cause of the hindered rotation of the phenyl groups about the C–N axes. Therefore, if an improbable strictly square-planar coordination is not considered, the ^{13}C NMR spectrum is consistent with a C_{2v} tetrahedral structure of complex 1 in solution but not with a static "pseudoplanar" structure (C_2), for which 13 carbon signals would be expected for the 2,6-iPr$_2$Ph-dad ligand.

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Synthesis of Functionalized Asymmetrical Bis(terpyridine)osmium(II) Complexes under Mild Conditions

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Introduction

The synthesis of (terpy)$_2$ complexes of osmium(II) (terpy = 2,2′:6′,2″-terpyridine) containing two differently substituted ligands at their 4′-position can be carried out in two successive steps,[1] using classical reactions.

$$\mathrm{OsCl_3 + terpy\text{-}X \xrightarrow[\text{ethanol, }\Delta]{} Os(terpy\text{-}X)Cl_3} \qquad (1)$$

$$\mathrm{Os(terpy\text{-}X)Cl_3 + terpy\text{-}Y \xrightarrow[\text{ethylene glycol}]{\text{refluxing}} Os(terpy\text{-}X)(terpy\text{-}Y)^{2+}} \qquad (2)$$

X, Y = substituents on the 4′-position of the terpy ligands

Due to the extreme stability of the Os(III)–Cl bond, the conditions of reaction 2 have to be particularly vigorous[2,3] whereas reaction 1 leads to monoterpy complexes under mild conditions.[4] In general, the preparation of OsN_6^{2+} complexes (N_6 represents six aromatic imine functions) requires long reaction times and high temperatures.[5] This method is unadapted to ligands bearing little robust chemical groups, as those used for building diades (diade = donor–acceptor linked system) and triades aimed to photoinduced charge separation[1,6] (Chart I). In the present paper, we report a new and very mild method allowing preparation of asymmetrical bis(2,2′:6′,2″-terpyridine)osmium(II) complexes in a stepwise procedure.

Experimental Section

All products were of reagent grade and were used as received. Acetonitrile (SDS) and tetrahydrofuran (SDS) were used without purification. The ligands Me-phterpy, Br-phterpy, and MeO-phterpy (phterpy = 4′-phenyl-2,2′:6′,2″-terpyridine) were prepared by modification of literature procedures[7] and purified by the method of Constable et al.[8] The ligands PTZ-phterpy (PTZ = phenothiazine–CH$_2$–) and PQ^{2+}-phterpy (PQ^{2+} = *N*-methyl-*N*′-methylene-4,4′-bipyridinium, paraquat) were synthesized as described previously.[1] The ligand Diaa-phterpy (Diaa = di-*p*-anisylamino) was obtained in the same way as Me-phterpy[7] by condensation of 2 equiv of 2-acetylpyridine with 1 equiv of *p*-(bis(*p*-methoxyphenyl)amino)benzaldehyde.

Chart I

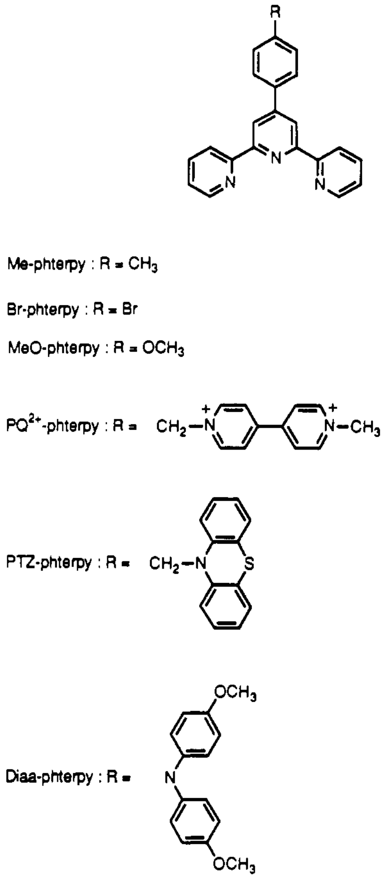

Table I

complex	yield, % *a*	yield, % *b*
Os(Me-phterpy)$_2$$^{2+}$		31
Os(Me-phterpy)(MeO-phterpy)$^{2+}$	66	49
Os(Me-phterpy)(Br-phterpy)$^{2+}$	35	32
Os(Me-phterpy)(PQ^{2+}-phterpy)$^{4+}$		48
Os(Me-phterpy)(PTZ-phterpy)$^{2+}$	17	8.5
Os(Me-phterpy)(Diaa-phterpy)$^{2+}$	35	17

[a] Reducing agent: Pt(0)/H$_2$. [b] Reducing agent: hydrazine.

The latter compound was synthesized by formylation of bis(*p*-methoxyphenyl)phenyl amine[9] according to Walter et al.[10] ^1H NMR spectra were acquired on a Bruker WP200SY instrument. Chemical shifts are reported vs. Me$_4$Si as an internal standard. Visible and UV spectra were obtained on a Kontron spectrophotometer. Cyclic voltammetry was carried out on a Bruker E1310 potentiostat connected to a XY Ifelec IF3802 recorder. FAB spectra were obtained by using a VG instruments ZAB-HF mass spectrometer. Elemental analyses of C, H, and N were performed by the Service de l'Institut de Chimie de Strasbourg.

Synthesis of the Complexes. Preparation of Os(Me-phterpy)(O)$_2$(OH)(NO$_3$)·H$_2$O. To an aqueous solution of Me-phterpy (88 mg in 120 mL) at pH = 3 (HNO$_3$) was added, in 5 h, 1 equiv of $K_2Os(O)_2(OH)_4$ in solid form. The pH of the solution was maintained at 3 ± 0.2 by HNO$_3$ during the addition. The solution was stirred overnight. After filtration on Millipore, the filtrate was reduced to 60 mL, and 10 mL of an aqueous saturated solution of KNO$_3$ was added. The pale green precipitate was filtered, washed with 10 mL of cold water, and dried under vacuum. Yield: 92%.

^1H NMR (CD$_3$OD): δ 9.62 (dd, 2 H), 9.01 (s, 2 H), 8.86 (d, 2 H), 8.67 (t, 2 H), 8.27 (t, 2 H), 8.80 (d, 2 H), 8.26 (d, 2 H), 2.41 (s, 3 H).

FAB MS (nitrobenzyl alcohol matrix): m/z = 564 [Os(Me-phterpy)(O)$_2$(OH)$^+$].

Anal. Calcd for Os(Me-phterpy)(O)$_2$(OH)(NO$_3$)H$_2$O: C, 40.00; H, 3.35; N, 8.48. Found: C, 40.08; H, 3.79; N, 8.62.

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Table II. Redox Potentials of Osmium Complexes[a]

complex	redox potentials, V					
	Os^{III}/Os^{II}	D^+/D^0 [b]	$PQ^{2+}/PQ^{\bullet+}$	$PQ^{\bullet+}/PQ^0$	Os^{II}/Os^I [c]	Os^I/Os^0 [c]
$Os(Me\text{-}phterpy)_2^{2+}$	+0.90				−1.20	−1.45
$Os(Me\text{-}phterpy)(PTZ\text{-}phterpy)^{2+}$	+0.90	+0.75			−1.20	−1.45
$Os(Me\text{-}phterpy)(Diaa\text{-}phterpy)^{2+}$	+0.94	+0.76			−1.20	−1.48
$Os(Me\text{-}phterpy)(PQ^{2+}\text{-}phterpy)^{4+}$	+0.90		−0.35	−0.75	−1.20	−1.45

[a] Cyclic voltammetry measurements on glassy-carbon electrode in CH_3CN, vs SCE; Bu_4NClO_4 (0.1 M) as supporting electrolyte; scan rate = 100 mV s^{-1}. [b] D^+/D^0 are the oxidized and reduced parts of PTZ-phterpy (line 2) and Diaa-phterpy (line 3). [c] The osmium oxidation states I and 0 are only formal.

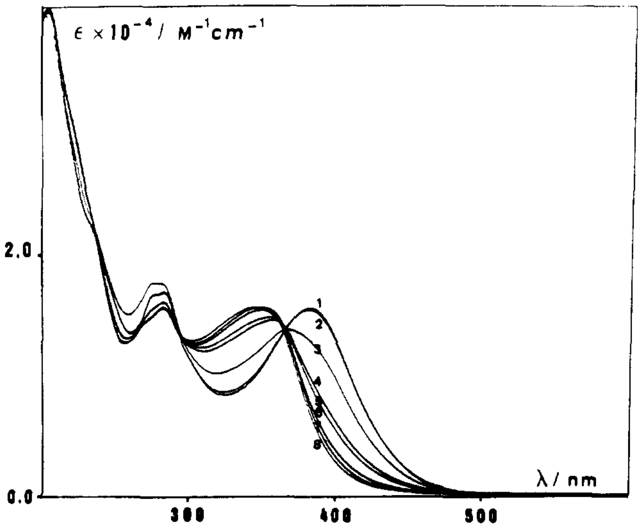

Figure 1. Electronic spectra of $[Os(Me\text{-}phterpy)(O)_2(OH)^+][NO_3^-]$ (7.0×10^{-5} M) in aqueous solution at pH = (1) 1.65, (2) 1.79, (3) 2.45, (4) 2.98, (5) 3.13, (6) 3.60, (7) 3.89, and (8) 5.47.

Preparation of $Os(Me\text{-}phterpy)(terpy\text{-}Y)(PF_6)_2$. Method A. A typical preparation is as follows. $[Os(Me\text{-}phterpy)(O_2)(OH)^+][NO_3^-]$ and a given functionalized terpy (in a stoichiometric amount) were dissolved in a H_2O/THF (1:1) mixture. A few drops of hydrazine were added while stirring, and the mixture was heated to 40 °C for 10 min. After evaporation of THF, the complex was precipitated out by addition of NH_4PF_6. It was further purified by column chromatography on silica (CH_3CN–aqueous KNO_3 as eluent).

Method B. With H_2/Pt(O), the experimental procedure was slightly different. The solvent used was methanol/H_2O (9:1) at pH = 3.0 (acid used: HNO_3). A solution of $[Os(Me\text{-}phterpy)(O)_2(OH)^+][NO_3^-]$ was added dropwise to a refluxing solution of the ligand under a hydrogen atmosphere and in presence of small amounts of platinum black (Ventron). This procedure minimizes oxidative degradation of the electron donor groups attached to the terpy chelate by the osmium(VI) starting complex.

Results

In order to avoid the presence of coordinating chlorine atoms, potassium osmate ($K_2Os(O)_2(OH)_4$) was used in the first step, leading to a monoterpy Os(VI) complex, by using a procedure analogous to that recently developed by Meyer et al.[11] $K_2Os(O)_2(OH)_4$ was added at room temperature to an aqueous solution of Me-phterpy at pH = 3. $[Os(Me\text{-}phterpy)(O)_2(OH)^+][NO_3^-]$ was obtained as a pale green solid in 92% yield.

It was characterized by ^1H NMR spectroscopy, FAB-MS, and elemental analysis. Its redox properties[12] and its electronic spectrum are strongly dependent on pH similar to its parent complex $[Os(terpy)(O)_2(OH)^+][NO_3^-]$,[11,12] as represented in Figure 1.

In the pH range 1–6, two redox couples can clearly be observed, one corresponding to a three-electron process (+0.36 V vs. SCE at pH = 2.5) and the other being a one-electron reaction (−0.06 V at pH = 2.5). As usual, the redox reactions are accompanied by protonation–deprotonation reactions.[12,13] At pH < 6, the four-electron reduction product is probably $Os(Me\text{-}phterpy)(OH_2)_3^{2+}$, which looks promising for substituting further the coordination sphere of the metal. Indeed, we found that the chemical reduction of $Os(Me\text{-}phterpy)(O)_2(OH)^+$ in the presence of a second terpy leads to the desired bis(2,2′:6′,2″-terpyridine)osmium(II) complex in a reproducible fashion with appreciable yields. Among the various reducing agents tested, hydrogen (in the presence of platinum(O)) and hydrazine in neutral medium gave the best results.

The various results obtained by using either of the two methods are collected in Table I.

Each complex was isolated pure (TLC control on silica) and characterized by ^1H NMR and FAB-MS. For example, ^1H NMR and elemental analysis are given for $Os(Me\text{-}phterpy)(PTZ\text{-}phterpy)^{2+}$. δ_H (CD_3CN): 9.01 (2 H, s); 9.00 (2 H, s); 8.61 (4 H, d, J = 8.4 Hz); 8.13 (2 H, d, J = 8.3 Hz); 8.07 (2 H, d, J = 8.3 Hz); 7.83–7.74 (6 H, m); 7.58 (2 H, d, J = 8.3 Hz); 7.31–6.92 (16 H, m); 5.37 (2 H, s); 2.57 (3 H, s). Anal. Calcd for $C_{56}H_{41}N_7SP_2F_{12}Os$: C, 50.79; H, 3.12; N, 7.40. Found: C, 50.97; C, 3.41; N, 7.15. Cyclic voltammetry confirmed in a convenient way the presence of the electroactive groups linked to the osmium complexes. Redox potentials of four osmium complexes are reported in Table II.

Discussion

From the results of Table I, it is clear that the best yields were obtained by using Pt/H_2 as a reductant, especially if one of the terpy ligands contains an oxidizable group (Diaa = di-*p*-anisylamino or PTZ = phenothiazine–CH_2–). In any case, the presence of these electrophores anchored to the complex seems to lower the yield significantly.

A possible limitation of the method resides in the high reactivity of the postulated intermediate complex $Os(Me\text{-}phterpy)(OH_2)_3^{2+}$. Clearly, reactions other than coordination to the second terpy may occur: deprotonation, formation of bridged polynuclear complexes (μ-hydroxo and μ-oxo), etc.[14]

The method described in the present report for preparing molecular diades built on osmium(II) complexes should allow the synthesis of electron-donor-osmium(II)–electron-acceptor complexes (triades) in a more preparative way than the use of classical thermal methods.

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The Ferrocene Assumption in Redox Thermodynamics: Implications from Optical Intervalence Studies of Ion Pairing to Ferrocenium

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The "ferrocene assumption" forms the basis of a popular approach to the ubiquitous problem of relating redox potentials