by following the method of Evans and co-workers.[27a] All compounds have been characterized by analyses and NMR spectroscopy.

Ru(TZ)(Me$_2$SO)$_2$(PF$_6$)$_2$ (2a). Ru(Me$_2$SO)$_4$Cl$_2$ (10^{-3} mol, 485 mg) and the macrocycle TZ (**1**) (10^{-3} mol, 376 mg) are heated at reflux for 3 h in 100 mL of a mixture of EtOH/H$_2$O, 75/25. Most of the EtOH is evaporated; the complex is precipitated as the hexafluorophosphate by a dropwise addition of a concentrated NH_4PF_6 aqueous solution. The precipitate is filtered, washed, and dried to give a yellow powder. Yield: 90%.

Ru(TZ)(CH$_3$CN)$_2$(PF$_6$)$_2$ (2b). This complex is obtained by refluxing complex **2a** for 3 h in CH_3CN. Yield: 100%. Anal. ($C_{24}H_{30}N_{10}RuP_2F_{12}$) C, H, N.

Ru(TZ)(py)$_2$(PF$_6$)$_2$ (2c). This complex may be obtained by two methods, the first one being cleaner.[36]

$Ru(Me_2SO)_4Cl_2$ (145 mg) and the macrocycle TZ (**1**) (113 mg) are refluxed for 3 h in 12 mL of a mixture of EtOH/H$_2$O, 75/25. Part of the solvent is evaporated; then the residue is heated at reflux for 5 h with 0.1 mL of pyridine. The solvent is evaporated to dryness, the solution obtained by addition of 14 mL of H$_2$O is filtered, an aqueous concentrated NH_4PF_6 solution is added to the filtrate, and the precipitate formed is filtered and washed three times with H$_2$O, twice with EtOH, and once with ether. Yield: 83%. Anal. ($C_{30}H_{34}N_{10}RuP_2F_{12}$) C, H, N.

$RuCl_3 \cdot 3H_2O$ (157 mg) and the macrocycle TZ (226 mg) are refluxed in 24 mL of H$_2$O for 4 h. After the addition of 2.4 mL of an aqueous Na_3PO_2 solution, the mixture is heated again at reflux for another 2 h. The solution is filtered on Celite, then 0.1 mL of pyridine is added, and the mixture is refluxed for 5 h. After evaporation to dryness, 2.8 mL of H$_2$O are added and the solution filtered, a NH_4PF_6 solution is added to the filtrate, and the precipitate obtained is filtered, washed with H$_2$O, and dried. Yield: 70%.

Ru(TZ)(Me$_2$SO)(py)(PF$_6$)$_2$ (2d). Ru(TZ)(Me$_2$SO)$_2$Cl$_2$ (352 mg) and pyridine (20 mg) are left at room temperature in 20 mL of a mixture of EtOH/H$_2$O, 75/25. The solvent is evaporated, 15 mL of H$_2$O are added, and the complex as the hexafluorophosphate is precipitated by an aqueous concentrated NH_4PF_6 solution. The precipitate is filtered and washed with H$_2$O. Yield: 90%. Anal. ($C_{27}H_{35}N_9OSRuP_2F_{12}$) C, H, N.

Ru(TZ)(CH$_3$CN)(py)(PF$_6$)$_2$ (2e). This complex is obtained by heating at reflux for 3 h the complex **2d** in CH_3CN. Yield: 100%. Anal. ($C_{27}H_{12}N_{10}RuP_2F_{12}$) C, H, N.

Ru(TZ)(4,4'-bpy)$_2$(PF$_6$)$_2$ (2f). Ru(Me$_2$SO)$_4$Cl$_2$ (145 mg) and the macrocycle TZ (113 mg) are heated at reflux for 3 h in a mixture of EtOH/H$_2$O, 75/25 (12 mL). Then a large excess of 4,4'-bipyridine (20 times) is added and the solution is refluxed for 6 h. The complex is precipitated as the hexafluorophosphate by a concentrated NH_4PF_6 aqueous solution. The precipitate dissolved in a minimum of DMF is loaded on a Sephadex LH 20 column and eluted with DMF. After evaporation of the solvent, the red complex **2f**[37] is obtained with a yield of 90%.

Registry No. **2a**, 101165-12-2; **2b**, 101165-14-4; **2c**, 101165-16-6; **2d**, 101165-18-8; **2e**, 101165-20-2; **2f**, 101165-22-4; Ru(Me$_2$SO)$_4$Cl$_2$, 89395-66-4.

(36) Complex **2c** may be also obtained directly from **2a** as PF_6^- salt by heating it in pyridine for 5 h.

(37) Complex **2f** has not been obtained analytically pure because of the presence of small quantities of polymeric impurities impossible to separate.

Contribution from the Laboratoire de Synthèse et d'Etudes Physicochimiques, Université des Sciences et Techniques du Languedoc, 34060 Montpellier Cedex, France

New Ligand-Bridged Polyruthenium(II) Complexes with Cofacial Tetrapyrazolic Macrocycles

C. Marzin,*† G. Tarrago,† I. Zidane,† E. Bienvenue,‡ P. Seta,‡ C. Andrieux,§ H. Gampp,§ and J. M. Savéant§

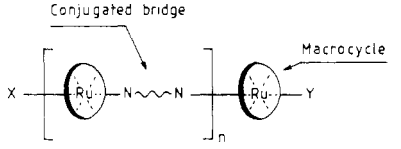
Received October 16, 1985

Three binuclear Ru(II) bimacrocyclic cofacial complexes X(TZ)Ru(bpy)Ru(TZ)X(PF$_6$)$_4$ (TZ = 2,7,12,17-tetramethyl-1,6,11,16-tetraazaporphyrinogen; X = Me$_2$SO, CH$_3$CN, or pyridine; bpy = 4,4'-bipyridine) and two tetranuclear tetramacrocyclic homologues have been prepared in order to study their capacities as electron carriers. ^{1}H NMR data and redox potential measurements show that no interaction occurs between the metal centers under these experimental conditions. The insertion in bilayer lipid membranes gives rise to stationary photocurrents of small amplitude.

Introduction

Lately the chemistry of biruthenium complexes has been widely investigated, especially with the aim to study the behavior of their mixed-valence species.[1-4] Most of the work has been based on complexes made of "Ru(NH$_3$)$_5^{2+}$" and "Ru(bpy)$_2^{2+}$" units linked by various bridging groups such as pyrazine, 4,4'-bipyridine, or cyano derivatives; the best example is the now well-known Creutz-Taube ion, the behavior of which is still the subject of controversy.[5-8] But few studies have been devoted to polymetallic complexes containing more than two ruthenium atoms.[9,10]

Our aim was to prepare a new series of polynuclear ruthenium(II) complexes such that one could expect an electron-transfer directionality through a known number of Ru atoms as represented in



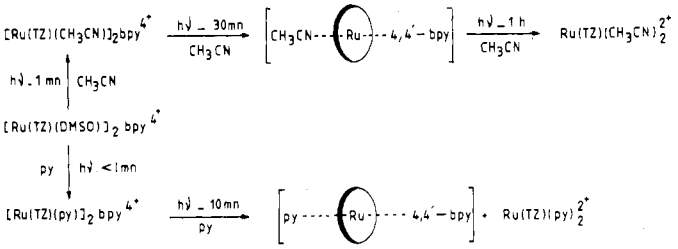
Such an arrangement has been described in long polymeric phthalocyanine, porphyrin, and hemiporphyrazine systems with

† Université des Sciences et Techniques du Languedoc, Montpellier; UA 468 au CNRS.
‡ Centre National de la Recherche Scientifique, Montpellier; LA 330 au CNRS.
§ Laboratoire d'Electrochimie, Université Paris VII; UA 438 au CNRS.

(1) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988; **1973**, *95*, 1086.
(2) Brown, D. B., Ed. *Mixed Valence Compounds*; D. Reidel: Dordrecht, The Netherlands 1980.
(3) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.
(4) Curtis, J. C.; Bernstein, J. S.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 385.
(5) Wong, K. Y. *Inorg. Chem.* **1984**, *23*, 1285.
(6) Fürholz, U.; Bürgi, H.-B.; Wagner, F. E.; Stebler, A.; Ammeter, J. H.; Krausz, E.; Clark, R. J. H.; Stead, M. J.; Ludi, A. *J. Am. Chem. Soc.* **1984**, *106*, 121.
(7) Stebler, A.; Ammeter, J. H.; Fürholz, U.; Ludi, A. *Inorg. Chem.* **1984**, *23*, 2764.
(8) Krausz, E.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 939. Fürholz, U.; Joss, S.; Bürgi, H.-B.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 943.

0020-1669/86/1325-1778$01.50/0

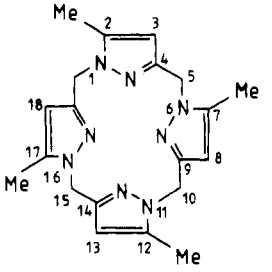
Scheme I



various metals and bridging ligands,[11] leading to one-dimensional conductors; a series was especially close to our system as the metal was iron and the bridging molecules were linear bidentate ligands such as pyrazine and 4,4′-bipyridine.[12] Our purpose is not to reach such long-chain polymers but rather to prepare series of complexes with a number of Ru atoms increasing step by step in order to observe the possible electron transfer in homogeneous solutions as well as in bilayer lipid membranes.

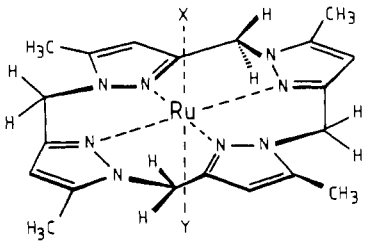
Results and Discussion

To obtain such complexes we have used the macrocycle described in the preceding contribution,[13] the tetrapyrazolic macrocycle **1**, and the occurrence of the axial-ligand lability of its Ru



1

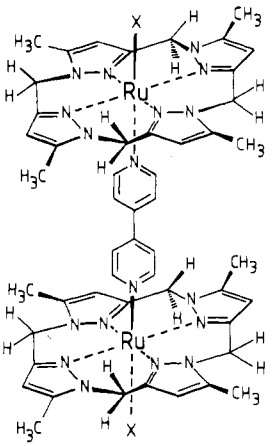
complexes. We have chosen as a bridging ligand 4,4′-bipyridine, which must have a behavior similar to a pyridine ligand as in **2**



2

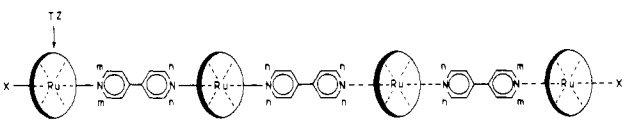
X = Me_2SO, CH_3CN, or py
Y = Me_2SO, CH_3CN, or py

(X and/or Y = pyridine) and which should not produce steric interactions between cofacial macrocycles. Thus, starting from 1 mol of complex **2** (X = Y = Me_2SO) with $^1/_2$ mol of 4,4′-bipyridine, we have obtained the red complex **3a**. As in the case



3a, X = Me_2SO
b, X = CH_3CN
c, X = py

of **2**, axial ligands are easily substituted by coordinating solvent molecules: thus from **3a** we have obtained **3b** and **3c** by reflux in CH_3CN and in pyridine, respectively. This last compound may also be prepared from complex **2** (X = Me_2SO, Y = py) with $^1/_2$ mol of 4,4′-bipyridine. From an equimolecular mixture of **2** (X = Y = Me_2SO) and 4,4′-bipyridine we have isolated complex **4a**



4a, X = Me_2SO
b, X = CH_3CN

with four cofacial macrocycles. Complex **4b** is obtained as **3b** by a thermal exchange of the axial Me_2SO ligands by CH_3CN molecules.

Photochemical Behavior. The bimacrocyclic compounds are even more sensitive to light than their monomacrocyclic analogues (see previous paper).[13] Irradiation with visible light in coordinating solvents leads to processes that are so fast that one sees generally only two steps. In the first one, a fast exchange of both end ligands occurs, which is completed in less than 1 min in the sunlight. Estimated quantum yields are close to unity. The second step is slower, on the time scale of 1 h, and leads to a multistep photolysis of the bimacrocyclic structure. This complex process gives at first an intermediate, the spectral characteristics of which point to a monomacrocyclic species, most probably bearing one 4,4′-bipyridine axial ligand; this intermediate is further photolyzed to the bis(solvato) end product. Quantum yields for the latter steps are in the range of 1% (see Scheme I).

^{1}H NMR Spectroscopy. The ^{1}H NMR chemical shifts and coupling constants concerning complexes **3** and **4** are gathered in Table I. As in the case of monomacrocyclic complexes (see preceding paper[13]), CH_2 macrocyclic signals allow an identification of the complexes obtained. In complexes **3a** and **3b** the eight CH_2 groups give rise to eight identical AB systems: one proton of each CH_2 faces the 4,4′-bipyridine and the other an X group. In the case of complex **3c** the axial ligands, pyridine and 4,4′-bipyridine, are not different enough to produce an anisochrony of the two CH_2 protons giving rise to eight identical A_2 systems. For the tetramacrocyclic complexes **4a,b** we have observed two kinds of systems for the CH_2 protons: one is due to eight identical A_2 systems corresponding to the two central macrocycles and the other to eight identical AB systems corresponding to the two external macrocycles. What is remarkable is the reproducibility of the CH_2 chemical shifts dependent on the axial-ligand nature but independent of the number of macrocycles concerned, one, two,

(9) Powers, M. J.; Callahan, R. W.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 894.
(10) von Kameke, A.; Tom, G. M.; Taube, H. *Inorg. Chem.* **1978**, *17*, 1790.
(11) Hanack, M.; Seelig, F. F.; Strähle, J. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1979**, *34A*, 983. Mitulla, K.; Hanack, M. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **1980**, *35B*, 1111. Dirk, C. N.; Inabe, T.; Schoch, K. F.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1539. Whangbo, M.-H.; Stewart, K. R. *Isr. J. Chem.* **1983**, *23*, 133. Canadell, E.; Alvarez, S. *Inorg. Chem.* **1984**, *23*, 573. Dirk, C. W.; Marks, T. J. *Inorg. Chem.* **1984**, *23*, 4325. Diel, B. N.; Inabe, T.; Jaggi, N. K.; Lyding, J. W.; Schneider, O.; Hanack, M.; Kannewurf, C. R.; Marks, T. J.; Schwartz, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 3207.
(12) Schneider, O.; Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 392. Metz, J.; Hanack, M. *Nouv. J. Chim.* **1981**, *5*, 541. Schneider, O.; Hanack, M. *Angew. Chem., Suppl.* **1982**, 41. Schneider, O.; Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 79. Hanack, M. *Chimia* **1983**, *37*, 238. Fischer, K.; Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 724. Schneider, O.; Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 784.
(13) Marzin, C.; Tarrago, G.; Gal, M.; Zidane, I.; Hours, T.; Lerner, D.; Andrieux, C.; Gampp, H.; Savéant, J. M. *Inorg. Chem.*, preceding paper in this issue.
(14) In fact the reaction leads to a mixture of complexes from which we have isolated the major one, compound **4a**.

Table I. ^{1}H NMR Data for Noncomplexed Ligands and Complexed[a] Macrocycles $(RuTZ)_2X_2(4,4'\text{-bpy})^{4+}$ (**3**) and $(RuTZ)_4X_2(4,4'\text{-bpy})_3^{8+}$ (**4**)

		δ(H)				
compd	X	H(pyr)	CH_3(pyr)	CH_2(mac)	X	bpy[c]
TZ		5.83	2.16	4.85		
4,4′-bpy						8.63 (α), 7.58 (β)
3a	Me_2SO	6.47 (+0.64)	2.47 (+0.31)	4.95 (+0.10)	2.44	7.24 (α) (−1.39), 7.38 (β) (−0.20)
				5.50 (+0.65)[e]		
3b	CH_3CN	6.47 (+0.64)	2.47 (+0.31)	4.80 (−0.05)	2.47	7.05 (α) (−1.58), 7.38 (β) (−0.20)
				5.29 (+0.44)[f]		
3c	py	6.44 (+0.61)	2.43 (+0.27)	4.73 (−0.12)		
4a	Me_2SO	6.40 (+0.57)	2.43 (+0.27)	4.73 (−0.12)		7.07 (α_n) (−1.56)[d]
		6.44 (+0.61)	2.47 (+0.31)	4.93 (+0.08)		7.24 (α_m) (−1.39)[d]
				5.47 (+0.62)[g]		7.47 (β) (−0.11)
4b	CH_3CN	6.46 (+0.63)	2.47 (+0.31)	4.80 (−0.05)		7.10 (α_n) (−1.53)[d]
			2.50 (+0.34)	4.81 (−0.04)		7.30 (α_m) (−1.33)[d]
				5.29 (+0.44)[g]		7.43 (β) (−0.15)

[a] In all cases the anion is PF_6^-. [b] Values in parentheses are the chemical shift differences between the complexed and noncomplexed ligands. [c] α and β refer to positions relative to the bipyridyl nitrogen atoms. [d] For the significance of n and m see molecules **4a** and **4b** in the text. [e] J = 17.2 Hz. [f] J = 17.0 Hz. [g] J = 16.8 Hz.

Table II. UV–Visible Absorption Spectral Data and Cyclic Voltammetry Data in CH_3CN of $(RuTZ)_2X_2(4,4'\text{-bpy})^{4+}$ (**3**) and $(RuTZ)_4X_2(4,4'\text{-bpy})_3^{8+}$ (**4**)

compd	X	λ_{max}, nm	ε, M^{-1} cm^{-1}	$E°_{ox}$, V vs. SCE	$E°_{red}$, V vs. SCE	i_p^{red}/i_p^{ox}
3a	Me_2SO	230		1.28	−1.31	0.55
		396	1750			
3b	CH_3CN	252		0.94	−1.31	0.55
		296				
		479	1290			
3c	py	251.5	1345	0.84	−1.35	0.55
		310	2250			
		500	5150			
4a	Me_2SO	478	23500	0.88	−1.35	0.81
				1.25		
4b	CH_3CN	488	25900	0.88	−1.32	0.75

or four: this shows again that CH_2 chemical shifts are mainly governed by the axial-ligand anisotropic effects. Pyrazole H and CH_3 chemical shifts are also independent of the number of macrocycles contained in the complex, showing no anisotropic influence of the macrocycles on each other.

UV–Visible Absorption. The low-energy transitions correspond to charge-transfer absorption as is the case in the homologous monomacrocyclic series. In the UV, a transition of $\pi-\pi^*$ character is certainly due to the presence of the 4,4′-bipyridine system (see Table II). In this series, one also notices the large bathochromic shift induced by replacement of Me_2SO ligands by CH_3CN or pyridine ones, and there is no large difference between those two last ligands as far as this shift is concerned. These two observations, already made in the monomacrocyclic series, show that each macrocyclic–Ru unit is independent of the other and that there is no important interaction between them. The bathochromic shift observed between the mono- and bimacrocyclic complexes may be only due to the presence of the 4,4′-bipyridine[15] [compare complexes **2** (X = Me_2SO, CH_3CN, or py) with **3a–c**]. A different behavior is observed for **4a** and **4b**: the lowest energy transition is about 10 times more intense than expected for noninteracting entities; this result seems to show some degree of conjugation, which, however, is not detected under the cyclic voltammetry or NMR experimental conditions.

None of the complexes described here, showed an emission at room temperature as well as at liquid-nitrogen temperature.

Electrochemistry. The binuclear compounds **3a–c** show one reversible oxidation wave each (see Table II).[16] Moreover, the shape of the wave cannot be distinguished from that of a monoelectronic wave. These findings clearly indicate very similar standard potentials of the two Ru(II) centers.[17] Thus, the 4,4′-bipyridine bridge does not act as an electron transmitter between the metal atoms, which therefore appear as independent under the conditions of the electrochemical experiments.

The values of the standard potentials of **3a–c** are in line with the values of the corresponding mononuclear complexes: in **3a**, where each Ru(II) is coordinated to a bipyridine and a Me_2SO ligand, the $E°$ of 1.28 V is very close to the value found for **2** (X = Me_2SO, Y = py) (1.26 V), where one Me_2SO and one pyridine are the axial ligands.[19] When Me_2SO is substituted by CH_3CN (**3b**) or pyridine (**3c**), the potentials are in excellent agreement with those of the mononuclear homologues **2** (X = CH_3CN, Y = py) (0.92 V), **2** (X = Y = py) (0.81 V), or **2** (X = Y = 4,4′-bpy) (0.84 V), respectively (Table II).

In reduction, **3a–c** feature a reversible wave around −1.3 V with a peak height half that of the corresponding oxidation wave. The standard potential is close to that of $Ru(2,2'\text{-bpy})_3^{2+}$,[18] and this can be explained by the fact that here the 4,4′-bipyridine is also bicoordinated. Since the reduction of the complex is centered on the bipyridines[18] [cf. the corresponding discussion of the mononuclear bipyridine complex **2** (X = Y = 4,4′-bpy)] the 2:1 ratio between oxidation and reduction peak heights is easily understood.

The same arguments can be used to understand the behavior of the tetranuclear complexes **4a** and **4b**. **4a** shows two oxidation waves, one at 0.88 V and one at 1.25 V. The first one occurs at a potential similar to those of **3c** and the mononuclear bis(bipyridine) complex **2** (X = Y = 4,4′-bpy) and can be assigned to the two central Ru atoms coordinated to the bridging ligands. The second wave corresponds to the one found for **3a** and can be attributed to the two terminal Ru(II).[19] As in the case of the binuclear complexes (vide supra) no interaction between the metal centers is observed. **4b**, for which two oxidation waves are to be expected at 0.84 V [central, cf. **3c** or **2** (X = Y = 4,4′-bpy)] and at 0.94 V (terminal, cf. **3b**), shows only one signal at 0.88 V, due to the facts that the expected splitting is small and that the electrochemistry had to be done on very diluted samples; the two waves are not resolved. The reduction potentials of the tetranuclear complexes **4a** and **4b** correspond to those of the binuclear complexes (Table II). The peak heights are about three-fourths the size of those of the corresponding oxidation peaks, as expected for three noninteracting reducible bipyridines and four oxidizable metal centers.

Phototransfer Behavior in BLM. Mono-, bi-, and tetramacrocyclic complexes described here and in the preceding paper[13] have been incorporated in bilayer lipid membranes (BLM) sep-

(15) Callahan, R. W.; Brown, G. M.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1443.

(16) In the sample of **3a** that was used for the electrochemistry, **3b** was present in 30% as an impurity due to fast exchange with the solvent.

(17) Ammar, F.; Savéant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *47*, 215.

(18) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.

(19) For both **3a** and **4a** an additional wave at 0.66 V is observed if the potential is set at the position of the oxidation wave. This may be due to the oxidation of the Me_2SO ligands (see ref 34 in the preceding paper).

arating two aqueous solutions, oxidant on one side and reductant on the other, in order to study the possible electron transfer from one solution to the other through the membrane under irradiation.[20] Complexes **2** (X = Y = py), **2** (X = Y = 4,4′-bpy), **3a**, **3b**, and **4a** have been tested; all these compounds appear very difficult to dissolve into the membrane forming solutions. Moreover, most of the time, they impede the thinning of the membrane. When the membrane reaches its bimolecular state, under the standard conditions generally used[21] to reveal redox photocurrents (ferric chloride as oxidant and ascorbic acid as reductant), we could however observe stationary photocurrents. These photocurrents were taken as the difference between the stationary current under illumination and the dark current (the latter ranges from 0 to about 40 pA for the less resistant membranes). They were in the direction of an electron flow from the reductant side to the oxidant side of the cell, they have a few picoamperes amplitude, and with **3a**, a 60-pA photocurrent is exceptionally reached. A better result might have been hoped for with the tetramacrocycle complex, the length of which is of the order of magnitude of the membrane thickness. However, due to the lack of amphiphilic properties, this compound probably does not take the transverse position that could lead to an efficient charge transfer. We are currently looking for compounds capable of a better insertion in bimolecular membranes; this seems to be a preliminary for a systematic study of the photocurrents induced in the ruthenium(II) complexes.

Experimental Section

Measurements. For ^{1}H NMR and UV-visible absorption spectra, electrochemical measurements, and photolysis procedures see the preceding paper.[13]

The pigmented BLM are formed on a 1 mm^2 hole in a Teflon septum separating two aqueous solutions, according to the classical method already described by Tien.[20] The pigment is incorporated into the membrane-forming solution in the approximate ratio of one pigment molecule to ten lipid molecules. A solution of the pigment [(2–8) × 10^{-3} M] in hexafluoro-2-propanol (Fluka) is added to a 2% (w/w) solution of azolectine in *n*-decane (Merck); the volatile alcohol partly vanishes from the mixture. With compound **3a** various experimental conditions have been tested, but in no case is the photocurrent higher than with the above standard conditions. Phosphatidylserine (PS, Sigma), glycerol monooleate (Serdary), phosphatidylcholine (PC, Sigma) and mixed PC/phosphatidylethanolamine/cholesterol/PS in the ratio 3.1/1.7/1.1/1.0 were tested as lipids, but the thinning of the membrane was no better. The use of dimethyl sulfoxide or acetonitrile (instead of hexafluoro-2-propanol) as pigment solvents leads to heterogeneous membrane-forming solutions. The aqueous solutions are 10^{-3} M ascorbic acid on one side and 2 × 10^{-3} M ferric chloride on the other side of the membrane. An Ag/AgCl electrode is immersed into each aqueous solution. The pigmented BLM are excited by means of a Coherent argon laser, Model Innova 90-3 (all lines excitation). The photocurrents have been recorded with a Keithley Model 427 current to voltage converter.

Materials. The macrocycle **1** has been obtained as already described.[22] $Ru(Me_2SO)_4Cl_2$ has been prepared by using the method of Evans.[23] Complexes **2** have been described in the preceding paper.[13]

$[Ru(Me_2SO)(TZ)]_2(4,4'\text{-bpy})(PF_6)_4$ (3a). A mixture of 10^{-3} mol of the macrocycle TZ (**1**) and 10^{-3} mol of $Ru(Me_2SO)_4Cl_2$ in EtOH/H_2O, 75% (60 mL), is refluxed for 3 h under nitrogen. Then 0.5 × 10^{-3} mol of 4,4′-bipyridine is added, and the mixture is kept at room temperature for 24 h. The solution is concentrated to dryness. The residue is first purified by chromatography on a Sephadex LH 20 column with water as eluant. A Cl^- to PF_6^- anion exchange is done by adding a concentrated aqueous solution of NH_4PF_6. The obtained precipitate is chromatographied again on Sephadex LH 20 but with DMF as eluant. After evaporation of the solvent, the dark red complex **3a** is obtained with a yield of 85%.

$[Ru(CH_3CN)(TZ)]_2(4,4'\text{-bpy})(PF_6)_4$ (3b). This complex is obtained by refluxing for 5 h the previous complex **3a** in CH_3CN. The product obtained is purified by chromatography on a Sephadex LH 20 column eluting with DMF. After evaporation the expected complex is obtained with a yield of 95%.

$[Ru(py)(TZ)]_2(4,4'\text{-bpy})(PF_6)_4$ (3c). This complex has been obtained by two methods. In the first method, it can be prepared from complex **3a** by refluxing it in pyridine for 10 h. The product obtained is purified by chromatography on Sephadex LH 20 eluting with DMF. Yield 95%. In the second method a mixture of complex **2** (X = Me_2SO, Y = py) (10^{-3} mol) and 4,4′-bipyridine (0.5 × 10^{-3} mol) is heated at 100 °C in DMF for 10 h. After purification on Sephadex LH 20 with DMF as eluant, the brown-red complex **3c** is obtained with a yield of 80%.

$[Ru(TZ)]_4(4,4'\text{-bpy})_3(Me_2SO)_2(PF_6)_8$ (4a). A mixture of the macrocycle TZ (10^{-3} mol) and $Ru(Me_2SO)_4Cl_2$ (10^{-3} mol) is refluxed for 3 h in EtOH/H_2O 75% (60 mL) under nitrogen. Then the 4,4′-bipyridine (10^{-3} mol) is added, and the solution is kept at 50 °C for 40 h. Purification is carried on as for complex **3a**. Yield 20%.

$[Ru(TZ)]_4(4,4'\text{-bpy})_3(CH_3CN)_2(PF_6)_8$ (4b). This complex is obtained by refluxing complex **4a** in CH_3CN for 3 h. After chromatography on Sephadex LH 20 with DMF as eluant, the expected dark red complex is obtained with a yield of 95%.

Registry No. **3a**, 101247-99-8; **3b**, 101248-00-4; **3c**, 101248-01-5; **4a**, 101248-02-6; **4b**, 101248-03-7.

(20) Tien, H. T. In *Bilayer Lipid Membranes Theory and Practice*; Dekker: New York, 1974; p 471.
(21) Wang, C. B.; Tien, H. T.; Lopez, J. R.; Liu, Q.-Y.; Joshi, N. B.; Hu, Q.-Y. *Photobiochem. Photobiophys.* **1982**, 177.
(22) Fifani, J.; Ramdani, A.; Tarrago, G. *Nouv. J. Chem.* **1977**, *1*, 521.
(23) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1006.