

# Highly Coupled Mixed-Valence Dinuclear Ruthenium and Osmium Complexes with a Bis-Cyclometalating Terpyridine Analogue as Bridging Ligand

Marc Beley, Jean-Paul Collin,\* and Jean-Pierre Sauvage

Contribution from the Laboratoire de Chimie Organo-Minérale, UA 422 au CNRS, Faculté de Chimie, Université Louis Pasteur, 67000 Strasbourg, France

Received June 22, 1993\*

The dinuclear complexes (tterpy)M(tpbp)M(tterpy)<sup>2+</sup> (M = Ru(II) or Os(II)), tterpy = 4',-p-tolyl-2,2':6',2''-terpyridine, tpbpH<sub>2</sub> = 3,3',5,5'-tetrapyritydylbiphenyl) have been prepared by oxidative coupling of the corresponding monomers M(tterpy)(dpb)<sup>+</sup> (dpbH = 1,3-di-*o*-pyridylbenzene). Spectrochemical and electrochemical properties of the monomers and dimers in different oxidation states are described. Chemical or electrochemical oxidation of the M(II)–M(II) species leads to the mixed-valence M(II)–M(III) dimer. The comproportionation constants *K*<sub>c</sub> determined by cyclic voltammetry (600 and 100 for Ru and Os, respectively) reflect the high stability of the M(II)–M(III) states. In addition, the near-infrared spectrum of each mixed-valence ion exhibits a very intense intervalence transfer (IT) transition. Although the two metal centers are separated by a large distance (11 Å), the matrix elements *V*<sub>ab</sub> are relatively large (0.15 and 0.12 eV for Ru and Os, respectively). This demonstrates the surprisingly high coupling ability of the bis-cyclometalating bridging ligand tpbp<sup>2-</sup>.

Long-range electron transfer and photoinduced charge separation are essential processes related to the development of molecular electronic<sup>1</sup> and solar energy conversion<sup>2</sup> devices. Molecular systems incorporating multivalent metals at a fixed relative distance and orientation are particularly attractive. Electronic coupling between metal centers varies strongly with the distance between the metals. It also strongly depends on the nature of the ligand bridging the two centers. If long-range electronic communication is desired, it will be important to design and use bridging ligands insuring as strong a coupling as possible. The seminal work of Creutz and Taube on 1,4-pyrazine-bridged Ru<sup>II</sup>,Ru<sup>III</sup> mixed-valence complexes<sup>3,4</sup> has been followed up by numerous studies on related d<sup>5</sup>–d<sup>6</sup> systems incorporating various bridging ligands.<sup>4,5</sup> Short bridges may sometimes lead to highly coupled systems due to  $\pi$ -communication. Various examples include (CN)<sub>2</sub>, N<sub>2</sub>,  $\mu$ - $\eta^2$ : $\eta^2$ -benzene, the anionic ligand N≡C–C(*t*-Bu)–C≡N<sup>4,6,7</sup> and bis-chelates containing an azo (–N=N–) group.<sup>8</sup>

Most of the other mixed-valence diruthenium complexes studied and containing more than five atoms between the two metal centers are only modestly coupled; i.e., they are class II complexes.<sup>4</sup> Among them, (bipy)<sub>2</sub>Ru(Cl)L(Cl)Ru(bipy)<sub>2</sub><sup>n+</sup> (bipy = 2,2'-bipyridine) systems (L = 4,4'-bipyridine or other bridge) have been particularly well studied by Meyer et al.<sup>9</sup> Very long bridges leading to a metal-to-metal distance in the nanometer range have also been examined. A few typical examples using Ru<sup>II</sup>,Ru<sup>III</sup> are those based on thioethers connected by a rigid saturated bridge<sup>10</sup> or 4,4'-bipyridyl ligands in which the two pyridine subunits are connected via their 4-positions either by a polyene<sup>11</sup> or a

polyphenylene<sup>12</sup> linker. Two recently reported examples exhibit relatively strong communication between dinuclear complexes bridged by ligands which span an appreciably long distance. The systems described make use of the dianion of 1,4-dicyanoamido-2,3,5,6-tetrachlorobenzene<sup>13</sup> or 4,4'-dithiobipyridine,<sup>14</sup> the latter case providing strong evidence for the marked efficiency of S–S bridges to conduct electrons.

In a preliminary communication, we recently reported that a bis-cyclometalating bridging ligand, tpbp<sup>2-</sup> (tpbpH<sub>2</sub> = 3,3',5,5'-tetrapyritydylbiphenyl) is able to strongly couple the two ruthenium centers in a mixed valence complex.<sup>15</sup> We now describe the bis-osmium analogue as well as some of the detailed physical properties of both the ruthenium and osmium systems.

## Experimental Section

**Instrumentation.** <sup>1</sup>H NMR spectra were acquired on a Bruker WP 200 SY instrument. Chemical shifts are reported referenced to Me<sub>4</sub>Si as an internal standard. Mass spectra were obtained by using VG ZAB-HF and Thomson THN 208 mass spectrometers. UV–visible absorption spectra were recorded with a Kontron Uvikon 860 and near-infrared spectra were recorded on a Cary Model 17D spectrophotometer.

Electrochemical measurements were made at room temperature on a Bruker EI 310M potentiostat with a three-electrode system in CH<sub>3</sub>CN containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte. The working electrode was a platinum disk electrode or a hanging mercury drop electrode. The potentials were reported versus saturated potassium chloride calomel electrode (SCE).

**Oxidation Experiments.** Oxidations to generate the mixed-valence M(II)–M(III) or the M(III)–M(III) species (M = Ru or Os) were performed in CH<sub>3</sub>CN using either Br<sub>2</sub> or controlled-potential electrolyses. Quantitative calculations on the mixed-valence dimers have been corrected for the small amounts of the M(II)–M(II) and M(III)–M(III) ions present at equilibrium.

**Chemicals.** High-purity commercial reagent grade materials were used without purification. Ru(tterpy)Cl<sub>3</sub><sup>16</sup> and Os(tterpy)(O<sub>2</sub>)(OH)(NO<sub>3</sub>)<sup>17</sup> were prepared as previously described.

- \* Abstract published in *Advance ACS Abstracts*, September 15, 1993.
- (1) *Molecular Electronics*; Ashwell, G. J., Ed., RSP Ltd.: Taunton, England, 1991.
  - (2) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: Chichester, England, 1991.
  - (3) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988.
  - (4) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.
  - (5) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.
  - (6) Krentzien, H.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 6379.
  - (7) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883.
  - (8) Ernst, S.; Kassack, V.; Kaim, W. *Inorg. Chem.* **1988**, *27*, 1146.
  - (9) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289 and references cited therein.
  - (10) Stein, C. A.; Lewis, N. A.; Seitz, G. J. *J. Am. Chem. Soc.* **1982**, *104*, 2596.
  - (11) Weitellier, S.; Launay, J. P.; Spangler, C. W. *Inorg. Chem.* **1989**, *28*, 758.

- (12) Kim, Y.; Lieber, C. M. *Inorg. Chem.* **1989**, *28*, 3990.
- (13) Aquino, M. A. S.; Lee, F. L.; Gabe, E. J.; Bensimon, C.; Greedan, J. E.; Crutchley, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5130.
- (14) De Sousa Moreira, I.; Wagner Franco, D. *J. Chem. Soc., Chem. Commun.* **1992**, 450.
- (15) Beley, M.; Collin, J.-P.; Louis, R.; Metz, B.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8521.
- (16) Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404.
- (17) Collin, J.-P.; Guillerez, S.; Sauvage, J.-P. *Inorg. Chem.* **1990**, *29*, 5009.

**1,3-Di-*o*-pyridylbenzene: dpb-H.** This ligand was prepared according to a synthetic method previously described for 1,4-di-*p*-pyridylbenzene.<sup>18</sup> 1,3-Dicyanobenzene (4 g, 31.2 mmol) and Co(Cp)COD (0.1 g, 0.43 mmol) dissolved in 40 mL of toluene were loaded in an autoclave under 10 atm of acetylene. The autoclave was heated to 130 °C for 3 days. After cooling, the toluene was evaporated. The oil obtained was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered through celite. After chromatography (silica; CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH as eluent), dpbH was obtained as a colorless oil (6.5 g, 90%). <sup>1</sup>H NMR (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.7 (m, 3H), 8.09 (d, 2H, 2 Hz), 8.06 (dd, 2H, 2 Hz), 7.85 (m, 4H), 7.58 (t, 1H, 8 Hz), 7.27 (ddd, 2H, 7, 4, 1.5 Hz). MS: *m/z* = 232; C<sub>16</sub>H<sub>12</sub>N<sub>2</sub> requires 232.

**Ru(tterpy)(dpb)(PF<sub>6</sub>)<sub>2</sub>: 1<sup>+</sup>PF<sub>6</sub><sup>-</sup>.** A mixture of Ru(tterpy)Cl<sub>3</sub> (0.53 g, 1.0 mmol) and AgBF<sub>4</sub> (0.63 g, 3.2 mmol) in acetone (100 mL) was refluxed for 2 h under air. After filtration, the solvent was evaporated and the mauve residue was dissolved in *n*-BuOH (50 mL). To this solution was added dpbH (0.23 g, 1.0 mmol) and the solution heated at reflux for 6 h. After cooling and filtration, the filtrate was added to an aqueous solution of KPF<sub>6</sub> (0.4 g in 100 mL of water). The precipitate formed was washed successively with water (100 mL), toluene (100 mL), and ether (50 mL). The residue was purified by silica gel chromatography eluting with CH<sub>3</sub>CN-aqueous solution of KNO<sub>3</sub> mixture (90:10, KNO<sub>3</sub> 0.1 M) (0.64 g, 80%). <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN): δ 8.98 (s, 2H), 8.55 (d, 2H, 8 Hz), 8.25 (d, 2H, 8 Hz), 8.16 (m, 4H), 7.70 (td, 2H, 8.2 Hz), 7.56 (m, 4H), 7.45 (t, 1H, 8 Hz), 7.09 (m, 4H), 6.94 (m, 2H), 6.65 (m, 2H), 2.51 (s, 3H). FAB-MS (nitrobenzyl alcohol matrix): *m/z* 656.1; Ru(tterpy)(dpb)<sup>+</sup> requires 656.

**Ru<sub>2</sub>(tterpy)<sub>2</sub>(tpbp)(PF<sub>6</sub>)<sub>2</sub>: 2<sup>2+</sup>[PF<sub>6</sub><sup>-</sup>]<sub>2</sub>.** A mixture of 1<sup>+</sup> (0.4 g, 0.5 mmol) and AgBF<sub>4</sub> (0.97 g, 5 mmol) in 20 mL of *n*-BuOH was refluxed for 5 h. After evaporation of *n*-BuOH, the residue was dissolved in CH<sub>3</sub>CN (50 mL). The black solution was treated by an aqueous solution of KPF<sub>6</sub> (0.2 g in 50 mL of water). The precipitate obtained was washed with water (100 mL), and the mixture of ruthenium complexes was separated by silica gel chromatography. Elution with KNO<sub>3</sub> in a CH<sub>3</sub>CN-water mixture (85:15; KNO<sub>3</sub> 0.1 M) gave 2<sup>2+</sup> (0.32 g, 80%). <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN): δ 9.05 (s, 4H), 8.97 (s, 4H), 8.62 (d, 4H, 8 Hz), 8.48 (d, 4H, 8 Hz), 8.14 (d, 4H, 8 Hz), 7.78 (d, 4H, 6 Hz), 7.04 (t, 4H, 6 Hz), 6.73 (t, 4H, 6 Hz), 2.53 (s, 6H). FAB-MS (nitrobenzyl alcohol matrix): *m/z* = 1455.2; Ru<sub>2</sub>(tterpy)<sub>2</sub>(tpbp)(PF<sub>6</sub>)<sub>2</sub> requires 1455.

**Ru(tterpy)(dpb)(PF<sub>6</sub>)<sub>2</sub> and Ru<sub>2</sub>(tterpy)<sub>2</sub>(tpbp)(PF<sub>6</sub>)<sub>4</sub>.** The starting ruthenium complex (25 μmol) was dissolved in 20 mL of CH<sub>3</sub>CN, and 0.2 mL of Br<sub>2</sub> was added to the stirring solution. Immediately, the solution turned from violet to green. Then, 20 mL of a saturated aqueous NH<sub>4</sub>PF<sub>6</sub> solution was added to the green solution. The green precipitate was isolated by filtration, washed with water (2 × 20 mL), and dried. A nearly quantitative yield of oxidized product was obtained.

**Os(tterpy)(dpb)(PF<sub>6</sub>)<sub>2</sub>: 3<sup>+</sup>PF<sub>6</sub><sup>-</sup>.** An aqueous solution (250 mL) of Os(tterpy)(O)<sub>2</sub>(OH)(NO<sub>3</sub>) (0.2 g, 0.32 mmol) was added to a solution of dpb-H (0.074 g, 0.32 mmol) in THF (250 mL). Hydrazine hydrate (5 drops) was added to the homogeneous solution previously heated to 50 °C. The mixture was stirred for 10 min and treated with an aqueous solution of KPF<sub>6</sub> (0.1 g in 40 mL of water). After removal of THF, the precipitate was separated by filtration and washed with water (50 mL). The crude product was submitted to silica gel chromatography under the same conditions as for compound 1<sup>+</sup>PF<sub>6</sub><sup>-</sup> (0.114 g, 40%). <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN): δ 9.00 (s, 2H), 8.57 (d, 2H, 8.2 Hz), 8.40 (d, 2H, 8 Hz), 8.12 (d, 2H, 8 Hz), 8.06 (d, 2H, 8 Hz), 7.55 (m, 4H), 7.43 (t, 1H, 8 Hz), 6.94 (m, 2H), 6.96 (d, 2H, 8 Hz), 6.50 (t, 2H, 7 Hz), 2.53 (s, 3H). FAB-MS: *m/z* = 746.2; Os(tterpy)(dpb)<sup>+</sup> requires 745.

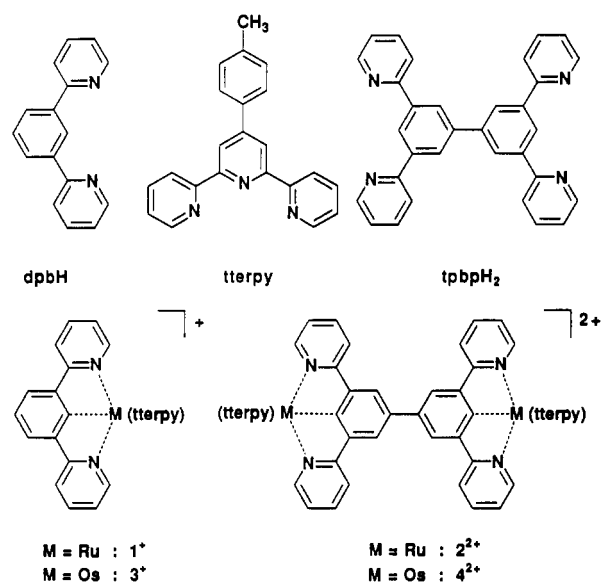
**Os<sub>2</sub>(tterpy)<sub>2</sub>(tpbp)(PF<sub>6</sub>)<sub>2</sub>: 4<sup>2+</sup>[PF<sub>6</sub><sup>-</sup>]<sub>2</sub>.** This compound was synthesized as described for 2<sup>2+</sup>. It was purified by silica gel chromatography. Elution with CH<sub>3</sub>CN-aqueous solution of KNO<sub>3</sub> mixture (85:15, KNO<sub>3</sub> 0.1 M); (0.037 g, 14%) <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN): δ 9.05 (s, 4H), 9.01 (s, 4H), 8.64 (d, 4H, 8 Hz), 8.49 (d, 4H, 8 Hz), 8.09 (d, 4H, 8 Hz), 7.53 (m, 12H), 7.27 (d, 4H, 6 Hz), 6.95 (m, 8H), 6.63 (t, 4H, 6 Hz), 2.5 (s, 6H). FAB-MS (nitrobenzyl alcohol matrix) *m/z* = 1633.3, [Os<sub>2</sub>(tterpy)<sub>2</sub>(tpbp)(PF<sub>6</sub>)<sub>2</sub>]<sup>+</sup> requires 1632.7.

## Results and Discussion

**Synthesis of Ligands and Complexes.** The compounds studied and their precursors are represented in Chart I.

The ligand precursor dpb-H was prepared in good yield from 1,3-dicyanobenzene and acetylene in the presence of a cobalt

Chart I



catalyst according to a synthetic method previously described by Bönneemann for 1,4-di-*p*-pyridylbenzene.<sup>18</sup> Contrary to the isomeric product 6-phenyl-2,2'-bipyridine, which is a crystalline white powder, dpb-H was obtained as a colorless oil despite its higher symmetry. The deprotonated product of dpb-H, dpb<sup>-</sup>, is a potentially terdentate ligand, isostructural to terpy (2,2':6',2''-terpyridine). It contains a central  $\sigma$ -phenyl coordination site. A related N-C-N terdentate ligand, the monoanionic aryldiamine [C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6]<sup>-</sup> has extensively been used in the preparation of various complexes including Ni(II), Pt(II), Pd(II), and Ta(IV) centers.<sup>19</sup> Originally we used a cyclometalating ligand in a ruthenium complex in order to better separate the MLCT and the LF states.<sup>20</sup> Indeed, replacing one neutral terpyridine ligand with an anionic C-N-N or N-C-N coordinating subunit leads to a luminescent ruthenium complex at room temperature.

The monomer complex 1<sup>+</sup> can easily be prepared by mixing the solvate precursor Ru(tterpy)L<sub>3</sub><sup>2+</sup> (L = acetone) with dpb-H in 1-butanol and heating the mixture under reflux for 6 h. The precursor Ru(tterpy)L<sub>3</sub><sup>2+</sup> was not isolated nor characterized. It was prepared from Ru(tterpy)Cl<sub>3</sub> and AgBF<sub>4</sub> in excess as dechlorinating agent. In the course of this preparation, depending upon the amount of AgBF<sub>4</sub> added, an additional dinuclear compound was obtained. It was assumed to be [Ru<sub>2</sub>(tterpy)<sub>2</sub>(tpbp)]<sup>2+</sup> on the basis of its <sup>1</sup>H NMR spectrum (sharp singlet for the 4'- and 6'- protons) and FAB-MS measurements. The X-ray structure of the complex shown in Figure 1 fully confirmed its chemical nature. This dinuclear complex could also be generated by reacting the mononuclear complex with a large excess of AgBF<sub>4</sub> used as an oxidant. In Table I are reported some factors related to the efficiency of the reaction affording the dinuclear ruthenium compound. Two main points should be noted. First, the presence of Ag<sup>+</sup> is essential to the production of the dimer. For example, increasing the amount of Ag<sup>+</sup> (runs 2, 3, and 4) leads to an increase of dimer formation. Second, the presence of oxygen during the reaction is also of great importance (runs 4 and 6). It seems that coordinating solvents such as acetonitrile or butyronitrile inhibit the dimer formation. Other additives used in catalytic amount, such as Ru(tterpy)Cl<sub>3</sub> or RuO<sub>2</sub>, have no measurable effect while the use of strong oxidants like Ce(IV) salts destroys the starting complex.

- (19) Abbenhuis, H. C. L.; Feiken, N.; Grove, D. M.; Jastrzebski, J. T. B. H.; Kooijman, H.; Van der Sluis, P.; Smeets, W. J. J.; Spek, A. L.; Van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9773 and references therein.  
 (20) Collin, J.-P.; Beley, M.; Sauvage, J.-P.; Barigelletti, F. *Inorg. Chim. Acta* **1991**, *186*, 91.

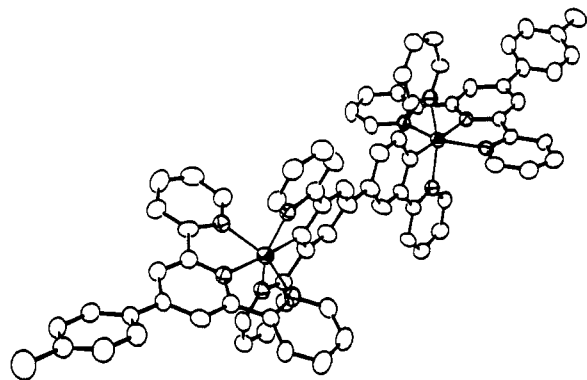


Figure 1. ORTEP drawing of the non-hydrogen atoms of the dinuclear complex  $2^{2+}$ .<sup>15</sup>

Table I. Preparation of the Mononuclear and Dinuclear Ruthenium(II) Complexes

run	starting complex	AgBF <sub>4</sub> in μmol	atmosphere	% yield	
				1 <sup>+</sup>	2 <sup>2+</sup>
1	Ru(tterpy)Cl <sub>3</sub> , 94 μmol	138	air	100	0
2		310		100	0
3		466		20	80
4		1540		40	60
5		310	argon	100	0
6		1540	argon	0	0
7	Ru(tterpy)(dpb) <sup>+</sup> , 6.2 μmol		air	100	0
8		120		20	80
9		310		20	80
10		250		90	10
11		310		0	0

<sup>a</sup> Conditions: runs 1–6, 94 μmol of dpb-H; runs 1–9, *n*-butanol as solvent; run 10, acetonitrile as solvent; run 11, butyronitrile as solvent.

Formation of a C–C coupling product from dpb-H is not obvious from a mechanistic viewpoint. It is likely to involve radicals located on the 5'-positions of the central ring. Once coordinated to the ruthenium (II) center, this position becomes relatively oxidizable after formation of the Ru–C<sub>2</sub> bond. In fact, coupling of radicals located on coordinated ligands has precedent.<sup>21,22</sup> What was completely unexpected in the present reaction was the dual function of Ag<sup>+</sup> acting both as a Lewis acid in order to displace the Cl<sup>-</sup> ligands in a very classical way and as an electron acceptor. The selectivity of the coupling reaction is also remarkable since no other coupling products than those involving the 5'-position of dpb<sup>-</sup> could be detected. It can even be speculated that the central ring of the coordinated dpb<sup>-</sup> ligand forms an intermediate  $\pi$ -complex with Ag<sup>+</sup> prior to electron transfer, radical generation, and deprotonation. The role of O<sub>2</sub> is at the present stage unclear.

The osmium (II) dinuclear complex [Os(tterpy)<sub>2</sub>]<sub>2</sub>tpbp<sup>2+</sup> has been prepared following a slightly different route. The mononuclear osmium(II) complex Os(tterpy)(dpb)(PF<sub>6</sub>) was synthesized from an osmium(VI) mono(terpyridine) complex where three coordination sites are oxo and hydroxo groups. This complex is a particularly attractive precursor in the synthesis of functionalized asymmetrical bis(terpyridine)osmium (II) complexes.<sup>17</sup> Its reduction by hydrazine in the presence of dpb-H leads to the coordination of N–C–N donor groups under very mild conditions. Treatment of the mononuclear osmium(II) complex under the same conditions as those used for the ruthenium complex (excess of Ag<sup>+</sup> in refluxing *n*-BuOH) affords the dinuclear osmium complex in 14% yield. Partial oxidation and decomposition during the purification step is probably the reason for this low yield.

**Electrochemical Measurements.** The electrochemical data for the mononuclear and dinuclear ruthenium and osmium compounds

Table II. Electrochemical Data for Ruthenium and Osmium Complexes Containing tterpy, dpb<sup>-</sup>, and tpbp<sup>2-</sup> Ligands

compound	E <sub>1/2</sub> , V vs SCE			K <sub>c</sub>
Ru(tterpy)(dpb) <sup>+</sup>	0.485		-1.610	
Ru <sub>2</sub> (tterpy) <sub>2</sub> (tpbp) <sup>2+</sup>	0.505	0.340	-1.550	600
Os(tterpy)(dpb) <sup>+</sup>	0.335		-1.600	
Os <sub>2</sub> (tterpy) <sub>2</sub> (tpbp) <sup>2+</sup>	0.340	0.220	-1.530	100
Ru(tterpy) <sub>2</sub> <sup>2+</sup> <sup>a</sup>	1.250		-1.240	
Os(tterpy) <sub>2</sub> <sup>2+</sup> <sup>a</sup>	0.890		-1.170	

<sup>a</sup> Collin, J.-P.; et al. *Inorg. Chem.* **1991**, *30*, 4230; **1992**, *31*, 4112.

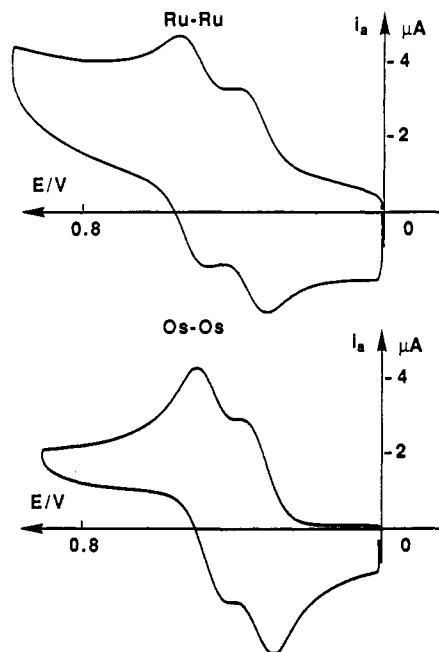


Figure 2. Cyclic voltammograms of the dinuclear complexes  $2^{2+}$  (top) and  $4^{2+}$  (bottom) in CH<sub>3</sub>CN (0.1 M *n*-Bu<sub>4</sub>BF<sub>4</sub>). Conditions: Pt electrode;  $\nu = 100$  mV s<sup>-1</sup>.

are presented in Table II. The anodic region of the cyclic voltammograms is dominated by reversible waves corresponding to one-electron oxidation of the M(II) state while the cathodic region exhibits poorly defined waves resulting from reduction of the coordinated polypyridine ligands. As expected, the oxidation potentials of the osmium (II) complexes are about 150 mV lower than those in the ruthenium analogues.

The effect of cyclometalating dpb<sup>-</sup> ligand on the stability of the M(III) state is illustrated by the drastic shift of potential between the M(tterpy)(dpb)<sup>+</sup> and M(tterpy)<sub>2</sub><sup>2+</sup> species. Typically, a shift of 500–700 mV demonstrates the strong  $\sigma$ -donating character of the anionic dpb<sup>-</sup> species as compared to a terpy type ligand. Cyclic voltammograms of the dimers Ru(II)–Ru(II) and Os(II)–Os(II) are shown in Figure 2. The comproportionation constant  $K_c$  for the reaction  $M^{II}M^{III} + M^{III}M^{III} \rightleftharpoons 2M^{II}M^{III}$  was determined from the difference between the potential of the couples  $M^{III}M^{III}/M^{III}M^{II}$  and  $M^{III}M^{II}/M^{II}M^{II}$ . The calculated  $K_c$  has been determined following the method described by Myers and Shain<sup>23</sup> and extended by Richardson and Taube<sup>24</sup> for overlapping waves.

The values of  $K_c$  indicate the high stability of the  $M^{II}M^{III}$  state and a large degree of electronic coupling in these mixed-valence complexes. In the ruthenium case, the  $K_c$  value (600) is comparable to that in ClRu(bipy)<sub>2</sub>(pz)Ru(bipy)<sub>2</sub>Cl<sup>3+</sup> (pz is 1,4-pyrazine) in spite of the much larger distance between the metals (11.0 Å as compared to 6.8 Å for pz).<sup>25</sup> Another interesting comparison can be made with the complex (NH<sub>3</sub>)<sub>5</sub>Ru(4,4'-bipy)-

(21) Espinet, P.; Alonso, M. Y.; Garcia-Herbosa, G.; Ramos, J. M.; Jeannin, Y.; Philoche-Levisalles, M. *Inorg. Chem.* **1992**, *31*, 2501.

(22) Mountford, H.-S.; Spreer, L. O.; Otvos, J. W.; Calvin, M.; Brewer, K. J.; Richter, M.; Scott, B. *Inorg. Chem.* **1992**, *31*, 718.

(23) Myers, R. L.; Shain, I. *Anal. Chem.* **1969**, *41*, 980.

(24) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(25) Callahan, R. W.; Meyer, T. J. *Chem. Phys. Lett.* **1976**, *39*, 82.

**Table III.** Ultraviolet-Visible Spectral Data for the Ruthenium and Osmium Complexes in Acetonitrile

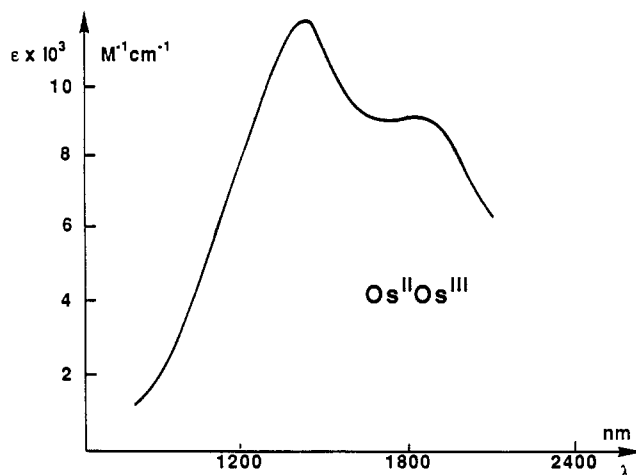
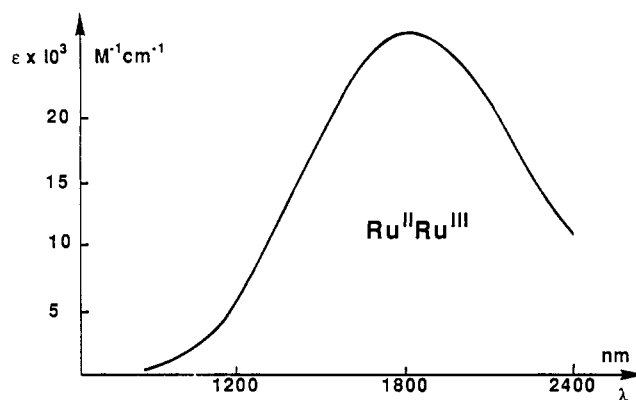
compound	$\lambda_{\max}$ , nm ( $\epsilon \times 10^4$ , $M^{-1} \text{ cm}^{-1}$ )
$\text{Ru}^{\text{II}}(\text{tterpy})(\text{dpb})^+$	506 (1.28), 372 (1.01), 286 (5.24), 244 (3.81)
$\text{Ru}^{\text{III}}(\text{tterpy})(\text{dpb})^{2+}$	656 (0.15), 414 (0.83), 272 (4.74)
$\text{Ru}^{\text{II}}\text{Ru}^{\text{II}}(\text{tterpy})_2(\text{tpbp})^{2+}$	543 (3.06), 516 (3.06), 287 (11.29), 220 (6.75)
$\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}(\text{tterpy})_2(\text{tpbp})^{2+}$	713 (8.3), 510 (0.44), 408 (1.78), 274 (20.4)
$\text{Os}^{\text{II}}(\text{tterpy})(\text{dpb})^+$	531 (1.28), 505 (1.32), 420 (1.18), 373 (1.36), 288 (4.78), 244 (3.98)
$\text{Os}^{\text{III}}(\text{tterpy})(\text{dpb})^+$	438 (0.49), 272 (3.78), 236 (1.54)
$\text{Os}^{\text{II}}\text{Os}^{\text{II}}(\text{tterpy})_2(\text{tpbp})^{2+}$	540 (3.54), 372 (4.52), 290 (12.25), 236 (7.91)
$\text{Os}^{\text{III}}\text{Os}^{\text{III}}(\text{tterpy})_2(\text{tpbp})^{2+}$	737 (5.43), 416 (2.39), 275 (18.76), 233 (7.93)

$\text{Ru}(\text{NH}_3)_5^{5+}$  in which the bridging ligand is 4,4'-bipyridine.<sup>9</sup> In this case a  $K_c$  value of 24 has been found for a distance (11.3 Å) very similar to that observed in the presently reported complex.

Otherwise, the difference between the  $K_c$  values of mixed-valence species of ruthenium and osmium is relatively small as previously observed for ruthenium and osmium complexes with diphosphine bridges.<sup>26,27</sup> Following the work of Sutton and Taube,<sup>5</sup> who had recognized four factors as determining the magnitude of the free energy of comproportionation ( $\Delta G_c$ ), we have estimated the weight of each factor. The contribution of the electrostatic factor has been taken as 150 cal mol<sup>-1</sup> by comparison with other mixed-valence complexes of analogous structure.<sup>5</sup> In the case of the  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  complex, we can conclude that the stabilization through electron delocalization of the valence (760 cal mol<sup>-1</sup> calculated from IT band) and the synergetic factor (570 cal mol<sup>-1</sup> of stabilization of  $\text{M}^{\text{II}}$  by  $\text{M}^{\text{III}}$  or vice versa) are the main contribution to  $\Delta G_c$  (1500 cal mol<sup>-1</sup>). The case of the  $\text{Os}^{\text{II}}\text{Os}^{\text{III}}$  complex is very similar with a predominance of synergetic factor (670 cal mol<sup>-1</sup>) in relation to the electronic delocalization (130 cal mol<sup>-1</sup>).

**Ultraviolet and Visible Spectra.** Table III lists  $\lambda_{\max}$  and  $\epsilon_{\max}$  values for the ruthenium and osmium dimers and related monomers in their +2 and +3 state. All the divalent complexes exhibit intense  $\pi\pi^*$  transitions in the UV region and broad metal-to-ligand charge-transfer (MLCT) bands in the visible region. The osmium complexes spectra are more complex than those of the ruthenium analogues because of greater spin-orbit coupling in the osmium case. As expected, an intense MLCT band is also present in the mixed-valence species  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  and  $\text{Os}^{\text{II}}\text{Os}^{\text{III}}$ . Contrary to those of their related mononuclear complexes the UV-visible spectra of the dinuclear  $\text{M}^{\text{III}}\text{M}^{\text{III}}$  complexes ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ) display a very intense band ( $\epsilon = 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) at 720–730 nm probably due to a LMCT transition. This possible assignment can be made by comparison with two other  $\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$  complexes in which the bridging ligand is under an anionic form.<sup>6,13</sup> A LMCT band is also observed in the fully oxidized monomer complex ( $\text{I}^{2+}$  or  $\text{3}^{2+}$ ) but, unexpectedly, it is much weaker than in the corresponding  $\text{M}^{\text{III}}\text{M}^{\text{III}}$  dimer ( $\text{2}^{4+}$  or  $\text{4}^{4+}$ , respectively).

**Near-Infrared Spectra.** The near-infrared spectra of the  $\text{M}^{\text{II}}\text{M}^{\text{II}}$ ,  $\text{M}^{\text{II}}\text{M}^{\text{III}}$ , and  $\text{M}^{\text{III}}\text{M}^{\text{III}}$  complexes ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ) were recorded in acetonitrile from 900 to 2400 nm. As shown in Figure 3 the mixed-valence ions display broad and intense bands while no bands are found for the  $\text{M}^{\text{II}}\text{M}^{\text{II}}$  and  $\text{M}^{\text{III}}\text{M}^{\text{III}}$  ions. Whereas the  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  complex shows a single band of Gaussian shape, the  $\text{Os}^{\text{II}}\text{Os}^{\text{III}}$  complex presents two overlapping bands observed previously in dinuclear osmium complexes where large spin-orbit coupling takes place.<sup>27</sup> These bands can be assigned as intervalence transitions (IT) on the basis of their low energy and large band width. However, these bands are narrower ( $\Delta\nu_{1/2} = 2800$

**Figure 3.** Intervalence transfer band of the mixed-valence dimers  $2^{3+}$  (top) and  $4^{3+}$  (bottom) in  $\text{CH}_3\text{CN}$ .**Table IV.** Near-Infrared Spectral Data for the  $\text{Mn}^{\text{II}}\text{M}^{\text{III}}$  Dimers in Acetonitrile ( $\text{M} = \text{Ru}$  or  $\text{Os}$ )

compound	$\lambda_{\max}$ , nm ( $\epsilon \times 10^4$ , $M^{-1} \text{ cm}^{-1}$ )	$\Delta\nu_{1/2}$ , $\text{cm}^{-1}$	$V_{\text{ab}}$ , $\text{eV}^a$
$\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}(\text{tterpy})_2(\text{tpbp})^{3+}$	1820 (2.7)	2820	0.15
$\text{Os}^{\text{II}}\text{Os}^{\text{III}}(\text{tterpy})_2(\text{tpbp})^{3+}$	1410 (1.18) 1800 (0.80)	3360	0.12 <sup>b</sup>

<sup>a</sup> Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135. <sup>b</sup> Estimation assuming the higher energy band and the same distance between the metal centers in the two dinuclear complexes.

$\text{cm}^{-1}$ ) than expected from calculations following Hush's theory (3500  $\text{cm}^{-1}$ ) for localized mixed-valence systems.<sup>28</sup> Moreover, in the case of  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  its position maximum is virtually independent of the solvent (1820, 1829, 1835, and 1835 nm in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{COCH}_3$ , DMF, and DMSO, respectively), which tends to indicate that the  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  complex behaves similarly to class III systems. For both ruthenium and osmium complexes the value of the extinction coefficient ( $(0.8\text{--}2.7) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) is of the same order of magnitude as in fully delocalized systems.<sup>4</sup> Strong valence delocalization is suggested by these observations. It seems therefore difficult to assign clearly a well defined class to these new complexes. The spectral characteristics of IT bands and their calculated matrix elements  $V_{\text{ab}}$  assuming class II are reported in Table IV. The structural specificity of the present systems relies on the strong  $\sigma$ -donating character of the cyclometalating bridging ligand. Although molecular orbital calculations have not been carried out as yet, simple considerations may explain the strong coupling observed. In the delocalization factor as previously discussed, two terms have to be considered. The first one deals with  $\text{Ru}^{\text{II}}(\text{d}\pi) \rightarrow$  bridging ligand ( $\text{tpbp}^{2-}, \pi^*$ )

(26) Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 752.(27) Kober, E. M.; Goldsby, K. A.; Narayana, D. N. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4303.(28) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

charge transfer. The energy matching between the metal d orbitals with the LUMO of the bridge will be better if the use of a strong  $\sigma$ -donor ligand raises the level of the d $\pi$  orbitals. This is reflected by the position of the MLCT band, lying at significantly lower energy than in normal bis(terpyridine) complexes. The second parameter to be considered is related to charge transfer between the filled ligand orbitals (HOMO) and the trivalent metal; i.e. ligand  $\rightarrow$  d $\pi$ (M<sup>III</sup>). It can be assumed that for tpbp<sup>2-</sup>, which is a strong electron donor, this charge transfer contribution will also be important. Again, this can be ascertained by the presence of low-lying LMCT (ligand-to-metal charge transfer) bands in the absorption spectra of most of the trivalent complexes. By comparison with other bridged systems in which the distance between the metal centers is 11 Å, the diphenyl bridge leads to extremely strong coupling. Indeed a bridge constituted by 4,4'-bipyridyl (d = 11.3 Å) or 1,4-dicyanobenzene (d = 11.8 Å) leads to  $V_{ab}$  = 0.05 and 0.04 eV, respectively.<sup>4</sup> Other bridges formed

by 1,4-dicyanoamidobenzene dianion and its derivatives<sup>13</sup> lead to a  $V_{ab}$  of 0.023 eV. Surprisingly, in the case of the 4,4'-dithiobipyridine bridge<sup>14</sup>, a large value of  $K_c$  ( $8 \times 10^4$ ) seems to indicate a more intense coupling than with the bis(4-pyridyl) sulfide. Finally, we have also observed a strong interaction between the ruthenium(III) sites in the fully oxidized state. Preliminary experiments by EPR and magnetic susceptibility<sup>29</sup> measurements showed that the Ru<sup>III</sup>Ru<sup>III</sup> complex is diamagnetic over a large range of temperature. Further studies of the magnetic behavior of the M<sup>III</sup>M<sup>III</sup> species as well as preparation of complexes in which terphenyl and quaterphenyl bridges are used in order to extend the distance between the metal centers are currently in progress.

**Acknowledgment.** We thank the CNRS for financial support.

(29) Kahn, O. Personal communication. We thank O. Kahn for preliminary magnetism measurements.