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[Re(CO)$_3$(3,3′-trimethylene-2,2′-biquinoline)(p-substituted-py)]$^+$ complexes. Preparation and characterization

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Abstract—A series of new rhenium(I) complexes of the type [Re(CO)$_3$(3,3′-trimethylene-2,2′-biquinoline)(L)](CF$_3$SO$_3$)$_n$, (L = CF$_3$SO$_3^-$, pyridine (py) or para-substituted pyridine like HO-py, ph-py or NC-py; $n = 0$ or 1) were prepared and characterized by FTIR, ^{1}H NMR, and UV–vis spectroscopies and by cyclic voltammetry. The pseudo-octahedral facial configuration of these compounds was established by FTIR. The differences found in the spectroscopical and electrochemical results were associated to the effect of the para-position substituent of the L pyridine ligand. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: metallic carbonyl complexes; rhenium complexes; heterocyclic nitrogen ligand.

The chemical, photochemical, and photocatalytic properties of rhenium(I) complexes with polypyridine ligands make them potential agents to promote thermal, photochemical and electrochemical catalysis [1]. Examples of this include the electroreduction and photoreduction of CO$_2$, the latter being a process of interest in the conversion and storage of solar energy [2].

The MLCT and LLCT transitions in this type of compounds have been proposed as key states in some photochemical processes [1c,3]. Thus, the control or modulation of the absorption and/or emission energy can provide a very important tool to modify the catalytic behaviour of these complexes.

In order to evaluate the effect of structural modifications in the polypyridine ligand on the properties of the ground and excited states in these complexes, we have studied complexes of the general structure ReBr(CO)$_3$(L) with L = bidentate polypyridine ligand [4]. In previous works with ReBr(CO)$_3$(3,3′-R,R′-2,2′-biquinoline), (with R = R′ = H, CH$_3$ or R-R′ = dimethylene and trimethylene bridge) we found that the extended conjugation in the biquinoline, as compared to 2,2′-bipyridine, causes a shift towards lower energy both in the MLCT band and in the reduction potential of the polypyridine ligand [4b,d]. Moreover, the distortion degree from the planarity in the polypyridine ligand induces a slight variation of these energies [4d]. We have associated the emissions in these complexes with parallel relaxation processes from an IL and a MLCT state [4e].

The substitution of the bromide atom in these compounds by para-substituted pyridines (L) with electron donating or electron attracting groups can be a good alternative to obtain an electronic state, *[Re(CO)$_3$(3,3′-R,R′-2,2′-biquinoline)(L)]$^+$, closer to the MLCT state [3,4e]. In order to have new rhenium complexes that can help prove the existence of this electronic state, we report here the synthesis and spectroscopical characterization of a new series of complexes of the type [Re(CO)$_3$(3,2N)(L)]$^{+n}$ (3,2N = 3,3′-trimethylene-2,2′-biquinoline, L = CF$_3$SO$_3^-$, pyridine (py), para-substituted pyridine like HO-py, bz-py (bz = benzyl) or NC-py; $n = 0$ or 1) (Fig. 1).

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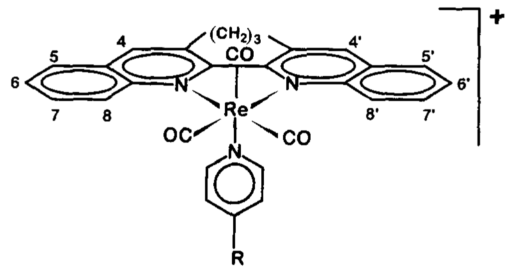

Fig. 1. $[Re(CO)_3(3,3'\text{-trimethylene-2,2'-biquinoline})(p\text{-R-pyridine})]^+$ complexes with R = H, CN, benzyl, or OH showing hydrogen positions for NMR discussions.

EXPERIMENTAL

Physical measurements

IR spectra were obtained from solid KBr disk and in $CHCl_3$ solution using a Bruker IFS-66 V FT-IR spectrophotometer. A 0.2 mm KBr cell was used scanning at least 100 times. ^1H NMR spectra were recorded in a 250 MHz Bruker spectrometer. Absorption spectra were recorded on a Shimadzu UV-160 spectrophotometer, using different and previously purified solvents, in quartz cells at ambient temperature. Molar conductivities were determined from 10^{-3} mol dm^{-3} solutions of complex in CH_3CN at 25°C using a Cole-Parmer 01481 conductivity meter. Electrochemical data were acquired in anhydrous acetonitrile solutions of the complexes containing 10^{-1} mol dm^{-3} tetrabutylammonium perchlorate (TBAP) via cyclic voltammetry using a Bank-Wenking POS 73 potentiostat with a Gould OS 4100 oscilloscope, and a Graphtec XY WX 4301 recorder. A three-electrode configuration, a working electrode was a platinum disk, the reference and counter electrodes were an aqueous calomel and a platinum wire, respectively. The test solution was separated from a reference electrode by Vycor bridge filled with corresponding solvent/supporting electrolyte system. A sweep rate of 200 mV s^{-1} was used for all the scans. Potentials were reported as $E_{\frac{1}{2}} = \frac{1}{2}(Ep_a + Ep_c)$, where Ep_a and Ep_c were the anodic and cathodic peak potentials, respectively. Ferrocene was used as an internal standard to compensate for the junction potential variability among experiments.

Materials

All the operations were carried out under purified nitrogen by standard Schlenk and vacuum-line techniques using freshly distilled, dried and degassed solvents. The solvents used in preparations, recrystallizations, and spectroscopic analysis (Mallinckrodt, grade HPLC) were treated and distilled prior to use. In electrochemical studies, anhydrous acetonitrile was dried using CaH_2 under nitrogen atmosphere at reflux for 2 h, and freshly distilled prior to use. Tetrabutylammonium perchlorate (TBAP) from Fluka was recrystallized twice from HPLC grade ethyl acetate (Mallinckrodt) prior to use. TBAP was stored in a vacuum desiccator over indicating Drierite ($CaSO_4$ anhydrous, Aldrich Chemical Co.) until needed for electrochemical studies. The pyridine ligand, $AgCF_3SO_3$, and $ReBr(CO)_5$, commercially available (Aldrich Chemical Co) were used without further purification. The synthesis of the biquinoline ligand (3,2N) and precursor complex $ReBr(CO)_3(3,2N)$ have been previously described [4b,d].

Synthesis of rhenium complexes

The new complexes were obtained at 50°C under an inert atmosphere through stoichiometric precipitation of the corresponding bromide with silver triflate in methylene chloride solutions. Silver bromide was filtered under nitrogen pressure through celite. The filtrate was stirred at 50°C with a stoichiometric amount of the specific pyridine. The resulting orange solution was concentrated and the product purified using a chromatographic column of alumina. The starting material was eluted with methylene chloride and the complexes were eluted with a 5% *v*/*v* methylene chloride/methanol mixture. The solution was concentrated and the microcrystalline orange product was obtained after dropwise addition of cool hexane.

The $[Re(CO)_3(3,2N)(CF_3SO_3)]$ complex was obtained by concentration of the solution obtained after that the silver bromide was filtered. The product was purified using a chromatographic column of alumina with methylene chloride as eluent and isolated as pure crystals.

$[Re(CO)_3(3,2N)(CF_3SO_3)]$. Yield: 81%. ν_{CO} (in KBr disk) 2014, 1900 (broad) cm^{-1}, (in $CHCl_3$ solution at 25°C) 2013, 1923, 1894 cm^{-1}. Molar conductivity (in acetonitrile) 30 S cm^2 mol^{-1}. Melting point 182°C (d).

$[Re(CO)_3(3,2N)(HO\text{-}py)]^+$. Yield: 58%. ν_{CO} (in KBr disk) 2016, 1895 (broad) cm^{-1}, (in $CHCl_3$ solution at 25°C) 2225, 1917 (broad) cm^{-1}. Molar conductivity (in acetonitrile) 113 S cm^2 mol^{-1}. Melting point 156°C (d).

$[Re(CO)_3(3,2N)(bz\text{-}py)]^+$. Yield: 21%. ν_{CO} (in KBr disk) 2015, 1900 (broad) cm^{-1}, (in $CHCl_3$ solution at 25°C) 2033, 1934 (broad) cm^{-1}. Molar conductivity (in acetonitrile) 140 S cm^2 mol^{-1}. Melting point 130°C (d).

$[Re(CO)_3(3,2N)(py)]^+$. Yield: 55%. ν_{CO} (in KBr disk) 2015, 1900 (broad) cm^{-1}, (in $CHCl_3$ solution at 25°C) 2019, 1830 (broad) cm^{-1}. Molar conductivity (in acetonitrile) 113 S cm^2 mol^{-1}. Melting point 135°C (d).

$[Re(CO)_3(3,2N)(NC\text{-}py)]^+$. Yield: 52%. ν_{CO} (in KBr disk) 2032, 1911 (broad) cm^{-1}, (in $CHCl_3$ solution at 25°C) 2034, 1930 (broad) cm^{-1}. Molar con-

ductivity (in acetonitrile) 140 S cm^2 mol^{-1}. Melting point 113°C (d).

RESULTS AND DISCUSSION

The prepared complexes are stable in air, either as solid or in solution. They are soluble in several solvents of medium polarity. The formulas proposed of the general type $[Re(CO)_3(3,3'\text{-trimethylene-}2,2'\text{-biquinoline})(L)]^{+n}$ for the products, are supported by melting points, conductivity measurements and spectroscopical results including FTIR, ^{1}H NMR and UV vis.

The conductivity values indicate a non-electrolyte compound for the $[Re(CO)_3(3,2N)(CF_3SO_3)]$ complex and the existence of a species constituted by two ions for the other complexes.

The IR spectra show no important differences when compared with the characteristic spectra of the co-ordinated and the free pyridine ligands. The spectrum in solution for the $[Re(CO)_3(3,2N)(CF_3SO_3)]$ complex show three strong bands in the carbonyl region which arise from a facial conformation with a local C_s symmetry around a hexacoordinated rhenium. For the other compounds with L = substituted pyridines, the spectra exhibit two intense bands in the typical carbonyl stretching region. This behaviour is consequent with a C_{3v} local symmetry for a facial stereochemistry in these complexes. The lowest energy signal for CO groups appears as a very broad band, which can be attributed to the decreasing of symmetry [5].

The proton NMR spectra of the complexes are summarized in Table 1. The assignments for the complexes were made considering the data and conclusions that we have reported previously for the free ligand and for the precursor complex [4d,6]. For those complexes we found that co-ordination shifts the signal of all the protons of the biquinoline ligand to lower fields. In the new complexes this deshielding increase. The effect is larger for the H_4 and $H_{4'}$ protons localized in the para-position to the co-ordinated heterocyclic nitrogens. This behaviour is a good indication that the pyridine ligand induces a lower electronic density over the rhenium atom as compared to bromide ligand in the precursor complex. In the same way, the differences in the $\delta_{complex}-\delta_{precursor}$ values for the series indicate that the substitution in para position of the co-ordinated pyridine also provides an effect that should be considered. Although the pyridine aromatic protons show signals at high field with a characteristic AB pattern in the complexes, in the benzylpyridine complex a multiplet signal is observed due to this proton appears overlapped with the five protons of the phenyl ring. The three-signal pattern (q, m, q) of the aliphatic methylene protons is a consequence of the impossibility of the biquinoline molecule to rotate around of the C_2—$C_{2'}$ bond, but it becomes a two-signal pattern (t, m) in the $[Re(CO)_3(3,2N)(bz\text{-}py)]^+$ complex. This change suggests, that rotation is allowed in this complex under the working temperature.

The UV–vis spectroscopical data for the complexes are shown in Table 2. Over 400 nm, one or two shoulders of low intensity can be clearly observed. Upon increasing the polarity of the solvent, these shoulders are shifted to the high energy region. This type of band can be assigned as a rhenium-to-biquinoline-charge-transfer (MLCT) transition. Because it is

Table 1. ^{1}H NMR spectral data for the $[Re(CO)_3(3,2N)(L)]^{+n}$ (n = 0 or 1) complexes and the free ligand (3,2N)[a]

	aromatic protons (3,2N)					aliphatic protons(3,2N)			L protons		
Compound	$H_{4,4'}$	$H_{6,6'}$	$H_{8,8'}$	$H_{5,5'}$	$H_{7,7'}$	H_a	H_b	H_c	H_α	H_β	
3,2N	8.00 s	7.54 t	8.35 d	7.81 d	7.69 t	2.70 t	2.20 q				
$ReBr(CO)_3(3,2N)$	8.25 s	7.69 t	8.82 d	7.90 m	7.90 m	2.83 q	2.74 m	2.43 q			
$[Re(CO)_3(3,2N)(CF_3SO_3)]$	8.33 s	7.77 t	8.89 d	7.97 m	7.97 m	3.01 q	2.81 m	2.50 q			
$\delta_{complex}-\delta_{precursor}$	+0.08	+0.08	+0.07	+0.07	+0.07						
$[Re(CO)_3(3,2N)(HO\text{-}py)]^+$	8.37 s	7.78 t	8.86 d	8.01 m	8.01 m	2.92 q	2.81 m	2.51 q	5.91 d	7.59 d	2.74 s[c]
$\delta_{complex}-\delta_{precursor}$	+0.12	+0.09	+0.04	+0.11	+0.11						
$[Re(CO)_3(3,2N)(bz\text{-}py)]^+$	8.67 s	7.89 t	8.79 d	8.20 d	8.09 t	2.58 t	2.43 m		6.70 to 7.30[b]		3.85 s[d]
$\delta_{complex}-\delta_{precursor}$	+0.42	+0.20	−0.03	+0.30	+0.19						
$[Re(CO)_3(3,2N)(NC\text{-}py)]^+$	8.61 s	7.93 m	8.83 d	8.15 m	8.15 m	2.98 q	2.80 m	2.56 q	7.93 m	7.65 d	
$\delta_{complex}-\delta_{precursor}$	+0.36	+0.24	+0.01	+0.25	+0.25						
$Re(CO)_3(3,2N)(py)]^+$	8.66 s	7.90 m	8.82 d	8.29 d	8.13 m	2.79 q	2.58 m	2.42 q	7.29 dd	7.14 dd	8.13 m[e]
$\delta_{complex}-\delta_{precursor}$	+0.41	0.21	0.00	+0.39	+0.23						

[a] δ in ppm relative to internal $SiMe_4$ at 25°C in $CDCl_3$.

[b] four pyridine protons and five phenyl protons signals.

[c] OH of p-hydroxypyridine.

[d] CH_2 of p-benzylpyridine.

[e] p-protons pyridine signal.

Table 2. UV–vis spectral data for rhenium complexes and ligand (3,2N) at 25°C

Compound	solvent[a]		λ_{abs},nm ($10^{-3}\,\varepsilon$, dm^3 mol^{-1} cm^{-1}) ($t_{2g}\rightarrow\pi_1^*$)	($\pi\rightarrow\pi^*$))
3,2N	DCM			319 (98.84)
ReBr(CO)$_3$(3,2N)[b]	TOL	491 (sh)	450 (3.15)	369 (h)
	DCM	480 (sh)	435 (2.85)	371 (151.55)
	ACET	467 (sh)	418 (2.85)	369 (153.89)
[Re(CO)$_3$(3,2N)(CF$_3$SO$_3$)]	DCM		425 (sh)	369 (49.50)
	ACET		424 (sh)	368 (18.60)
	AN	463 (sh)	414 (sh)	368 (114.0)
[Re(CO)$_3$(3,2N)(HO-py)]+	DCM		431 (sh)	384 (11.00)
	ACET		430 (sh)	367 (151.40)
	AN	441 (sh)	411 (sh)	367 (18.64)
[Re(CO)$_3$(3,2N)(bz-py)]+	DCM		430 (sh)	371 (32.50)
	ACET	434 (sh)	373 (21.80)	
	AN	462 (sh)	420 (sh)	370 (20.20)
[Re(CO)$_3$(3,2N)(NC-py)]+	DCM	471 (sh)	437 (sh)	421 (7.20)
	ACET		440 (sh)	372 (186.20)
	AN	431 (sh)	429 (sh)	386 (20.12)
[Re(CO)$_3$(3,2N)(py)]+	DCM		430 (sh)	471 (7.20)
	ACET		435 (sh)	372 (186.20)
	AN	450 (sh)	425 (sh)	371 (20.12)

[a] DCM : methylene chloride, TOL : toluene, ACET : acetone, AN : acetonitrile.
[b] Ref. 4d.

difficult to unequivocally assign the absorption maximum for this band, we cannot tell if the presence of the pyridine ligand has some influence over the energy of this transition. This difficulty is also related with the position, just under 400 nm, expected for the rhenium-to-p-substituted-pyridine charge transfer band according with the less extensive conjugation of the pyridine compared with the biquinoline [4d]. The latest band appears overlapped by more intense bands corresponding to intraligand transitions ($\pi\rightarrow\pi^*$ biquinoline).

The redox potentials obtained by cyclic voltammetry at 200 mV s^{-1} in acetonitrile solution of the rhenium complexes are collected in Table 3. The complexes showed two successive reversible or quasi-reversible reduction waves between 0.00 to -2.00 volts range (vs SCE). In every case, the first reduction wave could be attributed to the ligand-centered process which involves the addition of an electron to the π^* orbital on the biquinoline ligand. Each of the complexes displayed a reversible or irreversible oxidation in the 0.80 to 1.44 volts range (vs SCE) assigned to a metal-centered process Re(II/I). This processes involves removal of an electron from the dπ orbital on rhenium(I) [4d,7].

The differences in the redox potential values for the rhenium compounds do not show a relationship with the basicity of the pyridine ligand. Similar behaviour has been reported for analogous complexes [8].

Table 3. Electrochemical data of the new rhenium complexes[a]

Complex	redox potential redn		oxidn
ReBr(CO)$_3$(3,2N)[b]	-0.99	-1.58	$+1.18$
[Re(CO)$_3$(3,2N)(CF$_3$SO$_3$)]	-1.08	-1.41[d]	$+1.24$
[Re(CO)$_3$(3,2N)(HO-py)]$^+$	-1.03[e]	-1.51	$+1.35$[c]
[Re(CO)$_3$(3,2N)(bz-py)]$^+$	-0.88	-1.36	$+0.95$[c]
[Re(CO)$_3$(3,2N)(NC-py)]$^+$	-1.08[d]	-1.46	$+1.44$[c]
[Re(CO)$_3$(3,2N)(py)]$^+$	-1.00[d]	-1.42	$+1.40$[c]

[a] Potentials are in volts vs SCE in 10^{-1} mol dm^{-3} TBPA/acetonitrile solution at ambient temperature, scan rate was 200 mV s^{-1}.
[b] Ref. 4d.
[c] Values represent anodic peak potentials.
[d] $\Delta E_p = 170$ mV.
[e] $\Delta E_p = 180$ mV.

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REFERENCES

1. (a) Juris, A., Balzani, V., Barigelletti, F., Campagna, S., Belser, P. and von Zelewsky, A., *Coord. Chem. Rev.*, 1988, **84,** 85; (b) Barigelletti, F., Campagna, S., Belser, P. and von Zelewsky,

A., *Coord. Chem. Rev.*, 1988, **84,** 5; (c) Kalyanasundaram, K., *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, 1992; (d) Shoonover, J. R., Strouse, G. F., Dyer, R. B., Bates, W. D., Chen, P. and Meyer, T. J., *Inorg. Chem.*, 1996, **35,** 273; (e) Treadway, J. A., Loeb, B., Lopez, R., Anderson, P., Keene, F. R. and Meyer, T. J., *Inorg. Chem.*, 1996, **35,** 2242; (f) Rossenaar, B. D., Hartl, F. and Stufkens, D. J., *Inorg. Chem.*, 1996, **35,** 6194.

2. (a) Grätzel, M., *Energy Resources Through Photochemistry and Catalysis*, Academic Press, New York, 1983; (b) Ruiz, E., Wolcan, E., Capparelli, A. L. and Feliz, M. R., *J. Photochem. Photobiol. A. Chem.*, 1995, **89,** 61; (c) Hawecker, J., Lehn, J. M. and Ziessel, R., *J. Chem. Soc., Chem. Commun.*, 1983, 536; (d) Pac, C., Ishii, K. and Yanagida, S., *Chem. Lett.*, 1989, 765.
3. (a) Feliz, M., Ferraudi, G. and Altmiller, H., *J. Phys. Chem.*, 1992, **96,** 257; (b) Kutal, C., Corbin, A. J. and Ferraudi, G., *Organometallics*, 1987, **6,** 553.
4. (a) Moya, S. A., Pastene, R., Schmidt, R., Guerrero, J., Sariego, R. and Sartori, R., *Bol. Soc. Chil. Quim.*, 1992, **37,** 43; (b) Sartori, R., Guerrero, J., Pastene, R., Schmidt, R., Sariego, R. and Moya, S. A., *Bol. Soc. Chil. Quim.*, 1992, **37,** 311; (c) Moya, S. A., Pastene, R., Schmidt, R., Guerrero, J. and Sartori, R., *Polyhedron*, 1992, **11,** 1665; (d) Moya, S. A., Guerrero, J., Pastene, R., Schmidt, R., Sariego, R., Sartori, R., Sans-Aparicio, J., Fonseca, I. and Martinez-Ripoll, M., *Inorg. Chem.*, 1994, **33,** 2341; (e) Ferraudi, G., Feliz, M., Wolcan, E., Hsu, Y., Moya, S. A. and Guerrero, J., *J. Chem. Phys.*, 1995, **99,** 4929; (f) Moya, S. A., Pastene, R., Pardey, A. J. and Baricelli, P., *Bol. Soc. Chil. Quim.*, 1996, **41,** 251.
5. Bermejo, M. J., Ruiz, J. Y., Solans, X. and Vinaixa, J., *Inorg. Chem.*, 1988, **27,** 4385.
6. Thummel, R. P. and Lefoulon, F., *J. Org. Chem.*, 1985, **50,** 666.
7. (a) World, L. A., Duesing, R., Cheng, P., Dellaciana, L. and Meyer, T. J., *J. Chem. Soc., Dalton Trans*, 1991, 849; (b) Yang, W. and Schanze, K. S., *Inorg. Chem.*, 1994, **33,** 1354; (c) Moya, S. A., Pastene, R., Sartori, R., Dixneuf, P. and Le Bozec, H., *J. Braz. Chem. Soc.*, 1995, **6,** 29.
8. Sacksteder, L. A., Zipp, A. P., Brown, E. A., Streich, J., Demas, J. N. and De Graff, B. A., *Inorg. Chem.*, 1990, **29,** 4335.