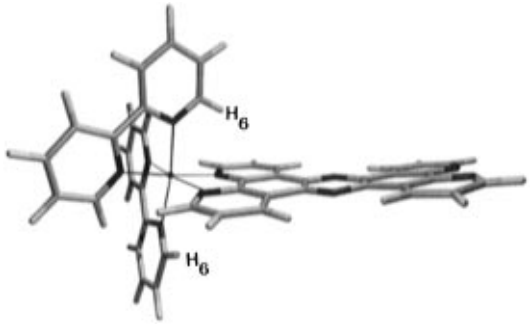

Figure 2. View of **4** obtained from the X-ray structure coordinates of **7**,[7] showing the position of the two H_6 atoms above the tpphz ligand.

ligand. It has no effect on the UV−visible spectra because MLCT band involving the tpphz phenazine part is overlapped by much stronger metal → bpy absorption bands (*vide infra*). Further interpretation of these chemical shift variations is not possible without accurate knowledge of the aggregation geometry and dynamics.

This behavior is reminiscent of the packing observed in crystals of the DNA cleavage agent $[RuO(dppz)(tpy)]^{2+}$ where it has been shown that the dppz quinoleine part has an innate propensity for π-stacking.[11] This property is probably even more pronounced in the case of tpphz complexes due to their larger and more accessible aromatic area. Besides, it is also reflected by the very low solublity of tpphz in most solvents when compared to dppz.

Bonding. Extended Hückel calculations were carried out in order to obtain compositions and energies of the tpphz ligand orbitals and to rationalize the electrochemical and spectroscopic results. Figure 3 shows a graphical representation of the squared

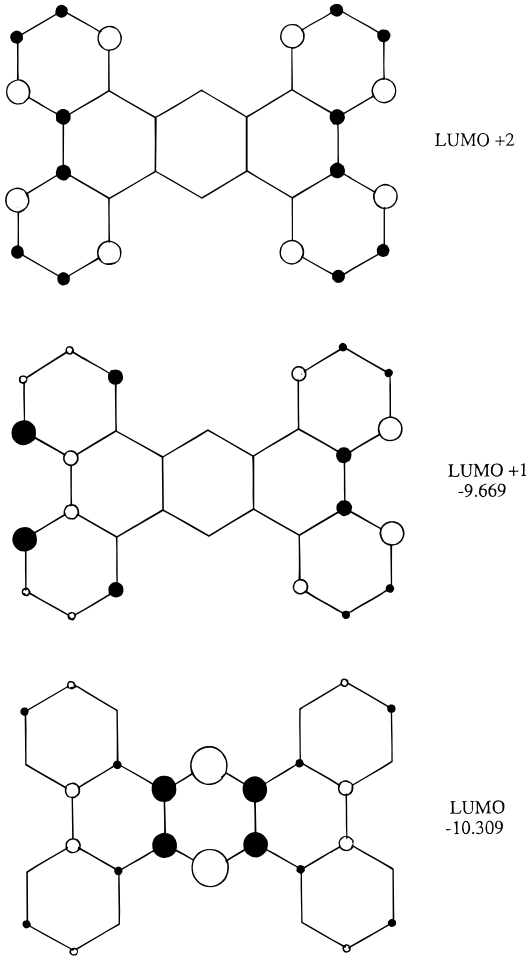

Figure 3. LUMO (−10.309 eV), LUMO+1 (−9.669 eV), and LUMO+2 (−9.651 eV) of **1** calculated by the extended-Hückel method.

MO coefficients for the three lowest lying unoccupied orbitals of **1**. The MO diagrams for the complexes are qualitatively very similar. The HOMO is mainly localized on the metal, the bpy ligands, and the phenanthroline part of **1**, with a very small contribution from the phenazine nitrogen atoms. On the other hand, the LUMO is mainly localized on the central phenazine part of the ligand, with little overlap with the bipyridine ends and small coefficients at the bipyridine nitrogen atoms. This orbital is at significantly lower energy than the LUMO in isolated bpy, which reflects a more pronounced π-accepting character of **1** vs bpy.

In contrast the next two MOs, LUMO+1 and LUMO+2, are only localized on the bipyridine ends of **1** without any contribution from the phenazine central part and with large coefficients on the nitrogen atoms bounded to the metallic center. In the case of metallic complexes, these LUMO+n ($n \geq 1$) also contain metal and 2,2′-bipyridine contributions. This very schematic MO diagram allows the interpretation of the main features of absorption spectra and electrochemical studies.

Absorption Spectra. As an example, the absorption spectra of **1** (protonated), **4**, **7**, and $[Ru(bpy)_3]^{2+}$ are shown in Figure 4, and Table 2 lists λ_{max} and extinction coefficients of the complexes with **1**. For comparison the data for $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ have also been included.

As observed for $[(bpy)_2Ru(dppz)]^{2+}$,[8b, 17] the spectra retain most of the features of the components $(bpy)_2M$ and tpphz. They display a strong MLCT band at 400−550 nm attributed to the overlap of $M^{II} \rightarrow bpy(\pi^*)$ and $M^{II} \rightarrow tpphz(\pi^*)$. This band is not red-shifted as might have been expected with a good π-accepting ligand as **1**, and the absorption wavelengths are

Table 2. Spectral Data[a]

species	absorption λ_{max}/nm ($10^{-3}\epsilon$/dm^3 mol^{-1} cm^{-1})	emission[b] λ_{max}/nm (rel int); λ_{irr}/nm
1, tpphz[c]	379 (21.3), 368 (13.0), 317 (29.3), 278 (72.3), 245 (29.3)	
$[Ru(bpy)_3]^{2+}$ [d]	452 (14.5), 345 (sh), 323 (sh), 285 (87.1), 250 (25.1)	607 (1); 450
$[Os(bpy)_3]^{2+}$ [e]	579 (3.3), 478 (11.1), 436 (10.7), 290 (78.0)	743[f]
4, $[Ru(bpy)_2tpphz]^{2+}$	450 (19.7), 380 (33.9), 361 (24.1), 284 (133.0), 246 (76.4)	616 (0.74); 450
5, $[Os(bpy)_2tpphz]^{2+}$	636 (3.84), 582 (4.42), 480 (15.6), 435 (14.1), 381 (30.2), 362 (21.8), 286 (87.7), 246 (56.4)	738 (0.009); 478
7, $[Ru(bpy)_2tpphzRu(bpy)_2]^{4+}$	442 (36.1), 370 (34.6), 351 (28.1), 281 (18.9), 244 (75.6)	671 (0.09); 443
8, $[Os(bpy)_2tpphzOs(bpy)_2]^{4+}$	630 (8.63), 587 (9.97), 477 (31.9), 432 (31.9), 370 (41.9), 352 (32.1), 285 (169.7), 245 (66.9)	
9, $[Ru(bpy)_2tpphzOs(bpy)_2]^{4+}$	628 (5.4), 439 (37.4), 370 (42.3), 351 (33.2), 284 (190.1), 245 (75.3)	618 (0.008); 440
6, $[Ru(bpy)_2tpphzRu(NH_3)_4]^{4+}$	455 (20.1), 373 (31.1), 354 (22.2), 280 (116.5), 246 (44.2)	617 (0.025); 455

[a] PF_6 salts in acetonitrile unless otherwise stated. [b] λ_{irr} = irradiation wavelength; rel int = relative intensity with respect to 3.18 μM $[Ru(bpy)_3]^{2+}$ in the same conditions, excitation at 450 nm; λ_{max} = maximum emission wavelength. [c] Measured in acetonitrile with drops of trifluoroacetic acid. [d] From ref 12 in water. [e] From ref 22. [f] From ref 23.

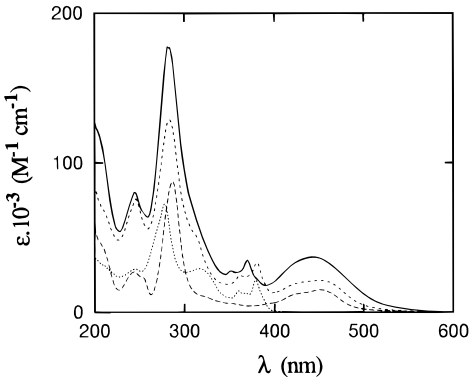

Figure 4. Absorption spectra of tpphz, **1** (protonated form) (···), $[(bpy)_2Ru(tpphz)]^{2+}$, **4** (---), $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$, **7** (—), and $[Ru(bpy)_3]^{2+}$ (— —) as their PF_6 salts, in acetonitrile solution at room temperature.

very close to that of the corresponding $[M^{II}(bpy)_3]^{2+}$. The lowest energy MLCT band related to HOMO → LUMO is probably very weak. As indicated above, this LUMO is mainly localized on the phenazine nitrogen atoms, with very small coefficients on the phenanthroline nitrogen atoms. It has been shown by Kaim et al.[24−28] that the extinction coefficients are directly correlated to the molecular orbital coefficients through small oscillator strength. This weak absorption is overlapped by the intense HOMO to LUMO+1 and HOMO to LUMO+2 bands involving two unoccupied orbitals with large coefficients on the phenanthroline part of **1** and on the $M(bpy)_2$ fragments and with a MO composition similar to that found in $[(M(bpy)_3]^{2+}$ complexes.

At higher energy (350−390 nm), the spectra display two sharp bands characteristic of **1**, corresponding to (tpphz)n → π^* and (tpphz)π → π^* transitions, with increasing energy from the free protonated ligand **1**, to **5**, **4**, **6**, and then **7**−**9**. Below 350 nm, the strong bands can be attributed to (bpy)π → π^* and (tpphz)π → π^*.

Electrochemistry. The electrochemical behaviors of the complexes **4**−**9** have been studied in acetonitrile and in DMF (Table 3). In acetonitrile, except for **5**, the reductions are not well-behaved, probably due to the adsorption of the reduced species onto the surface of the platinum electrode, and show abrupt and sharp adsorption and desorption spikes. In DMF this phenomenon disappears, and the complexes display several reversible reduction processes.[29] In this solvent, it was not always possible to observe the oxidative waves due to limitation by the solvent. Therefore, the oxidation potentials have been recorded in acetonitrile whereas the reduction potentials have been recorded in DMF (Table 3). Due to the poor solubility of the free tpphz, it has not been possible to study its electrochemical behavior. The number of electrons involved in each redox process has been estimated by linear and pulsed differential voltammetry.

Cyclic voltammograms of the monometallic complexes **4** and **5** and bimetallic complexes **6**−**9** are consistent with metal-based reversible oxidations and several ligand-based reductions. The oxidation potentials are very close to those of the corresponding $[(bpy)M(dppz)]^{2+}$ and $[M(bpy)_3]^{2+}$ (M = Ru or Os) analogues, with little influence of the strong π-accepting character of **1**. This is again consistent with the fact that the HOMO has little contribution from the phenazine part. For the dimetallic species, the oxidation potentials are not much affected by the second complexation. Hence, in **6**, the oxidation of the $(tpphz)Ru^{II}(NH_3)_4^{2+}$ moiety (0.61 V) is between that obtained in similar monometallic complex $[(bpym)Ru^{II}(NH_3)_4]^{2+}$ (0.66 V)[25] (bpym = 2,2′-bipyrimidine) and in $[(bpy)Ru^{II}(NH_3)_4]^{2+}$ (0.51 V).[30] Furthermore, the voltammograms of the homodinuclear complexes **7** and **8** show only one two-electron reversible oxidation wave. This confirms that the long intermetallic distance, 12.7 Å from the X-ray structure of **7**,[7] precludes any important coulombic interaction between these remote metallic centers. The complex **6** contains the solvent-sensitive moiety $Ru^{II}(NH_3)_4$ and is similar to other bimetallic complexes for which the redox potentials could be tuned by varying the solvent.[25] For instance, in DMF (Gutmann donor number (DN) = 26.6)[25b,26], $E_{1/2}(Ru^{II}(NH_3)_4)$ = 0.46 V. This cathodic shift of 0.15 V vs CH_3CN (DN = 14.1) is consistent with a better stabilization of the ammine part in DMF than in CH_3CN.

Except for **6**, which shows two irreversible waves, the reduction parts of the cyclic voltammograms display successive reversible reduction processes (Scheme 2). In contrast with the oxidation properties, the first one-electron reduction processes

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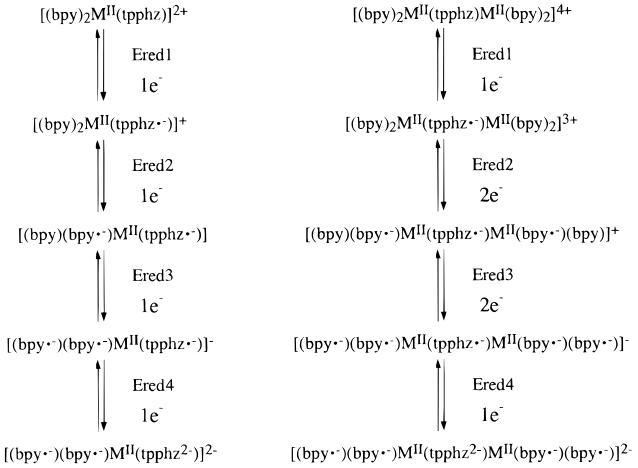
(29) This behavior has also been observed in similar complexes containing large aromatic ligands; see for example: (a) Richter, M. M.; Brewer, K. J. *Inorg. Chem.* **1993**, *32*, 2827. (b) Downard, A. J.; Honey, G. E.; Phillips, L. F.; Steel, P. J. *Inorg. Chem.* **1991**, *30*, 2259.
(30) Juris, A.; Barigelletti, S.; Campagna, S.; Balzani, V.; Belser, P.; von Zelewski, A. *Coord. Chem. Rev.* **1988**, *84*, 85 and references therein.

Table 3. Half-Wave Potentials E (V) for the Oxidation E_{ox} and the Reduction E_{red} of the Complexes[a,b]

species	E_{ox1}	E_{ox2}	E_{red1}	E_{red2}	E_{red3}	E_{red4}
$[Ru(bpy)_3]^{2+}$ [c]	1.27		−1.31	−1.50	−1.77	
$[Os(bpy)_3]^{2+}$ [d]	0.78		−1.30	−1.48	−1.78	
$[Ru(bpy)_2(dppz)]^{2+}$ [e]	1.33		−0.88	−1.31	−1.51	−1.83
4, $[Ru(bpy)_2(tpphz)]^{2+}$	1.33		−0.87	−1.33	−1.51	−1.73
5, $[Os(bpy)_2(tpphz)]^{2+}$	0.88		−0.87	−1.24	−1.53	−1.79
6, $[Ru(bpy)_2(tpphz)Ru(NH_3)_4]^{4+}$	0.61 $Ru(NH_3)_4$	1.32 $Ru(bpy)_2$	−0.81 *ir*	−1.27 *ir*	ca −1.51 *ir*	
7, $[Ru(bpy)_2(tpphz)Ru(bpy)_2]^{4+}$	1.34 (2 Ru)		−0.71	−1.31 (2 e$^-$)	−1.51 (2 e$^-$)	−1.72
8, $[Os(bpy)_2(tpphz)Os(bpy)_2]^{4+}$	0.89 (2 Os)		−0.70	−1.21 (2 e$^-$)	−1.44 (2 e$^-$)	
9, $[Ru(bpy)_2(tpphz)Os(bpy)_2]^{4+}$	0.89 (Os)	1.33 (Ru)	−0.70	−1.27 (2 e$^-$)	−1.48 (2 e$^-$)	−1.66[f]

[a] Unless otherwise noted the oxidation potentials are given *vs* SCE in CH_3CN and the reduction potentials are given *vs* SCE in DMF; in both cases the supporting electrolyte is 0.1 M NBu_4PF_6 at room temperature; scan speed 0.1 V s^{-1}. [b] All complexes are PF_6 salts unless otherwise stated. [c] From ref 27. [d] From ref 28 after reference electrode correction (−0.04 V). [e] Obtained vs SCE from ref 17 by addition of Fc/Fc^+ potential (0.48 V) correction. [f] Supplementary reversible wave at −2.06 V.

Scheme 2. Reduction Processes of the Monometallic **4** and **5** and the Dimetallic **7**−**9** Complexes



show that these complexes are significantly better electron acceptors than $[M(bpy)_3]^{2+}$ (M = Ru or Os) by *ca.* 0.4 V for the monometallic **4** and **5**, and by *ca.* 0.55 V for the bimetallic **6**−**9**. This is consistent with the addition of one electron on the low energy LUMO mainly localized on the phenazine part of **1** to give complexes $[(bpy)_2M(tpphz^{\bullet-})]^+$ or $[(bpy)_2M(tpphz^{\bullet-})M(bpy)_2]^{3+}$. Furthermore, addition of traces of water in the DMF solutions of **4** and **7** induces a 25 mV anodic shift which can be attributed to a protonation of the phenazine part. As expected, this π^* LUMO for the monometallic **4** or **5** is stabilized by further complexation by *ca.* 70 mV. In our case this stabilization of the tpphz π^* orbital by addition of a second $M(bpy)_2^{2+}$ is significantly smaller than for most bimetallic analogues, where the anodic shift of the first reduction is in the 300−400 mV range.[2f] Again, this small shift can be attributed to the small overlap of the LUMO with the metallic ends.

The second reductions at around −1.3 V add one (for **4** and **5**) or two (for **7**−**9**) electrons in the bpy type LUMO+1. These values are close to the first reduction potentials of $[M(bpy)_3]^{2+}$ (M = Ru or Os) and significantly less negative than the second reduction for most α-diimine complexes $[Ru(bpy)_2L]^{2+}$.[24b,26] This indicates that there is no interaction with the first electron in the LUMO, which would have shifted the potential toward more negative potentials. This contrasts with most other bridging ligands in which the second reduction in the bimetallic complex is at a potential comparable to the first reduction in the corresponding monometallic complex, and is attributed to a second reduction of the bridging ligand.[31] It is therefore very likely that this second electron is located on one of the two 2,2′-bipyridine ligands on each metallic end, to give the species $[(bpy)(bpy^{\bullet-})M(tpphz^{\bullet-})]$ or $[(bpy)(bpy^{\bullet-})M(tpphz^{\bullet-})M(bpy^{\bullet-})(bpy)]^+$. Just as for the oxidation, in the case of the dinuclear **7**−**9**, the two one-electron reductions of the remote bpy appear again at the same potential, indicating that the two sites are not interacting. The same reasoning can be applied to the third reductions which appear at around −1.5 V, *i.e.* only 0.2 V above the second reduction potential, at values close to the second reduction potentials for $[M(bpy)_3]^{2+}$ (M = Ru or Os). Therefore these third reductions yield the species $[(bpy^{\bullet-})(bpy^{\bullet-})M(tpphz^{\bullet-})]^-$ or $[(bpy^{\bullet-})(bpy^{\bullet-})M(tpphz^{\bullet-})M(bpy^{\bullet-})(bpy^{\bullet-})]^-$. As expected for bpy-localized processes, these second and third reductions are not sensitive to traces of water.

The fourth reduction potentials at around −1.7 V are one-electron processes for both the monometallic and the dimetallic complexes. They could correspond to a second reduction of the complexed tpphz. As noted by Kaim *et al.* for dppz complexes,[17] the potential difference between the first reduction and the second reduction of tpphz ($E_{red1} - E_{red4} = 0.9$ V for the mononuclear **4** and **5**, 1.0 V for the dinuclear complexes **7**−**9**) is the same as for phenazine.[32] Traces of water cause an anodic shift of 80 mV, again assumed to be related to a protonation of the very basic phenazine nitrogen atoms of the doubly charged $tpphz^{2-}$.

Luminescence. Preliminary luminescence studies show that all of the complexes **4**−**8**, but not the homodinuclear osmium complex **6**, are luminescent in dry acetonitrile when irradiated in the MLCT transition (Table 2). The mononuclear ruthenium complex **4** shows substantial luminescence with a maximum at 616 nm, a value very close to that of $[Ru(bpy)_3]^{2+}$. The mononuclear osmium complex **5** is also luminescent with a maximum at 738 nm, with a smaller luminescence quantum yield as always observed for the osmium complexes.[33] The emission wavelengths of the complexes **6** (617 nm) and **9** (618 nm), which can be considered to be made of a complex **4** linked to a nonemitting fragment $Ru(NH_3)_4$ or a weakly emitting $Os(bpy)_2$, are the same as for **4**. However, the quantum yields are much smaller, due to partial oxidative quenching of the luminescence of the $(bpy)_2Ru(tpphz)$ moiety.

This luminescence is quenched by water and only very weak emission is observed in aqueous medium (*ca.* 250-fold weaker than in acetonitrile). The luminescence of the mononuclear **4** and **5** in aqueous medium (Tris buffer, pH 7.5) is restored by

(31) See for example: (a) Richter, M. M.; Brewer, K. J. *Inorg. Chem.* **1992**, *31*, 1594. (b) Richter, M. M.; Brewer, K. J. *Inorg. Chem.* **1993**, *32*, 2827.
(32) (a) Kaim, W. *Angew. Chem., Int. Ed. Engl.* **1983**, 22, 171. (b) Schultz, A.; Kaim, W. *Chem. Ber.* **1991**, *124*, 129.
(33) Juris, A.; Balzani, V.; Campagna, S.; Denti, G.; Serroni, S.; Frei, G.; Güdel, H. *Inorg. Chem.* **1994**, *33*, 1491.

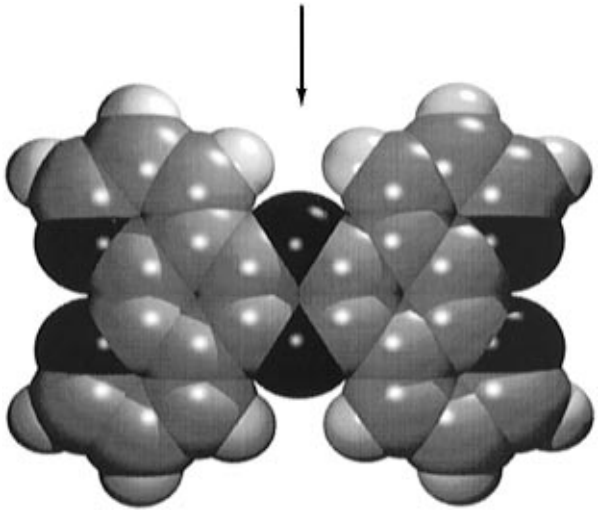


Figure 5. CPK model for **1** obtained from the X-ray structure coordinates of **7**.[7]

addition of DNA (enhancement 80 times). This behavior is very similar to that of $[(bpy)_2Ru(dppz)]^{2+}$ and can probably be interpreted in the same way. As indicated previously, upon irradiation in the MLCT band, the first charge transfer gives the excited state $*Ru^{III}(bpy)_2(tpphz^{\bullet -})$. In this state, the electron on the reduced tpphz is located in an orbital with high MO coefficients on the non-coordinating phenazine nitrogen atoms; this should significantly increase their basicity[34] and allow then proton transfer or H-bond formation. As shown in Figure 5, the access of electrophiles to these basic centers is partially impeded by steric crowding, which is even more important for **1** than for dppz. Only small electrophiles, such as H^+, can access the nitrogen atoms buried in this hydrophobic environment, and this access is even more difficult for tpphz than for dppz. In hydrophobic media, or when the complex is intercalated in DNA, the tpphz nitrogen atoms are fully shielded from water preventing then proton quenching.

In conclusion, we have synthesized two monometallic ruthenium and osmium complexes containing the fully conjugated tpphz ligand. Taking advantage of the bridging character of this ligand, we have prepared a series of homo and heterodinuclear ruthenium and osmium complexes. We are currently extending this strategy to longer bridging ligands and to oligonuclear complexes. Our findings have shown that, in many aspects, the "molecular switch" properties of these tpphz complexes were very close to that of the much studied dppz complexes. Future investigations will focus on interactions with DNA, and on photophysical and electrochemical properties of these products.

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(34) Kirsch-De Mesmaeker, A.; Jacquet, L.; Nasielski, J. *Inorg. Chem.* **1988**, *27*, 4451.