[6] I. Manners, *Angew. Chem.* **1996**, *108*, 1712–1731; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1603–1620.

[7] a) S. Takahashi, Y. Takai, H. Morimoto, K. Sonogashira, *J. Chem. Soc., Chem. Commun.* **1984**, 3–5; b) A. Altmann, V. Enkelmann, G. Lieser, U. H. F. Bunz, *Adv. Mater.* **1995**, *7*, 726.

[8] a) A. J. Bard, *Nature* **1995**, *374*, 13; b) D. Astruc, *New J. Chem.* **1992**, *16*, 305.

[9] B. Alonso, M. Morain, C. M. Casado, F. Lobete, J. Losada, I. Cuadrado, *Chem. Mater* **1995**, *7*, 1440–1442.

[10] A triskelion is a typical celtic symbol. Its stucture consists of three identical curved branches meeting in the center. [triskelia (plural), greek *triskeles* = three-legged].

[11] a) T. Weyland, C. Lapinte, G. Frapper, M. J. Calhorda, J.-F. Halet, L. Toupet, *Organometallics* **1997**, *16*, 2024–2031; b) H. Fink, N. J. Long, A. J. Martin, G. Opromolla, A. J. P. White, D. J. Williams, P. Zanello, *Organometallics* **1997**, *16*, 2646–2650.

[12] O. Lavastre, L. Ollivier, P. H. Dixneuf, S. Sinbandhit, *Tetrahedron* **1996**, *52*, 5495–5504.

[13] D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet, P. H. Dixneuf, *Organometallics*, **1997**, *16*, 3640–3648.

[14] Cyclic voltammograms were obtained in CH_2Cl_2 solutions $[0.5-1.10^{-3}\,M]$ with NBu_4PF_6 (0.1M) as electrolyte, 100 $mV\,s^{-1}$ scan rate, Pt working electrode and counter-electrode (1 mm diameter), standard calomel electrode (SCE) reference electrode. Potentials are given with respect to $E(Cp_2Fe^+/Cp_2Fe) =$ 0.45 V vs. SCE.

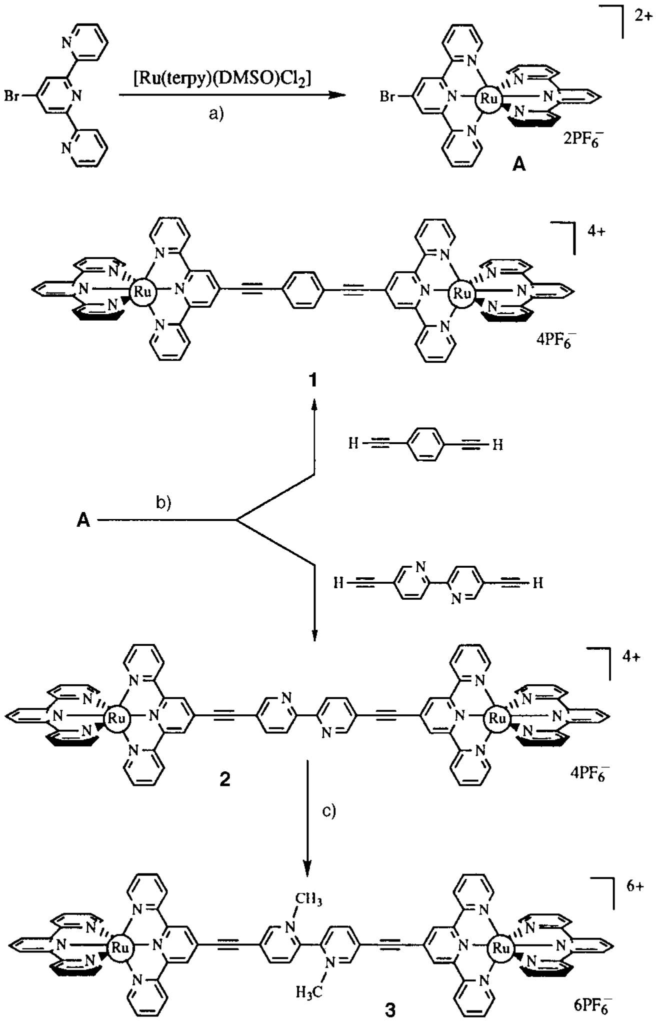
[15] C. Lebreton, D. Touchard, L. Le Pichon, A. Daridor, L. Toupet, P. H. Dixneuf, *Inorg. Chim. Acta* **1998**, *272*, 188–196.

Fine-Tuning the Electronic Properties of Binuclear Bis(terpyridyl)ruthenium(II) Complexes**

Muriel Hissler, Abdelkrim El-ghayoury, Anthony Harriman,* and Raymond Ziessel*

Bis(2,2′:6′,2″-terpyridine)ruthenium(II) is essentially nonemissive in fluid solution, and in deoxygenated acetonitrile at 20 °C the lifetime of the excited triplet state is about 550 ps.[1] Such photophysical properties compare unfavorably with tris(2,2′-bipyridine) ruthenium(II) and have restricted the utilization of $[Ru(terpy)_2]^{2+}$ as a building block for preparation of photoactive supramolecular assemblies. Recently, however, it was shown that attaching an acetylenic function at the 4′-position caused a dramatic prolongation of the triplet lifetime,[1, 2] especially in those cases where the acetylene group was the bridge for a ditopic ligand capped with "Ru(terpy)" metallo-fragments. This upgrade to the photophysical properties provides new opportunities to construct elaborate molecular assemblies around the photoactive Ru(terpy) unit.[3] The protracted triplet lifetime can be explained within the framework of the energy-gap law in terms of residence of the promoted electron in an extended π^* orbital that encompasses much of the bridging ligand.[4] Enlargement of the LUMO lowers the triplet energy, and thereby curtails mixing with higher-energy, metal-centered excited states.[5] In attempting to exploit this effect further we have found that the acetylene residue must be attached directly to the coordinated terpyridine ligand while the polyacetylenic bridge cannot comprise more than four ethynylene groups. Longer carbon chains act as a low-energy sink for photons absorbed by the terminal chromophores.[6] We now describe an alternative strategy for extending the length of the acetylenic bridge that involves the use of a central aromatic core.

Thus, two new Ru(terpy)-based binuclear complexes were synthesized in which the butadiynylene bridge is interspersed with either a 1,4-phenylene (**1**) or a 5,5′-(2,2′-bipyridylene) (**2**) spacer. Preparation of these complexes was accomplished with an original strategy by using a metallo-synthon bearing a bromide group in conjunction with 1,4-diethynylbenzene or 5,5′-diethynyl-2,2′-bipyridine in Sonogashira-type cross-coupling reactions (Scheme 1). These coupling reactions proceed



Scheme 1. Synthetic method used to prepare the binuclear Ru^{II} terpy-based complexes **1** and **2**: a) Ag^+ dehalogenation in methanol (6 h) followed by reaction with terpy-Br in methanol at 80 °C (19 h); b) $[Pd^{II}(PPh_3)_2Cl_2]$ 6 mol%, CH_3CN/C_6H_6, $(iPr_2)NH$, 25 °C (6 days); c) CH_3I (excess) in CH_3CN, 80 °C (5 days), anion exchange.

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[*] Prof. A. Harriman, Dr. R. Ziessel, M. Hissler, A. El-ghayoury
Laboratoire de Chimie
d'Electronique et Photonique Moléculaires
Ecole Européenne de Chimie, Polymères et Matériaux (ECPM)
Université Louis Pasteur
1, rue Blaise Pascal, F-67008 Strasbourg Cedex (France)
Fax: (+33) 388-41-68-25
E-mail: harriman@chimie.u-strasbg.fr

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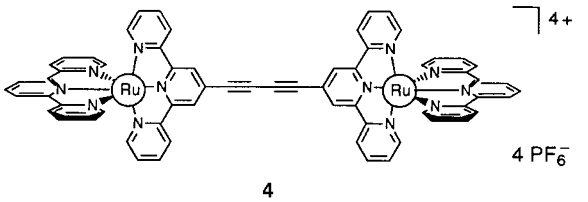
smoothly at ambient temperature in the presence of a catalytic quantity of Pd°. It is noteworthy that complex **2**, which could not be prepared by the classical method,[7] contains a vacant coordination site that remains freely accessible to incoming cations. Indeed, the N atoms of the central 2,2′-bipyridine are easily quaternized to give the viologen-like complex **3**, and in this respect **2** differs markedly from known systems of this general type.[8] The photophysical properties of all newly prepared complexes were recorded in deoxygenated acetonitrile at 20 °C with both steady-state and time-resolved luminescence spectroscopy.

Relative to $[Ru(terpy)_2]^{2+}$ both **1** and **2** are strongly emissive such that luminescence quantum yields (Φ_{lum}) could be estimated (Table 1). The luminescence maxima (λ_{lum}) are red-shifted with respect to that of $[Ru(terpy)_2]^{2+}$, while the triplet lifetimes (τ_T) are prolonged almost 200-fold (Table 1). Complexes **1** and **2** exhibit comparable behavior but stabilization of their triplet states is less significant than found[1] for the binuclear complex **4** having a butadiynylene bridge but without an interspersed aromatic core. In the latter case, the promoted electron is delocalized over the entire ditopic ligand. The poor sensitivity towards the nature of the central aromatic unit reflects a relatively small amount of mixing between π* orbitals localized on the aromatic group with those on the acetylene–terpyridine residue, presumably due to a mismatching of their LUMO energies. In this respect, the aromatic group can be regarded as imposing a high-energy barrier to electron delocalization.

Table 1. Photophysical and electrochemical properties of the bis-terpyridyl ruthenium(II) complexes as measured in deoxygenated acetonitrile at 20 °C.

Cmpd	λ_{lum} [nm][a]	Φ_{lum}[b]	τ_T [ns][c]	E_{red}[d]	E_{ox}[e]
1	685	0.0006	110	– 1.06	1.37
2	678	0.0006	100	– 1.06[f]	1.31
3	710	< 0.0001	4.0[g]	– 0.70[h]	1.37
4	735	0.0021	610	– 0.92	1.41
5	665	< 0.0001	5.8[g]	– 1.08	1.39
$[Ru(terpy)_2]^{2+}$	650	< 0.0001	0.56[g]	– 1.27	1.28

[a] Luminescence maximum, ± 5 nm. [b] Luminescence quantum yield, ± 25 %: The reproducibility is better than ± 3 % while comparative emission yields are accurate to within ± 5 %. [c] Triplet lifetime, ± 5 %. [d] Reduction potential, V vs. SCE, ± 15 mV. [e] Oxidation potential, V vs. SCE, ± 15 mV. [f] *N,N*-Dimethylformamide. [g] Measured by transient absorption spectroscopy. [h] First reduction peak of the central viologen unit.



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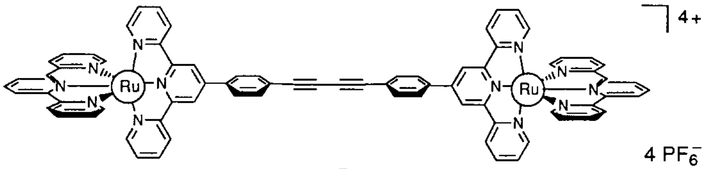

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It is instructive to compare the photophysical properties of **1** with those of the corresponding complex **5** in which the phenyl rings are attached directly to the coordinated terpyridine ligand. Complex **5** shows photophysical properties[1] that remain similar to those of $[Ru(terpy)_2]^{2+}$ and that are less impressive than those of **1** (Table 1). This comparison suggests poor orbital overlap at the LUMO level between the phenyl and pyridine rings, presumably because of their mutual orientation.[9] The symmetry of the acetylene group provides for increased orbital overlap with the pyridine ring and thereby favors extended delocalization of the promoted electron.[10] It is important to realize that the phenyl ring, which extends the molecular axis by approximately 4 Å, can be easily functionalized so as to modulate the local energetics and to provide an anchor for secondary groups.

A further important benefit of direct attachment of the acetylene to the coordinated ligand is that the one-electron reduction potential (E_{red}) of the latter becomes less negative (Table 1). Thus, comparison of the E_{red} values of $[Ru(terpy)_2]^{2+}$ and **1** shows that the acetylene substituent renders that ligand easier to reduce by ca. 210 mV. Inserting the phenylene group between pyridine and acetylene units loses approximately 20 mV whereas omitting the aromatic unit gains a further 140 mV. A less negative reduction potential of the ditopic ligand ensures selective charge injection into that ligand within the lowest energy, triplet excited state. Because this state is of metal-to-ligand charge-transfer (MLCT) character there is a substantial decrease in triplet energy upon raising E_{red} for the ditopic ligand since the corresponding one-electron oxidation potential (E_{ox}) is little affected by substitution. This effect serves to further decouple the MLCT triplet from higher energy excited states.[5]

Complex **2** is the prototype of a new class of rigid binuclear complexes possessing an accessible coordination site in the bridging ligand. Binding of adventitious cations to the central 2,2′-bipyridine provides a further simple means by which to tune the electronic properties of the bridge. This effect becomes apparent upon protonation of the vacant N atoms of the 2,2′-bipyridine group following addition of trifluoroacetic acid to an acetonitrile solution of **2**. A small red shift of the emission maximum and a slight increase in luminescence yield and lifetime (Table 2) is present, although the overall changes are small.[11] The process can be followed more conveniently in aqueous solution where the p*K* is 3.9 ± 0.1. This value is somewhat lower than that of 2,2′-bipyridine (p*K* = 4.5 ± 0.2) due to the presence of the acetylene functions and the neighboring ruthenium(II) cations. Protonation lowers the energy of the LUMO localized on the 2,2′-bipyridine unit, thereby increasing the extent of interaction with π* orbitals resident on the acetylene–terpyridine moiety. This, in turn, increases the propensity for electron delocalization along the ditopic ligand, but the effect is disappointingly small.

Other cations coordinate to the vacant 2,2′-bipyridine ligand in a manner that facilitates subtle control of the local

Table 2. Stability constants and photophysical properties of the cation complexes of **2** as measured in deoxygenated water at 20 °C and pH 7, when the ionic strength is kept constant at 0.1 by addition of KCl.

Cation	λ_{lum} [nm][a]	Φ/Φ°[b]	τ_T [ns][c]	log$K$[d]
H^+	683	1.13	115	3.95
Li^+	678	1.04	105	1.58
K^+	678	0.98	100	0.80
Mn^{2+}	682	1.07	110	1.73
Zn^{2+}	695	2.15	210	4.42
Cd^{2+}	700	2.43	255	3.64
Ba^{2+}	690	1.80	190	2.97
Hg^{2+} [d]	690	0.41	30	3.22
Ag^+ [f]	705	0.12	10	4.16

[a] Luminescence maximum recorded after complete complexation, ±5 nm. [b] Ratio of luminescence quantum yields recorded after complete complexation (Φ) and in the absence of cation (Φ°), ±9%. [c] Triplet lifetime recorded after complete complexation, ±8%. [d] Stability constant, ±7%. [e] Studied at pH 5 in the presence of 0.1 M KNO_3. [f] in 0.1 M KNO_3.

energetics (Table 2). Indeed, binding constants (K) were measured for several cations in neutral aqueous solution by monitoring the luminescence (or absorption) intensity for the terminal Ru(terpy) metallo-fragments as a function of cation concentration (Figure 1). Both the magnitude of K and the photophysical properties of the resultant 1:1 complexes depend on the nature of the added cation. Certain cations, notably Li^+, K^+, and Mn^{2+}, bind weakly to the vacant 2,2′-bipyridine ligand and barely perturb the photophysical properties of **2** in deoxygenated solution. Other cations, notably Ba^{2+}, Cd^{2+}, and Zn^{2+}, bind more avidly and cause a substantial increase in luminescence intensity and lifetime without apparent change to the absorption spectral profile. In these latter cases, coordination of the cation causes a pronounced red shift to the emission maximum (Table 2). The shape of each titration curve indicates that luminescence enhancement is associated only with the bound cation and there is no additional effect from any cation remaining in solution. This modulation of the luminescence intensity can be reversed by adding a competitive complexing agent, such as neocuproine or ethylenediamine. Identical behavior, at least in qualitative terms, was found in acetonitrile solution.

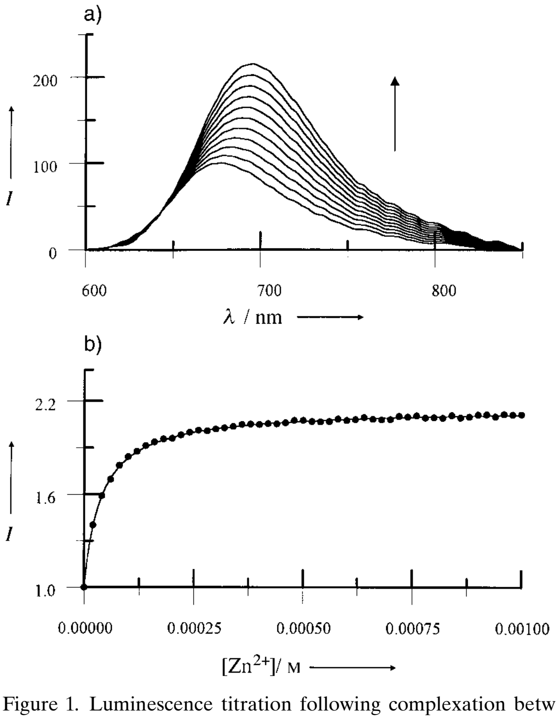

Figure 1. Luminescence titration following complexation between **2** and Zn^{2+} cations in acetonitrile at 20 °C. a) Overlay of luminescence spectra recorded during the titration showing the progressive increase in intensity and red-shift noted for the emission peak on coordination of the cation to the vacant 2,2′-bipyridine site. b) Correlation between emission quantum yield and concentration of added Zn^{2+} cations. The solid line represents a nonlinear, least-squares fit to formation of a 1:1 complex having log$K$ = 4.42 and Φ/Φ_{lum} = 2.15.

Complexation of cations such as Ag^+ and Hg^{2+}, these being strong 2,2′-bipyridine binders, causes a marked decrease in luminescence from the terminal Ru(terpy)-based chromophores (Table 2). A similar effect is observed upon methylation of the vacant N atoms of the 2,2′-bipyridine. In the case of **3**, luminescence quenching is most likely due to light-induced electron transfer[12] from a terminal metallo-chromophore to the central viologen unit. Since both Ag^+ and Hg^{2+} cations are easily reduced[13, 14] it seems reasonable to attribute luminescence quenching to electron transfer from the triplet state of a Ru(terpy)-based chromophore to a bound cation. In these cases, any free cation quenches the excited triplet state of the chromophore but such bimolecular processes are apparent only at very high concentration of cation.

Of the cations studied here those that amplify luminescence from the terminal chromophores are the most interesting since amplification is a measure of electron delocalization over the ditopic ligand. Binding of these cations to simple polypyridyl ligands is known to raise the one-electron reduction potential of the ligand.[15] Presumably, the same effect takes place with **2** such that coordination of Cd^{2+} or Zn^{2+} ions at the vacant 2,2′-bipyridine site pushes E_{red} for the 2,2′-bipyridine unit closer to that of the coordinated terpyridine ligands. This ensures better blending of LUMOs localized on the individual components that comprise the ditopic ligand so that an extended π* becomes available for the promoted electron. Cyclic voltammetry studies made with the Zn^{2+} complex of **2** support this hypothesis. Thus, reduction of **2** in *N,N*-dimethylformamide takes place progressively at the substituted terpyridine ($E_{red} = -1.06$ V vs. saturated calomel electrode (SCE), 2e process), parent terpyridine ($E_{red} = -1.42$ V vs. SCE, 2e process), and bipyridine ($E_{red} = -1.57$ V vs. SCE, 1e process) units. Upon coordination of Zn^{2+} to the central ligand, reduction of the substituted terpyridine ($E_{red} = -0.99$ V vs. SCE, 2e process) and bipyridine ($E_{red} = -1.23$ V vs. SCE, 1e process) becomes easier and takes place at more comparable potentials while reduction of the parent terpyridine ($E_{red} = -1.43$ V vs SCE, 2e process) remains unchanged. It seems likely that by more precise matching of the relevant LUMO energies it will be possible to create a giant π* orbital that encompasses the entire ditopic ligand. In following this strategy, however, it is essential that the central unit does not become too easily reduced such that the promoted electron becomes trapped at a low energy site, as seems to be the case with **3**.

For supermolecules of the type discussed here, extended electron delocalization at the triplet level demands that the acetylene function is attached directly to the coordinated terpyridine ligand. The molecular axis can be lengthened while retaining rigidity by including aromatic groups in the polyacetylene wire. Such groups provide a facile means by which to modify the solubility, electronic charge, molecular shape, and photoproperties of the emergent multicomponent array. The acetylene unit ensures selective charge injection into the ditopic ligand under illumination, while the nature of the central aromatic core controls the extent of electron delocalization over the ditopic ligand. These two molecular fragments are highly complementary, and they act cooperatively to direct electronic charge along the molecular axis. In the case of the prototypic system **2**, where the terminal Ru^{II} cations are separated by about 23 Å, the photophysical properties can be fine-tuned by selective coordination of additional cations. Presumably, external complexation of this type could be used to modulate the rates of light-induced energy or electron transfer through the bridge in mixed-metal analogues of **2**. Provided high binding constants prevail, this strategy could be used to stimulate electron transfer between remote reactants by injection of a low concentration of a specific cation into the system. This situation is reminescent of biological regulatory mechanisms and is a future goal for our research.

Experimental Section

Synthesis and characterization of all new complexes will be reported elsewhere, but a typical experimental procedure is given for **2**: A Schlenk flask was charged with 5,5′-diethynyl-2,2′-bipyridine (0.010 g, 0.49 mmol), $[Ru(terpy)(terpy\text{-}Br)](PF_6)_2$ (0.091 g, 0.98 mmol), 10 mL degassed CH_3CN, $[Pd(PPh_3)_2Cl_2]$ (0.004 g, 6% in mol) and CuI (0.002 g, 10% in mol). After purging with argon, $(i\mathrm{Pr})_2NH$ (5 mL) was added. The solution was stirred at room temperature for 6 days before KPF_6 (0.018 g, 4 equiv.) in water (5 mL) was added and the solvent removed. The crude product was chromatographed on alumina with a mixture of CH_3CN and H_2O (gradient of water 0–25%). The analytically pure compound was obtained by recrystallization from CH_3CN/diethyl ether. Yield 70%. $R_f = 0.45$ (alumina, $CH_3CN/H_2O/KNO_3$, 80/20/0.5 as eluent). ^1H NMR (CD_3OD): $\delta = 9.24$ (s, 3H), 9.12 (s, 1H), 9.02 (d, 4H, $^3J = 8.3$ Hz), 8.86–8.67 (m, 6 lines, 11H), 8.52 (t, 3H, $^3J = 5.9$ Hz), 8.38 (dd, 2H, $^3J = 8.3$ Hz, $^4J = 1.9$ Hz), 8.08-7.97 (m, 8H), 7.59–7.51 (m, 8H), 7.35–7.26 (m, 8H). FAB-MS: $m/z = 1772.1$ $[M - PF_6 + H]$, 1626.0 $[M - 2PF_6]$, 1481.0 $[M - 3PF_6]$. UV/Vis (CH_3CN) : λ_{max} nm (ε $M^{-1}cm^{-1}$) 495 (41400), 258 (45000), 332 (56000), 308 (69400), 272 (58400). Analysis calcd for $C_{74}H_{48}Ru_2N_{14}P_4F_{24}$ ($M_r = 1915.30$): C 46.41, H 2.53, N 10.24; found: C 46.29, H 2.42, N 10.15.

Luminescence lifetimes were measured by a time-correlated, single-photon counting methodology following laser excitation at 440 nm (detection at the peak of the emission spectrum). Binding constants were determined by monitoring absorption and/or luminescence spectral profiles as a function of cation concentration and using global analytical iterative routines provided by the SPECFIT commercial software. Reduction potentials were measured by conventional cyclic voltammetry with Pt discs as working and counterelectrodes and an SCE reference, calibrated vs. ferrocene.

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[1] A. C. Benniston, V. Grosshenny, A. Harriman, R. Ziessel, *Angew. Chem.* **1994**, *106*, 1956; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 18.
[2] A. Harriman, R. Ziessel, *Chem. Commun.* **1996**, 1707.
[3] For other approaches to the construction of functionalized terpyridine-based metal complexes see a) J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, *Chem. Rev.* **1994**, *94*, 993; b) M. Maestri, N. Armaroli, V. Balzani, E. C. Constable, A. M. W. Cargill Thompson, *Inorg. Chem.* **1995**, *34*, 2759; c) F. Barigelletti, L. Flamigni, M. Guardigli, A. Juris, M. Beley, S. Chodorowsky-Kimmes, J.-P. Collin, J.-P. Sauvage, *Inorg. Chem.* **1996**, *35*, 136; d) A. Harriman, J.-P. Sauvage, *Chem. Soc. Rev.* **1996**, 41.
[4] S. Boyde, G. F. Strouse, W. E. Jones, Jr., T. J. Meyer, *J. Am. Chem. Soc.* **1990**, *112*, 7395.
[5] V. Grosshenny, A. Harriman, F. M. Romero, R. Ziessel, *J. Phys. Chem.* **1996**, *100*, 17472.
[6] J. R. Shaw, R. T. Webb, R. H. Schmehl, *J. Am. Chem. Soc.* **1990**, *112*, 1117.
[7] V. Grosshenny, F. M. Romero, R. Ziessel, *J. Org. Chem.* **1997**, *62*, 1491.
[8] B. König, H. Zieg, M. Nimtz, L. De Cola, V. Balzani, *Chem. Ber.* **1997**, *130*, 529.
[9] A. Helms, D. Heiler, G. McLendon, *J. Am. Chem. Soc.* **1991**, *113*, 4325.
[10] M. P. Samanta, W. Tian, S. Datta, J. I. Henderson, C. P. Kubiak, *Phys. Rev. B* **1996**, *53*, 7626.
[11] F. Barigelletti, L. Flamigni, M. Guardigli, J.-P. Sauvage, A. Sour, *Chem. Commun.* **1996**, 1329.
[12] The thermodynamic driving force for light-induced electron transfer from the triplet state of a Ru(terpy)-based chromophore to the central viologen-like acceptor is $\Delta G^\circ \approx -0.07$ eV, as calculated from the redox potentials with the triplet energy estimated for **2**. For subsequent charge recombination, $\Delta G^\circ \approx -1.83$ eV.
[13] M. Gubelmann, A. Harriman, J. M. Lehn, J. L. Sessler, *J. Phys. Chem.* **1990**, *94*, 308.
[14] P. A. Christensen, W. Erbs, A. Harriman, *J. Chem. Soc. Faraday Trans. 2* **1985**, *81*, 575.
[15] C. Dietrich-Buchecker, J. M. Kern, J.-P. Sauvage, *J. Am. Chem. Soc.* **1989**, *111*, 7791.

Models for the Carbonyl–ene Cyclization Reaction: Open and Closed Transition States[**]

D. Christopher Braddock, King Kuok (Mimi) Hii, and John M. Brown[*]

During a study of stereospecific syntheses of menthol-related terpenoids we prepared racemic and enantiomerically pure 5-methyl-2-(1-methylethyl)hex-5-enal (**1**).[1] From preliminary experiments with simple Lewis acids, catalytic BCl_3, and catalytic or stoichiometric quantities of $SnCl_4$ gave cleanly the anticipated ene-cyclization products **2** and **3** (Scheme 1). In these two cases the ratio of **2** to **3** was 9:1, which is in accord with related results obtained by Snider and

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[*] Dr. J. M. Brown, Dr. D. C. Braddock, Dr. K. K. Hii
Dyson Perrins Laboratory
South Parks Road., Oxford OX1 3QY (UK)
Fax: (+44) 1865-275674
E-mail: bjm@ermine.ox.ac.uk

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