126. Ruthenium(II) Complexes with Three Different Diimine Ligands

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The synthesis of tris-heteroleptic complexes of Ru(II) with diimine ligands is described. Ten compounds $[Ru(R_2bpy)(biq)(L)][PF_6]_2$ (R = H, CH_3; L = 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy), 2,2′-bipyrimidine (bpm), 2,2′-biisoquinoline (biiq), 1,10-phenanthroline (phen), dipyrido[3,2-*c*:2′,3′-*e*]pyridazine (taphen), 2,2′-biquinoline (biq), 6,7-dihydrodipyrido[2,3-*b*:3,2-*j*][1,10]-phenanthroline (dinapy), 2-(2-pyridyl)quinoline (pq), 1-(2-pyrimidyl)pyrazole (pzpm), 2,2′-biimidazole (H_2biim)) are characterized by elemental analysis, electronic and ^1H-NMR spectroscopy. The relative photosubstitution rates of biq in MeCN are given at three temperatures.

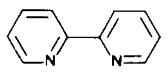
Introduction. – Ruthenium complexes with diimine ligands have been a matter of considerable interest in recent years [1] [2]. The parent complex ion $[Ru(bpy)_3]^{2+}$ has unusual redox properties in the ground state and in the first excited state, rendering it a useful photo-sensitizer [1] [3–5] which has been extensively studied with regard to the decomposition of H_2O [1] [6]. The complex has been modified or 'tuned' to accomplish even more useful properties in the ground and excited state [7–10]. Apart from synthesizing new homoleptic species $[Ru(II)(L')_3]^{2+}$ where L′ is a ligand different from bpy, mixed complexes of the type $[Ru(II)(L)_{3-n}(L')_n]^{2+}$ were prepared [10]. In the present communication, we extend the series of ruthenium-tris(diimine) complexes to tris-heteroleptic species of the type $[Ru(II)(L)(L')(L'')]^{2+}$ (L, L′, and L″ = bidentate ligands). Emission properties as well as redox potentials will be published in due course [11]. Altogether, a series of ten complexes of the type $[Ru(L)(L')(L'')]^{2+}$ were prepared. Two of these have already been mentioned in [12], using a different synthetic method [13] [14], and very recently one other analogous complex was reported [15].

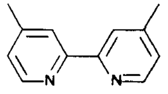
Experimental. – *Materials.* Chemicals were purchased from *Fluka, Merck,* or *Aldrich,* and used without further purification. The initial complex $[Ru(bpy)Cl_3]\cdot H_2O$ [16] and the polypyridine ligands, which are not commercially available, biiq [17], taphen [18], dinapy [19], H_2biim [20], pzpm [21], and pq [22], were prepared according to the literature methods. Column chromatography was carried out with silica gel *60* from *Merck* according to the method described by *Still et al.* [23].

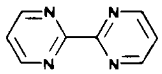
Measurements. The ^1H-NMR spectra were measured in (D_6)acetone with a *Bruker AM 360* spectrometer with TMS as internal standard. Absorption spectra were measured with a *Perkin-Elmer 555* spectrophotometer. Photosubstitution reactions were studied in diluted solns. ($8.5\cdot10^{-5}$M) in MeCN (3 ml). A 1-cm quartz cell was irradiated in a *Zeiss Pradovit Color 2000* slide projector with a 250-W lamp. The relative rate of substitution of each complex was monitored at three different temp. by following the changes in absorbance. Elemental analyses were performed in the Institute of Organic Chemistry, University of Fribourg.

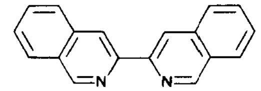
Preparation of Compounds. $[Ru(bpy)(biq)_2][PF_6]_2$ was prepared according to the method described in [24].

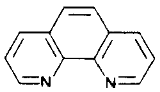
cis-$[Ru(bpy)(biq)(ACN)_2][PF_6]_2$. $[Ru(bpy)(biq)_2][PF_6]_2$ (150 mg, 0.141 mmol) was dissolved in MeCN (40 ml). The violet soln. was irradiated under Ar with stirring for 2 h. The soln. turned orange-brown, and the solvent was removed in the rotary evaporator. The solid material was redissolved in acetone (15 ml). The liberated

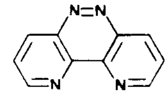

2,2'-Bipyridine
(bpy)

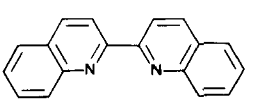

4,4'-Dimethyl-2,2'-bipyridine
(Me_2bpy)

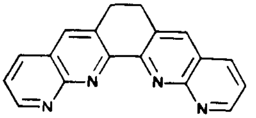

2,2-Bipyridine
(bpm)

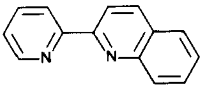

2,2'-Biisoquinoline
(biiq)

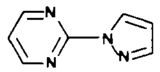

1,10-Phenantroline
(phen)

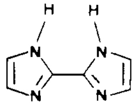

Dipyrido[3,2-*c*;2',3'-*e*]pyridazine
(taphen)


2,2'-Biquinoline
(biq)


6,7-Dihydrodipyrido[2,3-*b*;3,2-*j*]1,10-phenanthroline
(dinapy)


2-(2-Pyridyl)quinoline
(pq)


1-(2-Pyrimidyl)pyrazole
(pzpm)


2,2'-Biimidazole
(H_2biim)

2,2'-biquinoline was precipitated by addition of H_2O (15 ml) and removed by filtration. The product was then precipitated as the hexafluorophosphate salt by the addition of several ml of a conc. soln. of NH_4PF_6 in H_2O. The PF_6^- salt was collected by suction filtration, washed with H_2O, and dried overnight at 80°; yield 85%. Anal. calc. for $C_{32}H_{26}F_{12}N_6P_2Ru$: C, 43.40, H, 2.96, N, 9.49; found: C 43.42, H, 3.0, N, 9.39.

[Ru(bpy)(biq)(L'')][PF$_6$]$_2$. *cis*-[Ru(bpy)(biq)(MeCN)$_2$][PF$_6$]$_2$ (60 mg, $6.77 \cdot 10^{-5}$ mol) and the third diimine (1 equiv.) were suspended in a 1:1 H_2O/EtOH soln. (15 ml). The mixture was refluxed with stirring under Ar. Since the *cis*-[Ru(bpy)(biq)(MeCN)$_2$][PF$_6$]$_2$ was not completely dissolved, acetone (3 ml) was added and the refluxing continued for 3 h. Acetone (30 ml) was added to the cold soln. which was filtered. The product was precipitated by addition of H_2O (30 ml) and NH_4PF_6. The mixture was placed overnight at 0° to complete the precipitation. The PF_6^- salt was collected by suction filtration, washed with H_2O, and recrystallized from acetone/Et_2O.

Results and Discussion. – *Synthesis.* Several synthetic pathways to obtain tris-heteroleptic complexes were explored [25]. One possibility is the preparation of the intermediate [Ru(bpy)(biq)Cl$_2$] which then can react with L' to give the complex [Ru(bpy)(biq)(L')]$^{2+}$. Several of the tris-heteroleptic compounds (*Table 1*) were synthesized by this method. It yields generally mixtures of various complexes, which have to be separated by column chromatography.

The best way to prepare the tris-heteroleptic complexes is, however, by passing through the intermediate *cis*-[Ru(bpy)(biq)(MeCN)$_2$]$^{2+}$, which can be obtained by photolysis of [Ru(bpy)(biq)$_2$]$^{2+}$ (*Scheme 1*).

Table 1. *Elemental Analyses and Colors of Tris-heteroleptic Diimine Complex Salts of Ru(II)*

Complex		Calc.			Found			Color
		C	H	N	C	H	N	
$[Ru(bpy)(biq)(phen)][PF_6]_2$ $C_{40}H_{28}F_{12}N_6P_2Ru$	(**1**)	48.84	2.87	8.54	48.71	2.77	8.44	red-brown
$[Ru(bpy)(biq)(Me_2bpy)][PF_6]_2$ $C_{40}H_{32}F_{12}N_6P_2Ru$	(**2**)	48.64	3.26	8.51	48.81	3.30	8.50	red-brown
$[Ru(bpy)(biq)(biiq)][PF_6]_2$ $C_{46}H_{32}F_{12}N_6P_2Ru$	(**3**)	52.13	3.04	7.93	52.22	3.10	7.90	red
$[Ru(bpy)(biq)(bpm)][PF_6]_2$ $C_{36}H_{26}F_{12}N_8P_2Ru$	(**4**)	44.96	2.73	11.65	45.09	2.80	11.46	red-brown
$[Ru(Me_2bpy)(biq)(bpm)][PF_6]_2$ $C_{38}H_{30}F_{12}N_8P_2Ru$	(**5**)	46.12	3.06	11.32	45.14	3.04	11.05	red-brown
$[Ru(bpy)(biq)(dinapy)][PF_6]_2$ $C_{46}H_{32}F_{12}N_8P_2Ru$	(**6**)	50.79	2.97	10.30	50.77	3.00	10.28	blue-violet
$[Ru(bpy)(biq)(taphen)][PF_6]_2$ $C_{38}H_{26}F_{12}N_8P_2Ru$	(**7**)	46.30	2.66	11.37	46.55	2.87	11.09	red-brown
$[Ru(bpy)(biq)(H_2biim)][PF_6]_2$ $C_{34}H_{26}F_{12}N_8P_2Ru$	(**8**)	43.55	2.80	11.95	45.11	3.00	12.53	violet
$[Ru(bpy)(biq)(pq)][PF_6]_2$ $C_{42}H_{30}F_{12}N_6P_2Ru$	(**9**)	49.96	2.99	8.32	49.76	3.10	8.17	red-violet
$[Ru(bpy)(biq)(pzpm)][PF_6]_2$ $C_{35}H_{26}F_{12}N_8P_2Ru$	(**10**)	44.60	2.78	11.89	44.41	2.84	11.82	red-brown

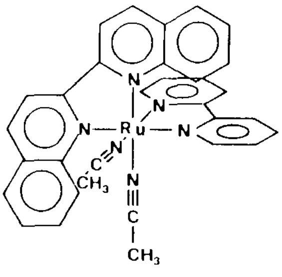
Scheme 1

$$[Ru(bpy)(biq)_2]^{2+} \xrightarrow[MeCN]{h\nu} [Ru(bpy)(biq)(MeCN)_2]^{2+} + biq$$

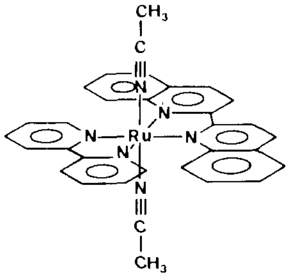
$$[Ru(bpy)(biq)(MeCN)_2]^{2+} + L'' \longrightarrow [Ru(bpy)(biq)(L'')]^{2+} + 2\ MeCN$$

$[Ru(bpy)(biq)(MeCN)_2]^{2+}$ can be isolated as its PF_6^- salt, and it reacts at relatively low temperatures with L′. The tris-complexes can be obtained in pure form by simple recrystallization.

^1H-NMR Spectroscopy. Signals have been assigned by the use of spin multiplicity, H,H coupling constants, selective decoupling, and in some cases by the use of nuclear *Overhauser* effect (NOE) experiments. The ^1H-NMR spectra of the tris-heteroleptic



cis



trans

Ru(II)-diimine complexes are relatively complicated. Since these complexes are unsymmetrical, all the protons are inequivalent in the ^{1}H-NMR spectra.

$[Ru(bpy)(biq)(MeCN)_2]^{2+}$ could give rise to two isomers. The *trans*-isomer has a C_2 symmetry, whereas the *cis*-isomer has C_1. The ^{1}H-NMR spectrum clearly shows the absence of C_2 symmetry excluding the *trans*-isomer. The spectrum shows 20 resonances in the aromatic region *(Fig. 1)* and two resonances in the aliphatic region due to the non-equivalent MeCN moieties. The chemical shifts are listed in *Table 2*. H–C(6′) of bpy is shifted by more than 1 ppm to low field by comparison of H–C(6) of bpy in tris-hetero-

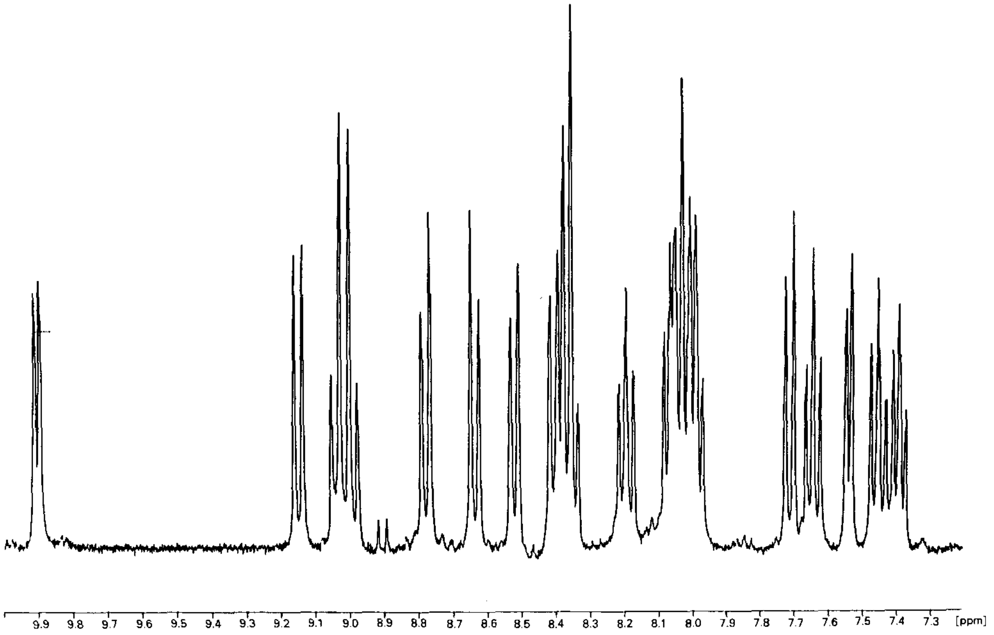


Fig. 1. *360-MHz ^{1}H-NMR Spectrum* ((D_6)acetone) *of $[Ru(bpy)(biq)(MeCN)_2]^{2+}$* (aromatic region)

Table 2. *^{1}H-NMR Chemical Shifts of $[Ru(bpy)(biq)(MeCN)_2]^{2+}$ in (D_6)Acetone*

bpy			
H–C(3)	8.38, 8.33	H–C(3′)	8.52 (*dd*, *J* = 8.18, 1.30)
H–C(4)	8.0 (*ddd*, *J* = 8.03, 7.34, 1.22)	H–C(4′)	8.38, 8.33
H–C(5)	7.39 (*ddd*, *J* = 7.50 5.87, 1.47)	H–C(5′)	8.07 (*ddd*, *J* = 7.49, 5.58, 1.35)
H–C(6)	7.54 (*ddd*, *J* = 5.83, 1.37, 0.61)	H–C(6′)	9.91 (*ddd*, *J* = 5.47, 1.33, 0.63)
biq			
H–C(3)	8.78 (*d*, *J* = 8.71)	H–C(3′)	9.04 (*d*, *J* = 8.78)
H–C(4)	8.64 (*d*, *J* = 8.78)	H–C(4′)	8.99 (*d*, *J* = 8.82)
H–C(5)	8.04 (*dd*, *J* = 8.32, 1.33)	H–C(5′)	8.41 (*dd*, *J* = 8.16, 1.31)
H–C(6)	7.64 (*ddd*, *J* = 8.08, 6.98, 1.04)	H–C(6′)	8.01 (*ddd*, *J* = 8.12, 7.02, 1.10)
H–C(7)	7.45 (*ddd*, *J* = 8.78, 7.03, 1.30)	H–C(7′)	8.20 (*ddd*, *J* = 8.79, 6.96, 1.60)
H–C(8)	7.71 (*dd*, *J* = 8.80, 0.52)	H–C(8′)	9.15 (*dd*, *J* = 9.04, 0.54)

leptic complexes. H–C(5′) of bpy shows a similar shift but less pronounced (*ca.* 0.5 ppm). H–C(8′) and H–C(7′) of biq show identical behavior (more than 1 ppm for H–C(8′) and *ca.* 0.7 ppm for H–C(7′)). These shifts can be explained by the fact that these protons are situated above the C≡N bond of MeCN. All other protons have chemical shifts more or less similar to those obtained in tris-heteroleptic complexes [25].

Electronic Absorption Spectroscopy. The electronic absorption data for heteroleptic Ru(II)-tris(diimine) complexes are summarized in *Table 3*. The spectra exhibit in the UV region strong bands due to ligand-centered transitions ($\pi \rightarrow \pi$) [26] [27]. In the VIS region, they also show intense bands which can be attributed to MLCT transitions (‘t_{2g}’$\rightarrow \pi^*$). *Fig. 2* shows the VIS spectra of some Ru(II)-tris(diimine) complexes that are illustrative of the whole series of the tris-heteroleptic compounds.

Table 3. *Spectral Data for the Complexes of the Type [Ru(bpy)(biq)(L″)]$^{2+}$*

L″	Absorption a): λ_{max} [nm] ($10^{-4}\varepsilon$ [$M^{-1} \cdot cm^{-1}$])
phen	525(0.95), 490(sh, 0.62), 438(0.88), 375(2.06), 354(2.07), 333(sh, 2.4), 320(2.46), 285(7.09), 265(10.87)
Me_2bpy	532(0.93), 500(sh, 0.63), 439(0.82), 376(1.77), 354(sh, 2.22), 326(2.79), 287(5.46), 267(5.61)
biiq	533(0.92), 500(sh, 0.58), 430(0.92), 376(2.48), 326(6.46), 287(4.36), 260(8.23)
bpm	518(0.76), 488(sh, 0.60), 441(0.66), 400(sh, 0.5), 376(2.37), 357(2.2), 337(sh, 2.33), 320(2.55), 284(3.55), 265(5.51)
bpm b)	524(0.77), 490(sh, 0.57), 445(0.62), 396(0.59), 375(2.3), 357(2.26), 336(sh, 2.43), 322(2.5), 278(3.4), 265
dinapy	612(sh, 0.52), 580(0.58), 486(0.61), 454(sh, 0.26), 396(1.93), 373(sh, 2.92), 354(3.18), 346(sh, 3.14), 283(4.75), 265(6.09), 245(4.92)
taphen	520(0.92), 437(0.78), 400(sh, 0.44), 376(2.43), 356(2.09), 330(sh, 2.63), 314(sh, 2.82), 282(4.16), 264(6.7)
H_2biim	552(0.89), 520(sh, 0.52), 448(0.35), 372(sh, 1.3), 289(4.0), 262(5.43)
pq	530(0.91), 458 (0.87), 412(sh, 0.3), 375(1.64), 354(2.3), 314(4.05), 288(3.85), 266(6.01), 257(sh, 5.12)
pzpm	510(0.79), 480(sh, 0.55), 418(0.66), 376(2.52), 357(2.25), 340(sh, 2.24), 285(3.59), 265(5.48), 256(sh, 4.63)
bpy c)	526(0.87), 494(sh, 0.58), 439(0.81), 400(sh, 0.44), 370(1.71), 350(sh, 2.04), 334(2.36), 318(sh, 2.57), 282(6.42), 261(5.67), 251(sh, 4.23)
biq c)	547(0.86), 481(0.66), 442(sh, 0.28), 408(0.3), 378(3.04), 359(3.07), 338(sh, 3.75), 323(4.26), 288(3.66), 267(10.7)

a) The spectra were measured at r.t. in MeCN solutions.
b) [Ru(Me_2bpy)(biq)(bpm)]$^{2+}$.
c) [9].

In the series of the bis-heteroleptic complexes [Ru(L)$_2$(L′)]$^{2+}$, one can observe two MLCT bands assignable to transitions into the lowest π^* orbitals of L and L′ [9] [24] [28]. The two bands are resolved, if the difference in the energies of the two π^* orbitals is sufficiently large [29].

In tris-heteroleptic complexes, we would predict, in principle, three different MLCT transitions. The differences of the energies of the π^* orbitals of the three diimine ligands are, however, in general not large enough to give a splitting into three bands, and consequently only two transitions can be discerned.

Except for [Ru(bpy)(biq)(dinapy)]$^{2+}$, where d$\rightarrow\pi^*$(dinapy) is the first MLCT band, the transition d$\rightarrow\pi^*$(biq) is at lowest energy. Possibly, three bands can be observed for [Ru(bpy)(biq)(bpm)]$^{2+}$. The d$\rightarrow\pi^*$(biq), d$\rightarrow\pi^*$(bpm), and d$\rightarrow\pi^*$(bpy) transitions would appear at 518, 441, and 400 nm, respectively.

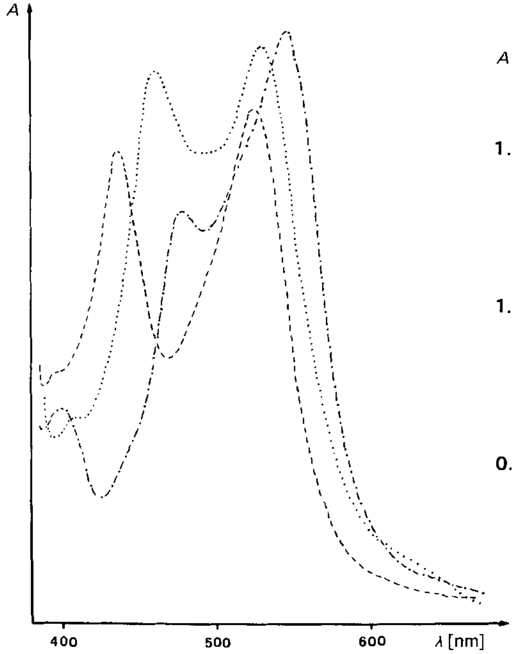


Fig. 2. *Electronic absorption spectra of* $[Ru(bpy)_2(biq)][PF_6]_2$ (——), $[Ru(bpy)(biq)_2][PF_6]_2$ (–·–·), *and* $[Ru(bpy)(biq)(pq)][PF_6]_2$ (····) *in the VIS region* (MeCN solutions)

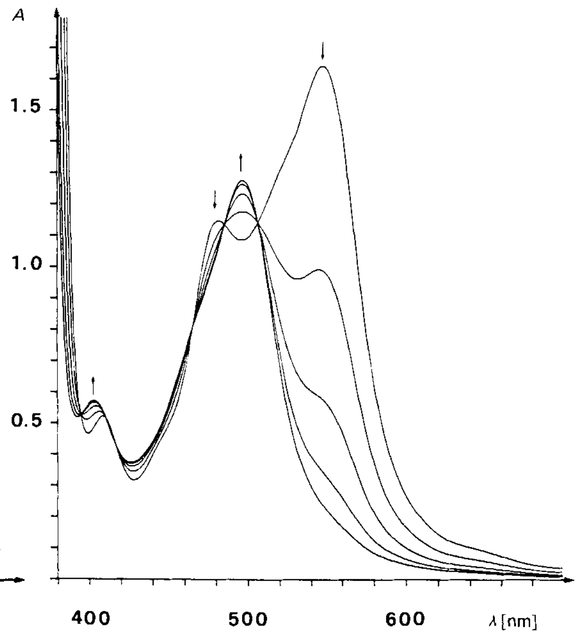


Fig. 3. *Change in the electronic absorption spectra of* $[Ru(bpy)(biq)_2][PF_6]_2$ *in MeCN upon irradiation with visible light* (irradiation times: 0 s, 5 s, 10 s, 15 s, 20 s)

Photoreactivity. The $[Ru(bpy)_n(biq)_{3-n}]^{2+}$ complexes ($n = 1,2$) are photolabile, and irradiation in acidic 1:1 H_2O/acetone soln. leads to $[Ru(bpy)_n(biq)_{2-n}(H_2O)_2]^{2+}$ [30][31]. *Marzin* and coworkers have found that $[Ru(bpy)_n(L)_{3-n}]^{2+}$ complexes ($n = 1,2$; L = 3,5-dimethyl-1-(2-pyridyl)-pyrazole) yield $[Ru(bpy)_n(L)_{2-n}(MeCN)_2]^{2+}$ when irradiated in pure MeCN [32]. The $[Ru(bpy)(biq)(L'')]^{2+}$ complexes are photolabile too, and in the case of $[Ru(bpy)(biq)_2]^{2+}$, irradiation in MeCN solution gives rise to *cis*-$[Ru(bpy)(biq)(MeCN)_2]^{2+}$ by substitution of one ligand biq. *Fig. 3* shows the change in the absorption spectra of $[Ru(bpy)(biq)_2]^{2+}$ upon irradiation with visible light. For all tris-heteroleptic complexes of the type $[Ru(bpy)(biq)(L'')]^{2+}$, the photoreaction in MeCN is outlined in *Scheme 2.*

Scheme 2

$$[Ru(bpy)(biq)(L'')]^{2+} \xrightarrow[\text{MeCN}]{h\nu} [Ru(bpy)(L'')(MeCN)_2]^{2+} + \text{biq}$$

The species $[Ru(bpy)(L'')(MeCN)_2]^{2+}$ were not isolated, but their VIS spectra indicate their constitution. The first MLCT band of $[Ru(bpy)(biq)(L'')]^{2+}$ disappears. In the photo-product the absorption of longest wavelenght is due to L″ or bpy. The relative quantum yields are temperature-dependent and have been measured at three different

Table 4. *Photoreactivity: Relative Quantum Yields* (Φ_{rel} for $[Ru(bpy)(biq)(dinapy)]^{2+}$ at 293.5 K is defined to be 1) *at 293.5 K, 303 K, and 311.5 K in MeCN*

Complexes	Φ_{rel}		
	293.5 K (±0.1)	303 K (±0.1)	311.5 K (±0.1)
$[Ru(bpy)(biq)(phen)]^{2+}$	9.1	23	38.6
$[Ru(bpy)(biq)(Me_2bpy)]^{2+}$	3	6.1	12.3
$[Ru(bpy)(biq)(biiq)]^{2+}$	2.2	4.8	9.1
$[Ru(bpy)(biq)(bpm)]^{2+}$	102	200	318
$[Ru(Me_2bpy)(biq)(bpm)]^{2+}$	59	109	159
$[Ru(bpy)(biq)(dinapy)]^{2+}$	1	1.6	2.5
$[Ru(bpy)(biq)(taphen)]^{2+}$	88.6	154	250
$[Ru(bpy)(biq)(H_2biim)]^{2+}$	–	–	0.25
$[Ru(bpy)(biq)(pq)]^{2+}$	72.7	138.6	220
$[Ru(bpy)(biq)(pzpm)]^{2+}$	31.8	43.2	61.4
$[Ru(bpy)(biq)_2]^{2+}$	1480	–	–
$[Ru(bpy)_2(biq)]^{2+}$	6.4	13	22.7

temperatures *(Table 4)*. It can be seen that noticeable differences exist in photoreactivity of the complexes. At 293.5 K, a linear correlation between the ln Φ_{rel} (Φ_{rel} = relative quantum yield) and the oxidation potential of the complexes was found *(Fig. 4)*. Only the values for $[Ru(bpy)(biq)_2]^{2+}$ (*c*) and for $[Ru(bpy)(biq)(pq)]^{2+}$ (*9*) deviate noticeably from the straight line. In these two complexes, the reactivity seems to be enhanced by the steric crowding of the ligands.

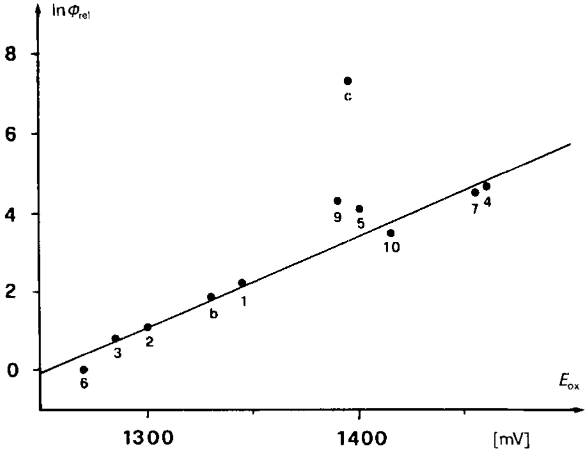


Fig. 4. *Correlation between ln Φ_{rel} and oxidation potential (Ru^{3+}/Ru^{2+}) of the complexes. 1* to *10* indicate the tris-heteroleptic complexes **1** to **10** *(cf. Table 1)*; *b* and *c* represent $[Ru(bpy)_2(biq)]^{2+}$ and $[Ru(bpy)(biq)_2]^{2+}$, resp., leaving aside $[Ru(bpy)(biq)_2]^{2+}$ and $[Ru(bpy)(biq)(pq)]^{2+}$, the best-fitting line has a correlation coefficient of 0.98.

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