Influence of the 4-Substituted Pyridine Ligand L' on both the Conformation and Spectroscopic Properties of the (2,2'-Biquinoline- $\kappa N^1,\kappa N^{1'}$)tricarbonyl(pyridine- κN^1)rhenium(1+) Complex ([Re(CO)₃-(bqui)(py)]⁺) and Its Derivatives [Re(CO)₃(L)(L')]⁺ (L=2,2'-Biquinoline and 3,3'-(Ethane-1,2-diyl)-2,2'-biquinoline)

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A series of new rhenium(I) complexes of the type $[\text{Re}^{I}(\text{CO})_{3}(\text{L})(\text{L}')]^{n+}$ (L = 2,2'-biquinoline (bqui) or 3,3'-(ethane-1,2-diyl)-2,2'-biquinoline (CH₂CN₂)bqui); L'=CF₃SO₃⁻, pyridine (py), or 4-substituted pyridine (HOpy, Bzpy, or NCpy); n = 0 or 1) were prepared and characterized by FT-IR, ¹H-NMR, UV/VIS and emission spectroscopy, luminescence lifetimes, and cyclic voltammetry. The pseudo-octahedral facial configuration was established by X-ray single-crystal diffraction analysis of two complexes and by a FT-IR study of all complexes. The $[\text{Re}(\text{CO})_{3}(\text{bqui})(\text{Bzpy})](\text{CF}_{3}\text{SO}_{3})$ complex crystallizes in the form of two mirror isomers arising from the conformational mobility of the biquinoline ligand. A correlation between the metal-to-ligand charge-transfer (MLCT) emission maxima and the σ^+ Hammett parameter was established for the complexes of the bqui series, while such correlation was not observed for the complexes of the (CH₂CH₂)bqui series. No correlation between oxidation potentials and the Hammett parameters was established. The results were rationalized in function of the effect of the 4-substituted pyridine ligand on the octahedral distortion and conformational characteristic of the complexes. The ¹H-NMR data confirmed these results.

Introduction. – Luminescent transition-metal complexes have been utilized as photosensitizers in areas such as solar-energy conversion, electron-transfer studies, chemiluminescent and electroluminescent systems, binding dynamics of heterogeneous media, and probes of macromolecular structure [1]. In this regard, much attention has been paid to Re^I complexes in recent years [2]. Many of these compounds exhibit a wide variety of energetically accessible metal-to-ligand charge transfer (MLCT), ligand-to-ligand charge transfer (LLCT), and intraligand (IL) excited states [3].

Their chemical, photochemical, and photocatalytic properties have made rhenium(I) complexes with polypyridine ligands potential thermal, photochemical, and electrochemical catalyzers [1a][4]. Examples of these include the electroreduction

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and photoreduction of CO_2 which could be of interest in the conversion and storage of solar energy [5].

The photophysical properties of the metal complexes are determined predominantly by the lowest-energy excited states [6]. However, the population of higher excited states leads to photochemical pathways. Thus, the control or modulation of the absorption and/or emission energy is a very important tool for the modification of the catalytic behavior of these complexes.

To evaluate the effect of structural modifications in the polypyridine ligand on the properties of the ground and excited states of these complexes, we have studied complexes of the general structure [ReBr(CO)₃(L)] with L = bidentate polypyridine ligand [3h][7]. In previous studies of [ReBr(CO)₃(R,R'bqui)], with R,R'bqui=3,3'-R,R'-2,2'-biquinoline and R = R' = H or Me, or $R - R' = CH_2CH_2$ or $CH_2CH_2CH_2$, we found that the extended conjugation in the 2,2'-biquinoline (=bqui) ligand, as compared to 2,2'-bipyridine (bpy) ligand, causes a shift towards lower energy both in the MLCT band and in the reduction potential of the polypyridine ligand [7b,d]. Moreover, the conformational characteristic of the complexes caused by the distortion degree from the planarity in the bqui ligand induces a slight variation of these energies [7d]. We have associated the emissions in these complexes with parallel relaxation processes from an IL and a MLCT state [7e].

The substitution of the Br-ligand in the complexes $[\text{ReBr}(\text{CO})_3(\text{R,R'bqui})]$ by 4substituted pyridine ligands (L') containing electron-donating or electron-attracting groups represents a viable alternative to obtain both a new MLCT electronic state, *i.e.*, $\text{Re} \rightarrow \text{pyridine}$, and inductive effects upon the energy of the $\text{Re} \rightarrow \text{bqui}$ MLCT [6][7e]. The objective of the present work is to rationalize the inductive effect of the 4-substituted pyridine ligand on the properties of biquinolinerhenium complexes. For this purpose, we report here the synthesis and spectroscopic studies of a new series of complexes of the type $[\text{Re}^1(\text{CO})_3(\text{L})(\text{L'})]^{n+}$, with L=2,2'-biquinoline (bqui¹) or 3,3'-(ethane-1,2-diyl)-2,2'-biquinoline (CH₂CH₂)bqui¹); $\text{L'}=\text{CF}_3\text{SO}_3^+$, pyridine (py), or 4-substituted pyridines Xpy, *i.e.*, HOpy, Bzpy (Bz=benzyl), or NCpy, and n=0 or 1.

Results and Discussion. – The prepared complexes $[Re^{I}(CO)_{3}(L)(L')]^{n+}$ are stable in air either as solids or in solution. They are soluble in several solvents of medium polarity. The conductivity values are in accordance with the formulae of the corresponding complexes.

The IR spectrum for the $[\text{Re}(\text{CO})_3(\text{L})(\text{CF}_3\text{SO}_3)]$ complexes $(\text{L}=\text{bqui} \text{ or }(\text{CH}_2\text{CH}_2)-\text{bqui})$ show three strong bands in the carbonyl stretching region that arise from a facial configuration with a local C_s symmetry of the carbonyl groups around a hexacoordinated Re-center. In case of complexes $[\text{Re}(\text{CO})_3(\text{L})(\text{L}')]$ with L'=4-substituted pyridine ligand = Xpy, the IR spectra exhibit two intense bands in the carbonyl stretching region. This behavior results from a C_{3v} local symmetry for the CO groups in a facial configuration. The lowest-energy band is very broad, which can be attributed to a

¹) Formerly, the following abbreviations were used instead of bqui and (CH₂CH₂)bqui; 2,2'-biquinoline=0,2N and 3,3'-dimethylene-2,2'-biquinoline=3,3'-(ethane-1,2-diyl)-2,2'-biquinoline=2,2N, respectively. For systematic names, see *Exper. Part.*

decrease of the octahedral symmetry in the complexes with 4-substituted pyridine ligands [8].

Crystal structures were obtained by X-ray single-crystal diffraction analysis for [Re(CO)₃(bqui)(py)](CF₃SO₃) and [Re(CO)₃(bqui)(Bzpy)](CF₃SO₃) (Table 1). The compounds are mononuclear, with [Re(CO)₃(bqui)(py)](CF₃SO₃) exhibiting just one molecule in the asymmetric unit while two mirror isomers, hereafter represented by A and B, are observed in the case of $[Re(CO)_3(bqui)(Bzpy)](CF_3SO_3)$. In both structures, the complex cations are electrically balanced by the triflate counteranions thus giving rise to neutral entities (Fig. 1). In both species, the Re environment conforms to a slightly distorted octahedron built up through the coordination of three carbonyl groups, the bidentate bqui ligand, and the py or Bzpy ligand. The N(3) atom of the pyridine ligand and the C(1) atom of one of the carbonyl units occupy the apical sites, and the basal plane is defined by C(2) and C(3) (of the remaining carbonyl groups) and N(1) and N(2) of the bqui ligand (arbitrary atom numbering, see Fig. 1). In all cases, the metal atom is slightly displaced from the mean plane along the apical line toward the py or Bzpy ligand (by 0.109(1)Å in [Re(CO)₃(bqui)(py)](CF₃SO₃) and by 0.114(1)and 0.108(1)Å in A and B, resp., of [Re(CO)₃(bqui)(Bzpy)](CF₃SO₃)), suggesting a base with the aspect of a depressed square pyramid. The apical axes are rather linear $(N(3)-Re(1)-C(1) \ 179.2(3)^{\circ}$ in $[Re(CO)_3(bqui)(py)](CF_3SO_3)$, and 178.0(5) and $179.3(5)^{\circ}$ in A and B, resp., of $[Re(CO)_3(bqui)(Bzpy)](CF_3SO_3))$ with small departures from the mean plane normals (4.3(2)° in [Re(CO)₃(bqui)(py)](CF₃SO₃), and 6.3(3) and $5.3(2)^{\circ}$ in A and B, resp., of bqui [Re(CO)₃(bqui)(Bzpy)](CF₃SO₃)). The Re-carbonyl interactions appear to be quite linear in [Re(CO)₃(bqui)(py)](CF₃SO₃) (range of the O-C-Re angle, $177.4-179.5^{\circ}$) and show a slightly larger deviation in [Re(CO)₃-

Table 1	. Crysta	llographic	Data
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	[Re(CO) ₃ (bqui)(py)](CF ₃ SO ₃)	[Re(CO) ₃ (bqui)(Bzpy)](CF ₃ SO ₃)
Formula	$C_{27}H_{17}F_3N_3O_6ReS$	$C_{34}H_{23}F_3N_3O_6ReS$
$M_{\rm r}$	754.70	844.81
System	monoclinic	monoclinic
Space group	P 21/c (no.14)	P 21/c (no.14)
Crystal dimensions [mm]	$0.30 \times 0.24 \times 0.16$	$0.25 \times 0.18 \times 0.16$
Crystal color, shape	orange, prisms	orange, prisms
a [Å]	11.614(1)	23.670(5)
<i>b</i> [Å]	12.597(1)	10.755(2)
<i>c</i> [Å]	18.234(2)	27.235(7)
β[°]	98.31(1)	111.84(2)
Cell volume [Å ³]	2639.8(4)	6436(2)
Ζ	4	8
$D_{\rm x} [\rm g cm^{-3}]$	1.90	1.74
F(000)	1464	3312
$\mu [{\rm mm}^{-1}]$	4.75	3.91
Max, min absorpt. correct.	0.39, 0.28	0.52, 0.43
Unique refl., R_{int} , parameters	4644, 0.051, 384	11317, 0.075, 880
R_1^{a} , wR_2^{b}) $(F^2 > 2\sigma(F^2))$	0.044, 0.104	0.064, 0.119
Final $\Delta \rho$ [eÅ ⁻³]	1.76, -1.68	0.77, -0.87
^{a)} $R_1: \Sigma F_o - F_c / \Sigma F_o $. ^{b)} $wR_2: [$	$\Sigma[w(F_{o}^{2}-F_{o}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]]^{\frac{1}{2}}.$	



Fig. 1. Molecular diagrams a) for $[Re(CO)_3(bqui)(py)]^+$ and b) for the isomers A and B of $[Re(CO)_3(bqui)-(Bzpy)]^+$. Arbitrary atom numbering; displacement ellipsoids drawn at a 40% level.

(bqui)(Bzpy)](CF₃SO₃) (ranges of the O–C–Re angle, $174.9-177.2^{\circ}$ in A and $171.9-174.6^{\circ}$ in B).

In the above complexes, the two independent moieties of the bqui ligand define a substantial dihedral angle $(17.7^{\circ} \text{ in } [\text{Re}(\text{CO})_3(\text{bqui})(\text{py})](\text{CF}_3\text{SO}_3)$, and 12.1° and 17.4° in *A* and *B*, resp., of $[\text{Re}(\text{CO})_3(\text{bqui})(\text{Bzpy})](\text{CF}_3\text{SO}_3)$), much larger than the corresponding N(1)–C(13)–C(14)–N(2) torsion angle that would be a measure of any eventual rotation around the C(13)–C(14) bond (-4.6° in $[\text{Re}(\text{CO})_3(\text{bqui})(\text{py})]$ (CF₃SO₃) and 3.6° and -1.4° in *A* and *B*, resp., of $[\text{Re}(\text{CO})_3(\text{bqui})(\text{Bzpy})](\text{CF}_3\text{SO}_3)$). This conformational effect probably is responsible for the presence of two conformational isomers.

This important deformation arises when the bqui ligand is bi-coordinate to the Recenter. The ligand is forced out of the octahedron's equatorial plane in the way discussed previously, presumably to avoid as much as possible the steric hindrance imposed by the eventual collision between the outermost H-atoms (H–C(8) and

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H–C(8')) of bqui and equatorial carbonyl groups (see below *Fig.* 2 for bqui numbering). Due to the nonplanar character of the ligand, the effect is difficult to quantify properly. However, its importance is suggested by the rather large dihedral angles that the lateral wings subtend with the polyhedron equatorial plane N(1)–N(2)– C(2)–C(3) (arbitrary numbering, see *Fig.* 1). In complexes with the same coordination pattern but containing the smaller pyridine ligands, this angle usually amounts to only a few degrees; but this dihedral angle is 35.3 and 37.7° in [Re(CO)₃(bqui)(py)](CF₃SO₃), and 32.9 and 35.1°, and 35.6 and 36.5° in *A* and *B*, respectively, of [Re(CO)₃ (bqui)(Bzpy)](CF₃SO₃). These observations reveal an additional effect on this angle caused by the L' ligands. In all cases, the bqui ligand is tilted towards the py or Bzpy side of the coordination sphere.

The ¹H-NMR spectra of the complexes are summarized in *Tables 2* and *3*. The assignments of the chemical shifts were made by comparison with data from previously reported studies of the free ligands and the precursor complexes [7d] [9]. Generally, the signals of the aromatic pyridine protons overlapped with those of the biquinoline protons. However, the characteristic *AB* pattern for the former protons are clearly distinguished in the spectra of the complexes with the Bzpy ligand.

The increase of deshielding of all the biquinoline protons observed in the new complexes relative to the precursor complexes with a Br-ligand, notably of H-C(4,4') localized in the *p*-position of the coordinated N-atom, is a good indication that the pyridine ligands induce a lower electron density on the Re-atom as compared to the Br and triflate ligands. Similarly, an effect of the 4-substituted pyridine ligand Xpy on the $\delta(H)$ of the aromatic biquinoline protons is observed in both complex series (*Tables 2* and *3*).

The two *m* signals of the CH₂CH₂ protons of the (CH₂CH₂)bqui ligand in the [Re(CO)₃{(CH₂CH₂)bqui}(CF₃SO₃)] complex is characteristic for an A_2B_2 system (*Table 3* and *Fig. 2*). This pattern is due to the presence, in solution, of two conformers in slow exchange. Both mirror-image isomers are generated by the distortion of the (CH₂CH₂)bqui ligand in the complexes (*Fig. 1,b*). This A_2B_2 pattern is also observed for the [ReBr(CO)₃{(CH₂CH₂)bqui]] precursor complex [7b,d], but the chemical-shift difference between the H_a and H_b protons decreases in the [Re(CO)₃{(CH₂-CH₂)bqui}(Xpy)]⁺ complexes. As shown in *Table 3*, these differences could be as small as those observed for the [Re(CO)₃{(CH₂CH₂)bqui}(py)]⁺ complex for which the A_2B_2 signals collapse to a quasi-*s* (*Fig. 2,b* and *c*). This behavior is expected for isomers in a fast exchange motion. The change in the shift difference between the H_a and H_b signals along the L' series of complexes indicates that the conformational-motion rate depends on the pyridine ligands at the working temperature.

The UV/VIS data of the complexes $[\text{Re}(\text{CO})_3(\text{L})(\text{CF}_3\text{SO}_3)]$ (*Table 4*) reveal one solvent-polarity-dependent band around 430 nm that has been assigned to a rhenium-to-biquinoline ($\text{Re} \rightarrow \text{bqui}$) charge-transfer (MLCT) transition [3c] [7b,d]; for the $[\text{Re}(\text{CO})_3(\text{L})(\text{Xpy})]^+$ complexes, this band can be clearly observed as one or two shoulders of low intensity above 400 nm. In the $[\text{Re}(\text{CO})_3(\text{L})(\text{Xpy})]^+$ complexes, these MLCT transitions are shifted to higher energies than those found in the complexes with Br or triflate ligands, in agreement with a lower electron density on the metal center induced by the pyridine ligand. However, it is not possible to evaluate the inductive effect of the Xpy ligand on the MLCT band due to partial overlap with the intraligand-transition bands ($\pi \rightarrow \pi^*$ biquinoline). The expected band below

	bqui						$\Gamma^{(p)}$		
	H–C(3,3′)	H-C(4,4')	H-C(6,6')	H-C(8,8')	H–C(5,5′)	H–C(7,7')	H_{α}	${\rm H}_{eta}$	\mathbf{H}_{x}
iupc	8.85 (d)	8.30(d)	7.58 (t)	8.25 (d)	7.86 (d)	7.75 (t)			
[ReBr(CO) ₃ (bqui)]	8.31(d)	8.50(d)	7.71(t)	8.96(d)	7.94 (m)	7.94 (m)			
Re(CO) ₃ (bqui)(CF ₃ SO ₃)]	8.39(d)	8.67 (d)	7.83 (m)	8.92(d)	8.03 (m)	8.03 (m)			
$\Delta \delta^{c}$)	-0.46	+0.37	+0.25	+0.67	+0.17	+0.28			
Re(CO) ₃ (bqui)(HOpy)] ⁺	8.35(d)	8.52(d)	7.70 (dt)	8.95(d)	(<i>m</i>) 06. <i>L</i>	(<i>m</i>) 06.2	7.70(d)	5.99(d)	$2.65(s)^{d}$
$\Delta \delta^{c}$	-0.50	+0.22	+0.12	+0.70	+0.04	+0.15			
[Re(CO) ₃ (bqui)(Bzpy)] ⁺	8.82(d)	8.84(d)	7.86 (dt)	8.84(d)	8.12(d)	8.09 (dt)	(6.95 (d))	6.72 (d)	$3.83 (s)^{e}$
∆∂°)	- 0.03	+0.54	+0.28	+0.59	+0.26	+0.34			7.16 $(m)^{f}$) 6.97 $(td)^{f}$) 7.16 $(m)^{f}$)
[Re(CO) ₃ (bqui)(NCpy)] ⁺	8.48(d)	8.80(d)	7.72 (t)	8.92(d)	8.10(d)	7.91 (dt)	8.20(d)	7.70(d)	
$\Delta \delta^{c}$)	-0.37	+0.50	+0.14	+0.67	+0.24	+0.16			
Re(CO) ₃ (bqui)(py)] ⁺	8.70 (AB)	8.70 (AB)	7.70 (t)	8.91 (d)	8.00 (m)	8.00 (m)	8.00 (m)	8.00 (<i>m</i>)	7.10 (dt)
$\Delta \delta^{c}$	-0.15	+0.40	+0.12	+0.66	+0.14	+0.25			

(CH ₂	2CH2)bq	ui ^b)					L'c)			
H-CI	(4,4') F	H–C(6,6′)	H-C(8,8')	H–(5,5')	H–C(7,7')	$H_{\rm a}$	H	H_{α}	H_{β}	H_x
(CH_2CH_2) bqui 8.05	(3 (s)	7.52(t)	8.43 (d)	(p) TT (d)	7.68 (t)	3.20 (s)				
[ReBr(CU) ₃ {(CH ₂ CH ₂)qbqul] 8.2. [Re(CO) ₃ {(CH,CH,)bqui}(CF ₃ SO ₃)] 8.38	1 (s) 8 (s)	7.74 (t)	8.84(d) 8.82(d)	(m) 08.1 7.97 (m)	(m) 08.1 (m) 7.97 (m)	$3.35 (A_2B_2)$ $3.32 (A_3B_3)$	$3.20 (A_2B_2)$ $3.54 (A_2B_2)$			
$\Delta \delta^{d}$ + 0.3:	تح ⊥	+0.22	+0.39	+0.20	+0.29	ì	1			
$[Re(CO)_{3}(CH_{2}CH_{2})bqui}(HOpy)]^{+} 8.3$	5 (s)	7.70 (dt)	8.84(d)	8.30(d)	7.91 (t)	$3.38~(A_2B_2)$	$3.42 (A_2 B_2)$	7.91	7.89~(AB)	$2.35(s)^{e}$
$\Delta \delta^{d}$) + 0.32	- ⁷	+0.18	+0.41	+0.53	+0.23					
$[Re(CO)_{3}[(CH_{2}CH_{2})bqui](Bzpy)]^{+} 8.5!$	(s) 6	7.80 (i)	8.72 (d)	(pp) 60.8	8.00 (dt)	$3.13 (A_2 B_2)$	$3.18 (A_2 B_2)$	7.0 7(d)	(9.83 (d))	$3.82 (s)^{f}$
$\Delta \delta^{d}$) + 0.5(+ 9	+0.28	+0.29	+0.32	+0.32			$(96.06 (dd)^g)$	$7.14 (d)^{g}$	$7.14 \ (m)^g)$
$[Re(CO)_{3}(CH_{2}CH_{2})bqui)\}(NCpy)]^{+} 8.3$	(2) (2)	7.85 (t)	8.76(d)	8.43(d)	7.90 (t)	$3.30 (A_2 B_2)$	$3.50 (A_2 B_2)$	7.95 (br.)	7.80(d)	
$\Delta \delta^{d}$) + 0.3	4	+0.33	+0.33	+0.66	+0.22					
$[Re(CO)_{3}(CH_{2}CH_{2})bqui)](py)]^{+}$ 8.62	(2 (s)	7.88 (m)	8.76(d)	8.20(d)	8.00 (dt)	3.26(s)	3.26 (s)	7.88 (m)	7.21 (<i>m</i>)	7.21 (m)
$\Delta \delta^{d}$) + 0.59	T 6	+0.36	+0.33	+0.43	+0.32					



Fig. 2. a) ¹*H*-NMR Spectrum of $[Re(CO)_{3}[(CH_{2}CH_{2})bqui](Bzpy)]^{+}$, b) $CH_{2}CH_{2}$ ¹*H*-NMR signals of the $ReBr(CO)_{3}[(CH_{2}CH_{2})bqui]]$ precursor, and c) $CH_{2}CH_{2}$ ¹*H*-NMR signals of $[Re(CO)_{3}[(CH_{2}CH_{2})bqui](Bzpy)]^{+}$. CDCl₃ solutions at room temperature; for atom numbering see formula and Footnotes b and c in Table 3.

400 nm for the Re-to-Xpy charge-transfer excited state [10][7d] was not observed because it is overlapped by more intense bands corresponding to L intraligand transitions.

Fig. 3, a shows the emission spectra for the bqui and (CH_2CH_2) bqui ligands and for the corresponding perchlorate salts, *i.e.*, $bqui \cdot 2 HClO_4$ and $(CH_2CH_2)bqui \cdot 2 HClO_4$, when these compounds are excited with λ_{exc} 250 nm in MeCN. The inset in *Fig. 3, a* illustrates the protonation effect upon the UV/VIS spectra of bqui and (CH₂CH₂)bqui. It is observed that both the absorption and emission maxima of (CH₂CH₂)bqui experience a shift to lower energies after protonation. The emission spectrum of bqui experiences minor changes towards lower energies after protonation; for bqui, the first excited singlet state is of $n\pi^*$ character, and its lowest triplet state is assigned as $\pi\pi^*$ [7i]. Inspection to Fig. 3, a suggests that, after protonation of (CH₂CH₂)bqui, fluorescence from the ${}^{l}n\pi^{*}$ state (λ_{em} ca. 360 nm) diminishes, as expected, and the phosphorescence from the ${}^{3}\pi\pi^{*}$ state (λ_{em} ca. 430 nm) is increased, for the unprotonated (CH₂CH₂)bqui ligand, there is a mixture of fluorescence and phosphorescence. Besides that, the emission quantum yield ϕ_{em} increases by a factor of 5 after the protonation of (CH₂CH₂)bqui. The bqui and (CH_2CH_2) bqui \cdot 2 HClO₄ compounds, however, show mainly fluorescence with a lower contribution from the ${}^{3}\pi\pi^{*}$ state to the total luminescence. Luminescence quantum yields for bqui and bqui 2 HClO4 are nearly the same. The emission quantum yield ϕ_{em} for (CH₂CH₂)bqui · 2 HClO₄, after excitation with λ_{exc} 250 nm, is nearly 10-fold higher than that of bqui \cdot 2 HClO₄. This can be explained by the hindrance to rotation

Table 4. UV/VIS Data for Rhenium(I) Complexes at 25°

Compound	Solvent	$\lambda_{abs} [nm] (10^{-3})$	$^{3} \varepsilon/\mathrm{dm}^{3} \mathrm{mol}^{-1} \mathrm{cm}^{-1}$)	
		$(t_{2g} \to \pi \ast_L)$		$(\pi ightarrow \pi^*)$
[Re(CO) ₃ (bqui)(CF ₃ SO ₃)]	CH_2Cl_2	440 (1.5)	374 (8.1)	356 (5.2)
	Me ₂ O	430 (sh)	373 (17.1)	265 (69.3)
	MeCN	424 (3.6)	371 (12.4)	354 (20.3)
[Re(CO) ₃ (bqui)(HOpy)] ⁺	CH_2Cl_2	430 (6.0)	374 (296.0)	262 (567.3)
	Me_2O	420 (sh)	373 (285.5)	357 (200.7)
	MeCN	420 (sh)	372 (254.4)	350 (sh)
[Re(CO) ₃ (bqui)(NCpy)] ⁺	CH_2Cl_2	425 (sh)	376 (234.0)	264 (411.9)
	Me ₂ O	420 (sh)	374 (262.2)	357 (226.4)
	MeCN	418 (sh)	379 (sh)	373 (366.0)
[Re(CO) ₃ (bqui)(py)] ⁺	CH_2Cl_2	420 (sh)	374 (295.9)	262 (567.3)
	Me_2O	414 (sh)	373 (285.5)	357 (200.7)
	MeCN	405 (sh)	372 (254.4)	267 (568.6)
[Re(CO) ₃ (bqui)(Bzpy)] ⁺	CH_2Cl_2	416 (sh)	379 (304.0)	362 (208.0)
	EtOH	410 (sh)	378 (279.3)	361 (197.2)
	MeCN	400 (sh)	377 (280.2)	268 (532.0)
[Re(CO) ₃ {(CH ₂ CH ₂)bqui}(CF ₃ SO ₃)]	CH_2Cl_2	450 (sh)	395 (5.5)	271 (17.7)
	EtOH	430 (sh)	394 (3.1)	266 (9.1)
	MeCN	426 (0.4)	371 (12.4)	354 (2.0)
[Re(CO) ₃ {(CH ₂ CH ₂)bqui}(HOpy)] ⁺	CH_2Cl_2	450 (sh)	394 (251.1)	378 (209.8)
	EtOH	438 (sh)	394 (165.1)	378 (143.1)
	MeCN	430 (sh)	392 (250.5)	268 (584.0)
[Re(CO) ₃ {(CH ₂ CH)bqui}(NCpy)] ⁺	CH_2Cl_2	451 (sh)	395 (199.3)	379 (168.0)
	EtOH	435 (sh)	393 (187.7)	377 (223.9)
	MeCN	425 (sh)	395 (254.8)	268 (473.3)
$[Re(CO)_3(CH_2CH_2)bqui](py)]^+$	CH_2Cl_2	445 (sh)	340 (250.0)	
	EtOH	430 (sh)	392 (81.6)	268 (178.9)
	MeCN	420 (sh)	391 (169.9)	267 (348.0)
[Re(CO) ₃ {(CH ₂ CH ₂)bqui}(Bzpy)] ⁺	CH_2Cl_2	451 (sh)	400 (350.6)	268 (533.1)
	EtOH	445 (sh)	399 (215.1)	269 (410.5)
	MeCN	435 (sh)	395 218.6)	269 (502.7)

imposed by the CH_2CH_2 group in (CH_2CH_2) bqui as compared to the 'free' bqui which leads to a smaller nonradiative rate constant.

When solutions of the Re¹ complexes are optically excited with λ_{ex} 250, 350, and 400 nm, three different emission spectra are obtained (*Fig. 3, b*) with λ_{em} near 370, 420, and 650 nm, respectively. The emission properties of the Re¹ complexes are shown in *Table* 5. The emission with λ_{em} near 370 nm (*Fig. 3, b*) exhibits some vibrational structure, and it was observed for all the complexes under study. Moreover, this emission is very similar to that obtained for bqui, (CH₂CH₂)bqui, and bqui \cdot 2 HClO₄ (see *Fig. 3, a*). The emission with λ_{em} near 370 nm could, therefore, be attributed to the fluorescence arising from the bqui moiety. The emission with λ_{em} near 650 nm which shifts to the red (*Fig. 4*) when the solvent polarity is increased, corresponds to a MLCT (Re \rightarrow bqui) excited state [7e].

To analyze the effect of the 4-substituted pyridine ligands on the HOMO of the Re^I complex, the emission maxima $(1/\lambda_{em})$ were plotted against the σ^+ Hammett parameters. Emission and absorption energies augment with an increase in the electron-withdraw-

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Fig. 3. a) Room-temperature emission spectra of the ligands bqui (\triangle) and $(CH_2CH_2)bqui (\bigcirc)$ and of the corresponding perchlorate salts bqui $\cdot 2 HClO_4$ (\bigtriangledown) and $(CH_2CH_2)bqui \cdot 2 HClO_4$ (\Box) after irradiation with λ_{exc} 250 nm (the corresponding UV/VIS spectra are given in the inset). b) Room-temperature emission spectra of $[Re(CO)_3(bqui)(Bzpy)]^+$ $(\bigcirc; \lambda_{exc}$ 250 nm) $[Re(CO)_3(CH_2CH_2)bqui](Bzpy)]^+$ $(\Box; \lambda_{exc}$ 250 nm), $[Re(CO)_3(CH_2CH_2)bqui](NCpy)]^+$ $(\Box; \lambda_{exc}$ 400 nm) in MeCN at different excitation wavelengths.

	F	Ľ,	Solvent	hexe 250nm	$\lambda_{\rm exc} 400 {\rm m}$	m	1 UCE 320 I	m	$\tau_{\rm em}$ [ns]	
				$\Phi_{ m em}$	$\lambda_{ m em} [m nm]$	${\pmb \Phi}_{ m em}$	$\lambda_{ m em} [m nm]$	$\Phi_{ m em}$	$\lambda_{\rm exc} 355 \text{ nm}$	$\lambda_{\rm exc}$ 337 nm
$[Re(CO_3(L)L')]^+$	bqui	HOpy	MeCN	$(3.0\pm1)\cdot10^{-3}$	692	$(3.8\pm0.4)\cdot10^{-4}$	416	$(1.0\pm0.1)\cdot10^{-5}$		
	bqui	Bzpy	MeCN	$(5.6\pm0.8)\cdot10^{-3}$	686	$(2.0\pm0.2)\cdot10^{-3}$	404	$(1.4\pm0.1)\cdot10^{-5}$		36 ^b)
	bqui	py	MeCN	$(1.9\pm0.4)\cdot10^{-3}$	675	$(2.3\pm0.2)\cdot10^{-3}$	404	$(1.7\pm0.2)\cdot10^{-5}$		40b)
	bqui	NCpy	C_6H_6		650		404		$11, 141^{a}$)	
			CH_2CI_2		664		470		8, 73 ^a)	
			C_2H_5O		666		404			
			MeCN	$(3.0\pm1)\cdot10^{-3}$	671	$(8.2\pm0.8)\cdot10^{-4}$	430	$(3.2\pm0.1)\cdot10^{-5}$	8, 44 ^a)	
	(CH ₂ CH ₂)bqui	HOpy	MeCN	$(1.8\pm0.1)\cdot10^{-3}$	670	$(6.7\pm0.7)\cdot10^{-5}$	401	$(1.2\pm0.1)\cdot10^{-4}$		
	(CH ₂ CH ₂)bqui	Bzpy	MeCN	$(2.0\pm0.4)\cdot10^{-3}$	686	$(1.4\pm0.1)\cdot10^{-3}$	401	$(4.6\pm0.5)\cdot10^{-5}$		35 ^b)
	(CH ₂ CH ₂)bqui	ру	MeCN	$(5.8\pm0.4)\cdot10^{-3}$	686	$(1.8\pm0.2)\cdot10^{-3}$	424	$(1.3\pm0.1)\cdot10^{-4}$	33 ^b)	35^{b})
	(CH ₂ CH ₂)bqui	NCpy	MeCN/CH2Cl2	$(4.0\pm0.6)\cdot10^{-3}$	699	$(6.8\pm0.7)\cdot10^{-4}$	418	$(4.3\pm0.4)\cdot10^{-4}$	$16, 97^{a}$)	
	• i								$11, 75^{a}$)	
	bqui	zd	MeOH/CH2Cl2	I	I	I	I	I	4, 113 ^c)	
			MeCN	I					$(6, 114^{c})$	
:	bqui	4,4′bpy	MeOH/CH ₂ Cl ₂	Ι	I	I	I	I	5, 58°	
Free ligands										
	ınba		MeCN	$(4.0 \pm 0.4) \cdot 10^{\circ}$						
	bqui · 2 HClO ₄		MeCN	$(3.6\pm0.4)\cdot10^{-3}$						
	(CH ₂ CH ₂)bqui		MeCN	$(6.9\pm0.7)\cdot10^{-3}$						
	(CH ₂ CH ₂)bqui	2 HCIO_4	MeCN	$(3.2\pm0.3)\cdot10^{-2}$						

Table 5. Photophysical Properties of the $[Re(CO)_3(L)(L')]^+$ Complexes and the L Ligands at Room Temperature

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Fig. 4. Lippert Plot for the dependence of the emission energy of $[Re(CO)_3(bqui)(NCpy)]^+$ on solvent polarity (top of x axis) and dependence of the emission energy of the bqui complexes on Hammett parameter σ^+ (bottom of x axis). For σ^+ values, see Exper. Part; for details see Table 6.

ing power of the pyridine substituents, with more positive σ^+ 's providing more electronwithdrawing power. It is known that σ^+ shows a better correlation with cationic species. The formation of a MLCT excited state (Re \rightarrow bqui) makes the metal more positive (Re^{II}) with the resultant formation of positive charge on the pyridine ligand as the consequence of partial withdrawal of electron density from the metal. Therefore, ligands with more basic (more negative) σ^+ values, like OH⁻ will drive electron density into the Re, making it more easily oxidized and lowering the MLCT energy; for the bqui series, a linear correlation is observed between $1/\lambda_{em}$ and σ^+ (*Fig. 4*). However, the (CH₂CH₂)bqui series did not show a good correlation (*Table 5*). This lack of correlation in the (CH₂CH₂)bqui series could reflect the conformational effect of the pyridine ligand on the whole complex that may modify both the LUMO and HOMO energies [7d]. This conformational effect is better compensated in the series of the [Re(CO)₃-(bqui)L']⁺ complexes than in that of the [Re(CO)₃{(CH₂CH₂)bqui}L']⁺ complexes due to the major restriction of the conformational motion in this latter series.

Another emission, with λ_{em} near 420 nm, is illustrated in *Fig. 3, b* for the [Re(CO)₃{(CH₂CH₂)bqui}(py)]⁺ complex but was observed for all the complexes of both the bqui and the (CH₂CH₂)bqui series after excitation with λ_{exc} 350 nm (*Table 5*). This emission is strongly dependent on the solvent, but no correlation could be established between emission maxima and solvent polarity. However, the emission near 420 nm is similar to that of (CH₂CH₂)bqui · 2 HCl in *Fig. 3, a*. It could be assigned

to the ${}^{3}\pi\pi^{*}$ (³IL) excited states of the bqui and (CH₂CH₂)bqui ligands in the Re^I complexes. It is noteworthy that the emission quantum yield ϕ_{em} (λ_{exc} 350 nm) is higher by a factor of 10 for the complexes of the (CH₂CH₂)bqui series than for those of the bqui series (see the comment above concerning the difference of ϕ_{m} for (CH₂CH₂)bqui · 2 HClO₄ and bqui · 2 HClO₄)

After excitation with λ_{exc} 400 nm (MLCT (Re \rightarrow bqui) excited state) in both the bqui and (CH₂CH₂)bqui series, the lowest emission quantum yields ϕ_{em} are obtained for the complexes with the 4-substituted ligand HOpy, while the highest values are obtained for those with the py and Bzpy ligands (*Table 5*). After excitation with λ_{exc} 350 nm, the ϕ_{em} are between two and ten-fold lower than the corresponding ϕ_{em} after excitation with λ_{exc} 400 nm in both the bqui and (CH₂CH₂)bqui complex series. After excitation with λ_{exc} 250 nm, the ϕ_{em} amount to 2–6·10⁻³ for all the bqui and (CH₂CH₂)bqui complexes and are in general higher than the ϕ_{em} after excitation with λ_{exc} 400 nm.

It is possible to account for the biexponential decay of the luminescence in the $[ReBr(CO)_3(CH_2CH_2CH_2)bqui]$ complex $((CH_2CH_2CH_2)bqui=3,3'-(propane-1,3-))$ diyl)-2,2'-biquinoline) by considering the parallel relaxations of the lowest lying $^{3}MLCT$ and ^{3}IL states [7e]. Moreover, [Re(CO)₃(bqui)L]⁺ complexes with L = pyrazine (pz) and 4,4'-bipyridine (4,4'bpy) (see Table 5) showed a biexponential decay of the luminescence with a longer lifetime, τ_{em} 58 ns for L=4,4'bpy and τ_{em} 114 ns for L=pz, assigned to the radiative and nonradiative relaxations of the ³MLCT (Re \rightarrow bqui) excited state, and a shorter lifetime, τ_{em} ca. 6 ns, assigned to the decay of the ³IL states [3i]. In the present study (see *Table 5*), the luminescence lifetimes for the Re¹ complexes were obtained after a curve fitting analysis of the oscillographic traces, monitoring wavelengths between 400 and 650 nm. However, the longer lifetime was not observed at monitoring wavelengths between 400 and 500 (where there is no ${}^{3}MLCT$ $(\text{Re} \rightarrow \text{bqui})$ emission). Only monitoring wavelengths between 550 and 650 showed the longer luminescence lifetime. Therefore, it can be stated that the longer luminescence lifetimes (ranging from 33 to 141 ns in *Table 5*) for $[Re(CO)_3(bqui)(NCpy)]^+$, $[Re(CO)_3\{(CH_2Cl_2)bqui\}(NCpy)]^+,$ $[Re(CO)_3[(CH_2CH_2)bqui](py)]^+,$ $[Re(CO)_3-$ (bqui)(py)⁺, $[Re(CO)_3(CH_2CH_2)bqui](Bzpy)$ ⁺, and $[Re(CO)_3(bqui)(Bzpy)]$ ⁺ can be ascribed to the luminescence decay of the ³MLCT (Re \rightarrow bqui) excited state. The $[Re(CO)_3$ weak luminescence of $[Re(CO)_3[(CH_2CH_2)bqui](OHpy)]^+$ and $(bqui)(OHpy)^{+}$ did not allow us to measure emission lifetimes with λ_{exc} 355 or 337 nm. The shorter lifetime, $\tau_{em} ca. 8-16$ ns, which was mainly observed with monitoring wavelengths between 400 and 500 nm, must be ascribed to the ³IL state.

The excitation spectra in *Fig. 5*, which are normalized to the emission-quantumyield values of *Table 5*, show that the highest ϕ_{em} are observed on irradiations at λ_{ex} 420 nm when monitoring the emission at λ_{em} 650 nm, and at λ_{ex} 340 nm when the emission is monitored at λ_{em} 420 nm. Nevertheless, the emission corresponding to the ³MLCT (Re \rightarrow bqui) is still significant when the excitation energy is near λ_{ex} 340 nm. Some contribution from the IL excited state to the emission with λ_{em} near 650 nm can not be discarded when exciting with λ_{ex} 350 nm since the biquinoline absorption spectrum is still significant at that wavelength. In *Fig. 5*, the UV/VIS spectrum of the [Re(CO)₃{(CH₂CH₂)bqui}(NCpy)⁺ complex in MeCN is shown for comparison. The lowest absorption band for this complex is placed between the two peaks of the two excitation spectra. It was established in a previous work [7e] that a short-lived ³IL state of the bqui ligand is placed between 15 and 20 kJ above the ³MLCT (Re \rightarrow bqui) state. Intersystem crossing from the ³IL to the ³MLCT (Re \rightarrow bqui) state has been proposed in [3i]. The shortening of the ³IL-state lifetime, τ_{em} ca. 8–16 ns, in both the bqui and (CH₂CH₂)bqui complex series can be compared to the longer lifetimes (ca. 900 ns) of the ³IL excited states in [ReCl(CO)₃L₂] complexes (L=quinoline or isoquinoline) where the MLCT state is placed at higher energy than the ³IL excited state [7j]. The shortening of the the ³IL-state lifetime in the [Re(CO)₃(bqui)(L')]⁺ and [Re(CO)₃{(CH₂CH₂)bqui}(L')]⁺ complexes can be explained by a fast intersystem crossing, *i.e.*, on a time scale $\tau < 20$ ns, between ³IL and ³MLCT excited states.

Redox potentials of the rhenium complexes are shown in *Table 6*. The complexes may be divided into two groups based on their electrochemical properties. The first group involves the py and Bzpy derivatives of the bqui and (CH_2CH_2) bqui series and is characterized by two successive reversible reduction waves between 0.00 and -2.00 V (*vs.* SCE) and only one reversible oxidation wave between 0.00 and +2.00 V (*vs.* SCE). The second group includes the OHpy and NCpy derivatives of both series, where four reversible reduction waves are found between 0.00 and -2.00 V (*vs.* SCE) and one irreversible oxidation wave between 0.00 and -2.00 V (*vs.* SCE).

According to previous studies [7b,d], the first reduction wave of the first group could be attributed to a ligand-centered process that involves the addition of an electron to the π^* orbital on the bqui moiety. Three possible processes could be assigned to the second reduction wave, *i*) a metal-centered Re^I/Re⁰ reduction, *ii*) a pyridine-ligand reduction, and *iii*) a second reduction of the bqui moiety.



Fig. 5. Excitation spectra of $[Re(CO)_{3}[(CH_{2}CH_{2})bqui](NCpy)]^{+}$ in MeCN monitored at the emission wavelength: λ_{em} 650 nm (—) and 420 nm (...) and absorption spectrum of $[Re(CO)_{3}[(CH_{2}CH_{2})_{2}bqui](NCpy)]^{+}$ $(-\cdot - \cdot -)$ in MeCN

	Redox potential		
	$E_{\rm red}/{ m V}$		$E_{\rm ox}/{ m V}$
[Re(CO) ₃ (bqui)(HOpy)] ⁺	-0.79, -0.89	-1.38, -1.57	$+1.54^{b}$)
[Re(CO) ₃ (bqui)(Bzpy)] ⁺	-0.71	-1.24	+1.71
$[\text{Re}(\text{CO})_3(\text{bqui})(\text{py})]^+$	-0.71	-1.24	+1.72
[Re(CO) ₃ (bqui)(NPpy)] ⁺	-0.71, -0.90	-1.26, -1.47	$+1.41^{b}$)
[Re(CO) ₃ (bqui)(HOpy)] ⁺	-0.75, -0.90	-1.29, -1.40	$+1.55^{b}$)
$[Re(CO)_3[(CH_2CH_2)bqui](Pzpy)]^+$	-0.71	-1.25	$+1.70^{\circ}$
$[Re(CO)_3[(CH_2CH_2)bqui](Py)]^+$	-0.71	-1.24	+1.72
$[Re(CO)_3[(CH_2CH_2)bqui](NCpy)]^+$	-0.77, -0.90	-1.23, -1.49	$+1.56^{b}$)

Table 6. Electrochemical Data of the Complexes^a)

The change in the pyridine-ligand basicity should affect the complex mainly by destabilizing the e_g orbitals. The lack of such an effect of the substituent at the pyridine ligand on the second reduction potential values eliminates process *i*) as a possible explanation. Process *ii*) may also be discarded considering that the reduction values are the same for both the Bzpy and py complexes. Therefore, a second reduction of the bqui moiety must be involved in the second reduction wave. Moreover, a difference of *ca.* 500 mV between the first and the second reduction potential is consistent with previous findings for similar complexes showing a similar electrochemical behavior [11].

For the second group, the appearance of four reversible waves might be explained by considering that the OHpy and NCpy ligands could generate a slow conformational motion between both enantiomers (established by X-ray and NMR). Consequently, two bqui moieties with different electrochemical behavior may be observed.

Each of the complexes displayed a reversible or irreversible oxidation between 1.00 and 2.00 V (*vs.* SCE) corresponding to a metal-centered process $Re^{1/11}$. This process involves the removal of an electron from the t_{2g} orbitals of Re^{I} [7d][12].

The effect of the basicity of the L' ligand on the metal was analyzed considering the correlation between the oxidation potentials and the *Hammett* parameter. The lack of this correlation can be rationalized taking three aspects into account: first, the complexes with the OHpy and NCpy ligands show irreversible oxidation waves; second, the t_{2g} orbitals should be, by symmetry, less affected by altering the pyridine basicities rather than the e_g ones; and finally, the substituent at the pyridine ligand provides a different influence on the planarity of the bqui moiety, which may affect sterically the t_{2g} energy. In accordance with the previous discussion, the importance of the latter effect is notable and has been also observed in related complexes [7d][13].

Conclusion. – X-Rays studies of rhenium and manganese complexes containing the same bqui and (CH_2CH_2) bqui ligands have revealed that the symmetry of the compounds is departing by various degrees from a perfect octahedron [7d,g,h][13b]. This deviation has a significant influence on the spectroscopic and electrochemical properties of the complexes [7]. Changes in the electronic repulsion between the d orbital of the metal and the bqui orbitals as the consequence of biquinoline conformational dis-

tortions are responsible for these influences. Destabilization of the LUMO and stabilization of the HOMO will usually result from an increase of this conformational distortion.

The bqui complexes with L' ligands show different correlations with the *Hammett* parameter. The lack of a similar correlation for the corresponding (CH_2CH_2) bqui complexes reveals an additional influence of the L' ligand on both the conformational- and exchange-motion rate of the complexes. This influence can presumably not be evaluated. However, it constitutes a promising alternative to modulate the complex properties.

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Experimental Part

General. The values of σ^+ in the Lippert plot (Fig. 4) are taken from [17]. All the operations were carried out under purified N₂ by standard Schlenk and vacuum-line techniques and by using freshly distilled, dried, and degassed solvents. The solvents used in preparations, crystallizations, and spectroscopic analysis (Mallinckrodt, grade HPLC) were distilled prior to use. For electrochemical studies, anh. MeCN was dried over CaH₂ under N₂ by refluxing for 2 h and then freshly distilled prior to use. Commercially available (Aldrich) 2,2'-biquinoline (bqui)¹) and pyridine ligands, AgCF₃SO₃, [ReBr(CO)₅], and precursor compounds were used without further purification. The synthesis of the 3,3'-(ethane-1,2-diyl)-2,2'-biquinoline ligand (=6,7-dihydrodibenzo[b,j][1,10]phenanthroline; (CH₂CH₂)bqui¹) [9] and precursor complexes [ReBr(CO)₃(L)] have been previously described [7b,d]. Molar conductivities: Cole-Parmer-01481 conductivity meter; 10⁻³ M solns, in MeCN at 25°. UV/VIS Spectra: Shimadzu-UV-160 spectrophotometer; quartz cells; solns. in purified solvents of different polarity at least 100 times; in cm⁻¹. ¹H-NMR Spectra: 250-MHz-Bruker spectrometer. Microanalyses were performed at the Facultad de Química y Farmacia, Universidad de Chile.

X-Ray Crystal-Structure Analyses. The X-ray single-crystal diffraction data were collected in a *Siemens-R3m* four-circle diffractometer, with the $\omega/2\theta$ scan mode and a variable scan speed of $4.2-29.3^{\circ}$ min⁻¹. Structures were solved by direct methods [14] and refined by full-matrix least squares in F^2 [15]. Anisotropic displacement factors were used for non-H-atoms, while H-atoms (all of which were unambiguously defined by the configuration) were included at their idealized positions and allowed to consider their presence onto their host atoms. A check for higher symmetry present in [Re(CO)₃(bqui)(Bzpy)](CF₃SO₃) was unsuccessful. The results are given in *Table 1* and *Fig. 1* (see [16] for the drawn displacement ellipsoids). CCDC-169685 and -169686 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the *Cambridge Crystallographic Data Center via* www.ccdc.can.ac.uk/data_request/cif.

Cyclic Voltammetry. The measurements were performed by standard techniques [7d]. A sweep rate of 200 mV s⁻¹ was used for all the scans. Potentials are reported as $E_{\frac{1}{2}} = \frac{1}{2} (E_{p_a} + E_{p_c})$, where E_{p_a} and E_{p_c} are the anodic and cathodic peak potentials, respectively.

Photophysical Measurements. The luminescence of the Re¹ complexes at r.t. was investigated with an *SLM-Aminco-4800* or a *Perkin-Elmer-LS-50B* spectrofluorimeter connected to a PC. The spectra were corrected for differences in instrumental response and light scattering. Solns. were deoxygenated by bubbling N₂ of high purity in a gas-tight apparatus before recording the spectra. Emission quantum yields were measured relative to rhodamine B in EtOH. Quantum yields were calculated according to *Eqn. 1*, where *I* is the integral of the emission spectrum, *A* is the absorbance of the sample or standard at the excitation wavelength, and *n* is the solvent refraction index. Luminescence lifetime measurements were performed by excitation with the third harmonic of a *Spectron-Nd-YAG* laser (18 ns FWHM and 12 mJ/pulse at 355 nm) or with a *Laseroptics* nitrogen laser (7 ns FWHM and 2mJ/pulse at 337 nm).

 $\phi_{\rm em} = (A_{\rm standard}/A_{\rm sample})(I_{\rm sample}/I_{\rm standard})\phi_{\rm em, standard}(n_{\rm sample}/n_{\rm standard})^2$

(1)

Synthesis of Rhenium Complexes. The $[Re(CO)_3(L)(CF_3SO_3)]$ complexes [13b] were obtained by reaction of the $[ReBr(CO_3)(L)]$ complex with silver trifluoromethanesulfonate in CH_2Cl_2 at 50° during 4 h, under an inert atmosphere. AgBr was separated by passing the mixture through *Celite*. The filtrate was evaporated and the obtained solid purified by column chromatography (alumina, CH_2Cl_2). The eluate was evaporated, and pure crystals were isolated after crystallization.

The $[\text{Re}(\text{CO})_3(L)(L')](\text{CF}_3\text{SO}_3)$ complexes [13b] were obtained at 50° under an inert atmosphere by addition of the corresponding 4-substituted pyridine in stoichiometric amounts to the $[\text{Re}(\text{CO})_3(L)(\text{CF}_3\text{SO}_3)]$ complex dissolved in CH₂Cl₂. After 2 h, The resulting orange soln. was evaporated and the solid product purified by column chromatography (alumina, CH₂Cl₂/MeOH 95:5) The eluate was evaporated and a microcrystalline orange product was obtained after dropwise addition of cool hexane. All the complexes were characterized by elemental analysis, IR, molar conductivities, and melting points.

(2,2'-Biquinoline- κ N^{*I*}, κ N^{*I*})tricarbonyl(trifluoromethanesulfonato- κ O)rhenium ([Re(CO)₃(bqui)(CF₃SO₃)]: Yield 84%. Molar conductivity: 21 Scm²mol⁻¹. M.p. 333° (dec.). IR 2029vs, 1935vs, 1914vs. Anal. calc. for C₂₂H₁₂F₃N₂O₆ReS: C 39.11, H 1.79, N 4.15; found: C 39.71, H 1.84, N 4.32.

 $\begin{array}{l} (2,2'-Biquinoline \kappa N^{l},\kappa N^{l'}) tricarbonyl(pyridin-4-ol-\kappa N^{l}) rhenium(1+) \ Trifluoromethanesulfonate ([Re(CO)_{3}-(bqui)(HOpy)](CF_{3}SO_{3})): Yield 79\%. Molar conductivity: 110 S cm² mol⁻¹. M.p. 154° (dec.). IR: 2015vs, 1901vs. Anal. calc. for C_{27}H_{17}F_{3}N_{3}O_{7}ReS: C 42.08, H 2.22, N 5.45; found: C 41.74, H 2.40, N 5.65. \end{array}$

 $\begin{array}{ll} (2,2'-Biquinoline \kappa N^{l},\kappa N^{l'}) tricarbonyl[4-(phenylmethyl)pyridine \kappa N^{l}]rhenium(1+) & Trifluoromethanesulfonate ([Re(CO)_3(bqui)(Bzpy)](CF_3SO_3)): Yield 83\%. Molar conductivity: 130 Scm²mol⁻¹. M.p. 213° (dec.). IR: 2030vs, 1922vs. Anal. calc. for C_{34}H_{22}F_3N_3O_6ReS: C 48.34, H 2.74, N, 4.97; found: C 48.13, H 2.76, N 5.15. \end{array}$

(2,2'-Biquinoline- κ N¹, κ N^{1'})tricarbonyl(pyridine- κ N¹)rhenium(1+) Trifluoromethanesulfonate ([Re(CO)₃-(bqui)(py)](CF₃SO₃)): Yield 30%. Molar conductivity: 105 Scm²mol⁻¹. M.p. 213° (dec.). IR: 2015vs, 1898vs. Anal. calc. for C₂₇H₁₇F₃N₃O₆ReS: C 42.97, H 2.27, N 5.57; found: C 43.24, H 2.33, N 5.81.

 $\begin{array}{ll} (2,2'-Biquinoline{\kappa}N^{l},\kappa N^{l'}) tricarbonyl(pyridine{-4-carbonitrile{-\kappa}N^{l}}) rhenium(1+) & Trifluoromethanesulfonate ([Re(CO)_3(bqui)(NCpy)](CF_3SO_3)): Yield 23\%. Molar conductivity: 99 Scm²mol⁻¹. M.p. 103° (dec.). IR: 2020vs, 1904vs. Anal. calc. for C₂₈H₁₆F_3N_4O_6ReS: C 43.13, H 2.07, N 7.19; found: C 43.49, H 2.26, N 7.47.$ $Tricarbonyl(6,7-dihydrodibenzo[b,j][1,10]phenanthroline{-\kappa}N^{l_3},\kappa N^{l_4})(trifluoromethanesulfonato-\kappaO)rhe-$

nium ([Re(CO)₃{(CH₂CH₂)bqui}](CF₃SO₃)): Yield 87%. Molar conductivity: 18 Scm²mol⁻¹. M.p. 347° (dec.). IR: 2031vs, 1927vs, 1903vs. Anal. calc. for $C_{24}H_{14}F_3N_2O_6ReS$: C 41.09, H 2.01, N 3.99; found: C 41.41, H 2.31, N 4.15.

 $\label{eq:relation} Tricarbonyl(6,7-dihydrodibenzo[b;j][1,10]phenanthroline-\kappa N^{13}, \kappa N^{14}) (pyridin-4-ol-\kappa N^1)rhenium(1+) Trifluo$ $romethanesulfonate [Re(CO)_3{(CH_2CH_2)bqui}(HOpy)](CF_3SO_3)): Yield 63\%. Molar conductivity: 109 Scm^2mol^{-1}. M.p. 141° (dec.). IR: 2020vs, 1897vs. Anal. calc. for C_{29}H_{19}F_3N_3O_7ReS: C 43.72, H 2.40, N 5.27; found: C 44.08, H 2.51, N 5.01.$

 $\label{eq:tricarbonyl} Tricarbonyl(6,7-dihydrodibenzo[b_j][1,10]phenanthroline-\kappa N^{13}, \kappa N^{14}][4-(phenylmethyl)pyridine-\kappa N^1)rhe$ $nium(1+) Trifluoromethanesulfonate ([Re(CO)_3((CH_2CH_2)bqui](Bzpy)](CF_3SO_3)): Yield 83\%. Molar conduc$ $tivity: 120 Scm²mol⁻¹(MeCN). M.p. 115° (dec.). IR: 2029vs, 1911vs. Anal. calc. for C_{36}H_{25}F_3N_3O_6ReS: C 49.65, H$ 2.89, N 4.83; found: C 48.80, H 2.78, N 5.04.

Tricarbonyl(6,7-*dihydrodibenzo*[b,j][1,10]*phenanthroline*- κ N¹³, κ N¹⁴)(*pyridine*- κ N¹)*rhenium*(1+) *Trifluoromethanesulfonate* [Re(CO)₃{(CH₂CH₂)bqui}(py)](CF₃SO₃): Yield 22%. Molar conductivity: 100 Scm²mol⁻¹. M.p. 365° (dec.). IR: 2016vs, 1898vs. Anal. calc. for C₂₉H₁₉F₃N₃O₆ReS: C 44.61, H 2.45, N 5.38; found: C 44.65, H 2.26, N 5.52.

Tricarbonyl(6,7-*dihydrodibenzo*[b,j]/[1,10]*phenanthroline*- κ N¹³, κ N¹⁴)(*pyridine-4-carbonitrile-\kappaN¹)rhenium*(1+) *Trilfuoromethanesulfonate* ([Re(CO)₃{(CH₂CH₂)bqui}(NCpy)](CF₃SO₃)): Yield 66%. Molar conductivity: 123 Scm²mol⁻¹. M.p. 144° (dec.). IR: 2024v*s*, 1899v*s*. Anal. calc. for C₃₀H₁₈F₃N₄O₆ReS: C 44.72, H 2.25, N 6.95; found: C 45.01, H 2.57, N 6.55.

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