Synthesis and Characterization of Polypiridine-Based Rhenium(I) Complexes with Pyrazino[2,3-*f*][1,10]phenanthroline

by **Ramiro Díaz***[a]), **Angélica Francois**[a]), **Ana María Leiva**[b]), **Bárbara Loeb**[b]), **Ester Norambuena**[c]), and **Mauricio Yañez**[a])

[a]) Facultad de Recursos Naturales, Universidad Católica de Temuco, Manuel Montt 56, Temuco, Chile (e-mail: ramdiazh@uct.cl)

[b]) Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago, Chile

[c]) Departamento de Química, Universidad Metropolitana de Ciencias de la Educación, Av. José Pedro Alessandri 774, Santiago, Chile

Dedicated to the memory of Dr. *Carlos Andrade*, great mentor and friend

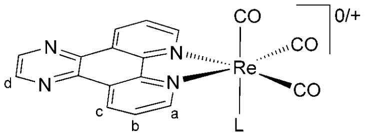
A series of tricarbonyl rhenium(I) complexes of the type *fac*-$[Re^I(CO)_3(ppl)(L)]^{0/+}$, where ppl is pyrazino[2,3-*f*][1,10]phenanthroline, and where L is Cl^-, TfO^-, 4-(*tert*-butyl)pyridine (^{t}Bu-py), 4-methoxypyridine (MeO-py), 4,4′-bipyridyl (bpy), or 10-(picolin-4-yl)phenothiazine (pptz), were synthesized and fully characterized. In all complexes, an increment in the electron-acceptor properties of ppl compared to the free ligand was observed. This effect was more significant for pyridine-type ligands, especially for pptz, compared to Cl^- or TfO^-. The properties of *fac*-$[Re(CO)_3(ppl)(pptz)]PF_6$ were compared with those of the analogous compound *fac*-$[Re(CO)_3(dppz)(pptz)]PF_6$, where dppz is dipyrido(3,2-*a*:2′,3′-*c*)phenazine, the goal being to generate long-lived excited charge-transfer (CT) states. In this respect, *fac*-$[Re(CO)_3(ppl)(pptz)]PF_6$ seems to be a promising candidate.

Introduction. – Based on the early studies reported by *Wrighton* and *Morse* [1], rhenium(I) tricarbonyl complexes with polypyridine ligands have attracted the attention of several research groups [2–6]. Among other properties, these complexes have the advantage of being synthetically manageable. $[Re(CO)_5Cl]$ is usually used as a starting material, given that the substitution of two C=O groups by a polypyridine-type, bidentate (N,N) ligand is feasible [2]. The product obtained is a complex of the type *fac*-$[Re(CO)_3(N,N)Cl]$. Moreover, the Cl-atom can be substituted by a monodentate ligand (L) such as pyridine proper or substituted pyridines, which gives rise to complexes of the general type *fac*-$[Re(CO)_3(N,N)L]^+$ (**1**) [3][4].

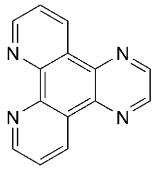
Most complexes of the above type are luminescent [4] due to metal-to-ligand charge-transfer (MLCT; d → π^*) processes or $\pi \rightarrow \pi^*$ transitions. MLCT is of interest for possible applications in solar-energy-conversion devices [5]. In many cases, the redox and photophysical properties of such complexes are determined mainly by the properties of the ligands [6]. The use of planar, conjugate ligands with acceptor properties, combined with donor ligands coordinated to the $Re^I(CO)_3$ moiety, allows one to induce charge-separated excited states [7a,b].

Pyrazino[2,3-*f*][1,10]phenanthroline (ppl; **2**) is a bidentate polypyridine ligand with several phenathroline-type coordination sites; it is planar and highly conjugated. As a consequence, it is only sparingly soluble in most polar solvents. Compared to related ligands such as dppz (**3**), there are only few literature reports on complexes with ppl [6b]. For example, some Ru complexes with ppl have been reported both in both basic studies and in DNA-intercalation experiments [8].

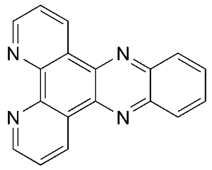
In this paper, the syntheses and properties of a series of *fac*-$[Re(CO)_3(ppl)L]^{0/+}$ complexes **1** with different ligands L are reported[1]), including TfO^-, py, ^{t}Bu-py, 4-MeO-py, bpy, and pptz; and their potential as light-emitting charge-transfer (CT) complexes for different applications is discussed.



fac-$[Re(CO)_3(N,N)L]$ (**1**)



ppl (**2**)



dppz (**3**)

Results and Discussion. – 1. *Synthesis and Properties of Pyrazino[2,3-*f*][1,10]phenanthroline.* The ppl ligand **2** was prepared according to a previously published procedure [8a], and characterized by UV/VIS, IR, and ^{1}H-NMR spectroscopy, as well as by elemental analysis (see *Exper. Part*). In the cyclic voltammogram of ppl, a reversible reduction at – 1.51 V was observed, which can be assigned to the reduction on the pyrazine fragment of the ligand [8a]. The electron spin resonance (ESR) spectrum of mono-electronic-reduced ppl (**2**), obtained by *in situ* electrochemical reduction in DMSO, is shown in *Fig. 1*; in *Table 1*, the hyperfine-coupling constants are listed, and the magnetic centers are identified.

Twelve signals with hyperfine structures appeared in the ESR spectrum, in agreement with the number of magnetic centers in the molecule. A good correlation with the simulated spectrum was observed (insert in *Fig. 1*). The pattern is characteristic of a highly conjugated species. The additional electron is delocalized over the whole structure, but not in a uniform way; the pyrazine N-atoms concentrate more electronic density than the rest of the molecule, as evidenced by the magnitude of the coupling constants (positions 2,2′, and d,d′).

2. *Synthesis and Properties of Rhenium Complexes.* All complexes were prepared from $[Re(CO)_5Cl]$, which was first converted to *fac*-$[Re(CO)_3(ppl)Cl]$ by heating with ppl (**2**) in toluene. After exchange of Cl^- by TfO^-, the resulting *fac*-$[Re(CO)_3(ppl)(TfO)]$ complex was converted to *fac*-$[Re(CO)_3(ppl)L]$ by reaction with the appropriate ligand[1]) in hot MeOH. For details, see the *Exper. Part.*

2.1. *IR and UV/VIS Properties.* The IR spectra of the neutral Re complexes were characterized by two very intense bands at *ca.* 2030 and 1930 cm^{-1}, inherent of a facial CO coordination in Re^I complexes [9]. In case of cationic complexes, both ν(CO) bands

---

[1]) Ligand abbreviations: ppl (**2**), pyrazino[2,3-*f*][1,10]phenanthroline; py, pyridine; ^{t}Bu-py, 4-(*tert*-butyl)pyridine; MeO-py, 4-methoxypyridine; bpy, 4,4′-bipyridyl; pptz, 10-(picolin-4-yl)phenothiazine; dppz (**3**), dipyrido[3,2-*a*:2′,3′-*c*]phenazine; TfO^-, trifluoromethanesulfonate anion; phen = 1,10-phenanthroline.

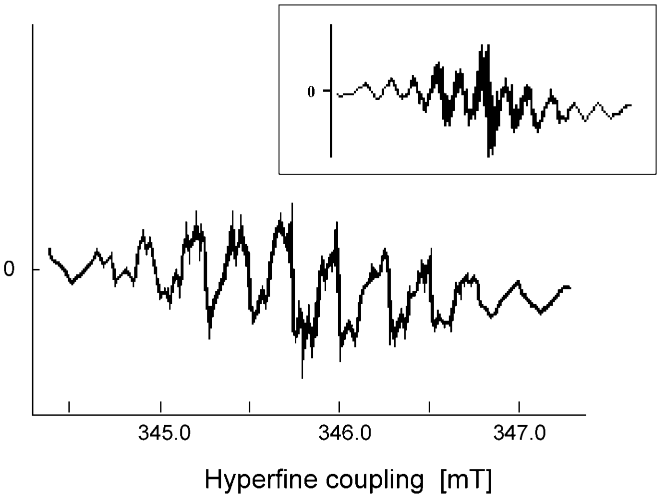
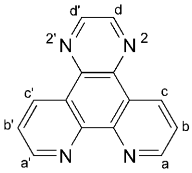


Fig. 1. *ESR Spectrum of free ppl* (**2**) *in DMSO obtained by electrochemical reduction* in situ. The insert shows the simulated spectrum.

Table 1. *Hyperfine-Coupling Constants from the ESR Spectrum of Mono-Electronic-Reduced ppl* (**2**) *in DMSO*



Magnetic center	Atoms	Coupling constant [mT]
2,2′	N,N	0.505
d,d′	H,H	0.250
b,b′	H,H	0.094
a,a′	H,H	0.056
1,1′	N,N	0.021
c,c′	H,H	<0.007

were shifted to lower energies due to the change in symmetry from C_s ($L = Cl^-$) to pseudo C_{3v}, ($L = py$) [10]. For the band at 2030 cm^{-1}, related to the A_1 mode, a similar shift for all complexes was observed. Conversely, the band at lower energy, related to the E mode, reflects the effect of the py substituent on Re–CO back-bonding. The following trend was observed for its displacement: pptz > MeO-py > ^{t}Bu-py > bpy. In other words: the trend followed the donor capacity of the substituent. Finally, the band at 840 cm^{-1}, assigned to ν(P–F), indicated the presence of the PF_6^- counterion in the cationic complexes.

The UV/VIS spectrum of *fac*-[Re(CO)$_3$(ppl)Cl] is shown in *Fig. 2*. Two intra-ligand (IL) transitions were observed at 258 nm ($\pi \rightarrow \pi^*$) and 290 nm (broad; n $\rightarrow \pi^*$). A shoulder at 380 nm, absent in the spectrum of the free ligand, was assigned to an

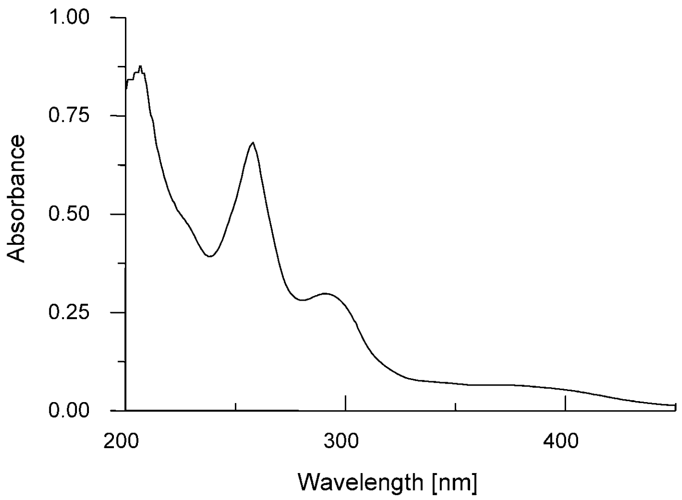


Fig. 2. *UV/VIS Spectrum of* fac-*[Re(CO)$_3$(ppl)Cl] in MeCN*

MLCT process (d → π*). Similar spectra were obtained for the cationic complexes (data not shown). The presence and position of the MLCT was determined by difference absorption spectra relative to free ppl (**2**). The data obtained for the IL bands were similar to those reported by *Lo* and *Hui* [6b] for complexes of the type *fac*-[Re(CO)$_3$(ppl)L]$^+$ possessing electron-accepting ligands L. We observed that the MLCT band was shifted by 20–30 nm to shorter wavelengths for ligands with electron-donor properties. The presence of an electron donor should increase the Re–C and Re–N (ppl) retro-donation effect. Consequently, the d → π* transition appears at higher energy than for electron-accepting ligands. In *Table 2*, the IR and UV properties of all studied complexes are summarized.

Table 2. *IR and UV/VIS Spectroscopic Data for* fac-*[Re(CO)$_3$(ppl)L]$^{0/+}$ Complexes.* IL and MLCT refer to 'intra-ligand' and 'metal-to-ligand charge transfer', resp.

Ligand[1])	ν(CO) [cm^{-1}]	λ_{max} [nm][a])	
		IL	MLCT
Cl$^-$	2020 1920	258 (4.44) 290 (1.95)	380 (0.445)
TfO$^-$	2045 1962	257 (5.21) 287 (2.23)	360 (0.511)
bpy	2033 1939	258, 275 (sh)	360
^{t}Bu-py	2034 1931	258 (12.76), 288 (5.94)	360 (0.862)
MeO-py	2033 1925	256 (8.14), 339 (3.56)	380 (0.067)
Pptz	2034 1919	255, 287 (sh)	370

[a]) In parentheses, molar-extinction coefficients, ε (in 10^5 M^{-1} cm^{-1}), are given.

2.2. *^{1}H-NMR Properties.* The ^{1}H-NMR spectra of the *fac*-[Re(CO)$_3$(ppl)L] (**1**) complexes showed a similar pattern as those of the free ligands. The coordination to the metal was evidenced by a shift of all signals to lower field. The spectra of *fac*-[Re(CO)$_3$(ppl)(TfO)] and *fac*-[Re(CO)$_3$(ppl)(pptz)]PF$_6$ are shown as examples in *Fig. 3*. When we compared the chemical shifts for the series of cationic *fac*-[Re(CO)$_3$(ppl)L]$^+$ complexes with that of free ppl (**2**), an effect of the substituent in the pyridine ring on the phenanthroline H-atom resonances was clearly manifested, as well as on the pyrazine resonances. Specifically, in the phenanthroline fragment, a lowfield shift for the H-atoms in positions a, a′, b, and b′ was observed, with the following trend: pptz < MeO-py < ^{t}Bu-py < bpy (*Table 3*). In a sense, this tendency reflects the electron-donating properties of the substituents, since the shift gets smaller as the deshielding effect of the metal is balanced by the donor effect of the substituent. For the H-atoms in positions c and c′, no significant change was observed. Here, deshielding is largely due to the anisotropic effect of the pyrazine N-atoms [8a][10], which is not affected by the auxiliary ligand. For the pyrazine H-atoms in positions d and d′, no clear trend was observed. However, it is necessary to point out that, for L = pptz, the signals were shifted to lower field, confirming the effect of the donor capacity of L to the metal.

Table 3. *^{1}H-NMR Chemical Shifts* (in ppm) *of* fac-*[Re(CO)$_3$(ppl)L]$^{0/+}$ Complexes*. At 200 MHz in CD$_3$CN.

Position	ppl[a])	Cl$^-$ [b])	TfO$^-$	^{t}Bu-py	MeO-py	bpy	pptz
a,a′	9.29 (*dd*)	9.50 (*dd*)	9.40 (*dd*)	9.80 (*dd*)	9.73 (*dd*)	9.84 (*dd*)	9.70 (*dd*)
b,b′	7.29 (*dd*)	8.04 (*dd*)	8.30 (*dd*)	8.34 (*dd*)	8.30 (*dd*)	8.36 (*dd*)	8.25 (*dd*)
c,c′	9.47 (*dd*)	9.73 (*d*)	9.81 (*dd*)	9.91 (*dd*)	9.84 (*dd*)	9.90 (*dd*)	9.83 (*dd*)
d,d′	8.96 (*s*)	9.17 (*s*)	9.25 (*s*)	9.22 (*s*)	9.26 (*s*)	9.22 (*s*)	9.19 (*s*)
e,e′	–	–	–	8.36 (*d*)	8.12 (*d*)	8.59 (*d*)	8.36 (*d*)
f,f′	–	–	–	7.33 (*dd*)	6.73 (*d*)	7.64 (*d*)	7.28 (*d*)
g,g′	–	–	–	–	–	7.60 (*dd*)	7.00 (*d*)
h,h′	–	–	–	–	–	8.59 (*dd*)	6.76 (*td*)
i,i′	–	–	–	–	–	–	6.72 (*td*)
j,j′	–	–	–	–	–	–	6.47 (*dd*)
CH$_2$/Me	–	–	–	3.62 (*s*)	3.75 (*s*)	–	5.00 (*s*)

[a]) Free ligand; in CDCl$_3$. [b]) In CD$_3$OD.

2.3. *Cyclic Voltammetry.* The results obtained by cyclic voltammetry (CV) for the above Re complexes are collected in *Table 4*. Most of the reduction processes were found to be reversible. As for free ppl (**2**), the first reduction process in all compounds was assigned to the reduction of the pyrazine portion of the ligand. A good correlation with the ^{1}H-NMR data was observed, in the sense that coordination enhances the electron-acceptor properties of the ppl ligand. Our results indicate that a photo-excited electron should occupy the $^3\pi_{\mathrm{LUMO}}$ orbital of the ppl ligand.

The CV properties of *fac*-[Re(CO)$_3$(ppl)Cl] were compared with those of related *fac*-[Re(CO)$_3$(N,N)Cl] complexes (N,N = phen [11] or dppz [12]; *Table 5*). By increasing the aromaticity of the acceptor ligand, the reduction potential was diminished, as expected. No clear tendency was observed for the corresponding oxidation processes, although a good correlation was observed between ΔE ($= E(\mathrm{ox}) - E_{1/2}(\mathrm{red})$) and the MLCT ($\mathrm{d} \rightarrow \pi^*$) absorption band. For *fac*-[Re(CO)$_3$(ppl)(TfO)], two irreversible

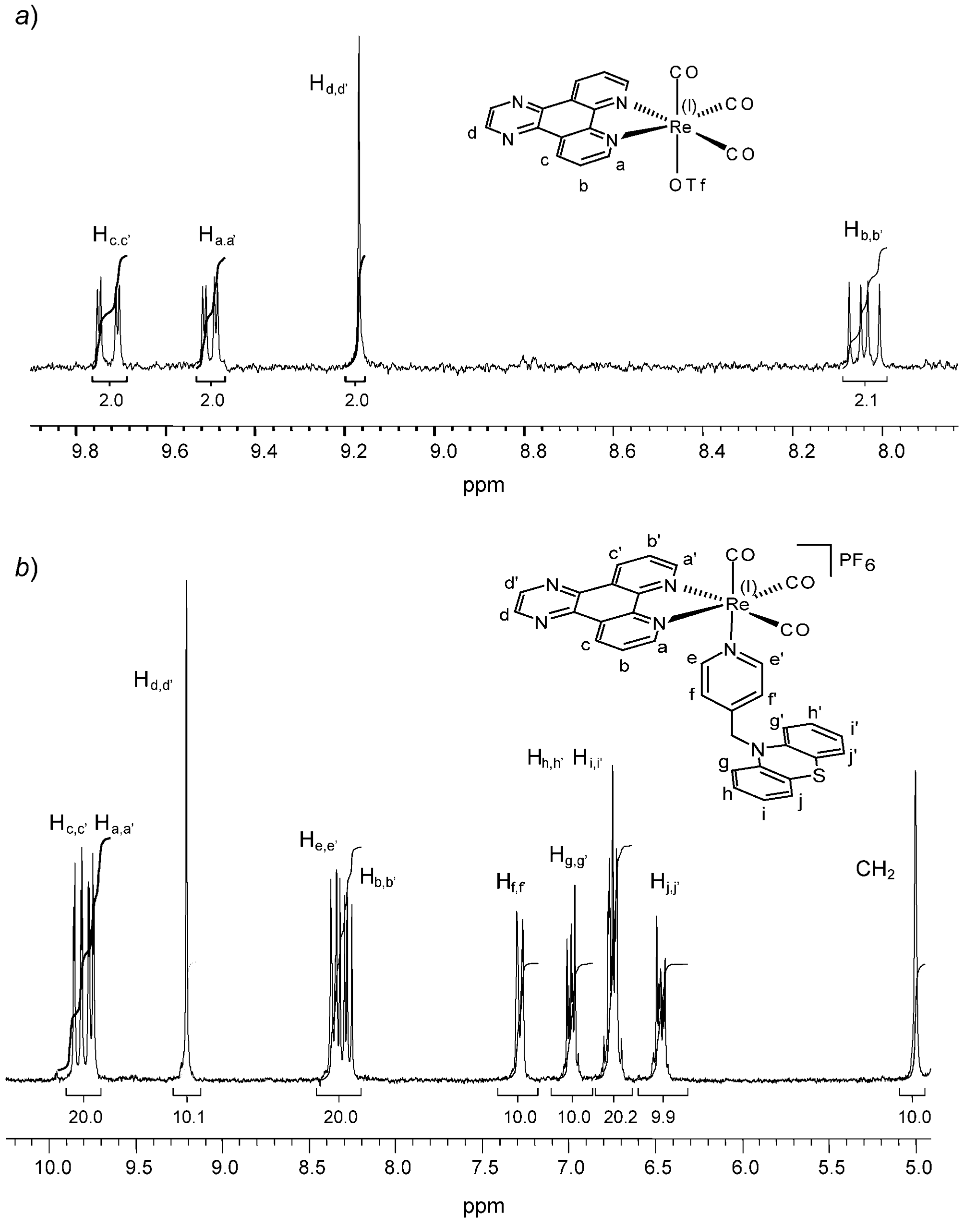


Fig. 3. ^{1}H-NMR spectra of a) fac-[Re(CO)$_3$(ppl)(TfO)] and b) fac-[Re(CO)$_3$(ppl)(pptz)]PF$_6$. At 200 MHz in CD$_3$CN.

reductions were observed: one at −1.21 V, involving the pyrazine portion of the ligand, the other at −1.44 V, probably due to reduction of the phenanthroline moiety.

Table 4. *Cyclovoltammetric Data of* fac-*[Re(CO$_3$)(ppl)L] Complexes* **1**. Potentials (in V) were determined with the Ag/AgCl system in MeCN relative to the standard calomel electrode (SCE).

Ligand[1])	E_p (ox)[a])	$E_{1/2}$ (red)
Cl$^-$	+1.53	−1.16, −1.44
TfO$^-$	+1.44	−1.21[b]), −1.44[b])
bpy	+1.15	−1.38
^{t}Bu-py[c])	+1.21	−1.31
MeO-py	+1.14	−1.06, −1.21
pptz	+1.57, +0.89[d])	−0.99

[a]) Irreversible wave for Re^{II}/Re^{I}. [b]) Irreversible wave. [c]) In 1,2-dichloroethane. [d]) (pptz)$^{+/0}$, reversible wave.

Table 5. *Electrochemical and UV/VIS Data for Selected* fac-*[Re(CO)$_3$(N,N)Cl] Complexes*

(N,N)	Electrochemical data [V]			λ_{max} [nm] (MeOH)
	E_p (Re$^{II/I}$)[a])	$E_{1/2}$ ((N,N)$^{0/-}$)[b])	ΔE[c])	MLCT
phen[d])	+1.41	−1.36	2.77	365[e])
ppl[f])	+1.53	−1.16	2.69	381
dppz[g])	+1.42	−1.04	2.46	400

[a]) Irreversible wave. [b]) First reduction potential. [c]) $\Delta E = E$ (ox) – E (red). [d]) Electrochemical data from [11a] (in MeCN). [e]) Data from [11b]. [f]) Electrochemical data: in MeCN. [g]) Electrochemical data from [12] (in 1,2-dichloroethane).

In the cationic complexes with bpy and ^{t}Bu-py ligands, an increase in the reduction potential of ppl was noticed relative to the neutral complexes. In this way, a certain degree of electronic interaction between the donor and acceptor ligands in the complex is manifested. When the ligand was MeO-py or pptz, the reduction potentials were, unexpectedly, lowered. This effect is not clear yet, but it could have its origin in the increase of the Re–CO retro-donation character, which might diminish the electron density on ppl, making it more susceptible to reduction.

The oxidation process ascribed to the Re^{II}/Re^{I} couple is irreversible, as typically observed for these types of complexes [3][6][12][13]. As a general trend, the CV results obtained for the complexes with electron-donor ligands studied in this paper are not as pronounced as in the case of similar complexes with monodentate electron-acceptor ligands [6]. For *fac*-[Re(CO)$_3$(ppl)(pptz)]$^+$, an additional oxidation was observed at 0.89 V (*Fig. 4*). This signal is characteristic for the (pptz)$^+$/(pptz)^0 redox reaction, and has been reported for other Re^{I} complexes containing this ligand [7a][14].

As can be deduced from the data collected in *Table 4*, the auxiliary ligands bpy, ^{t}Bu-py, and MeO-py lower the energy of the involved Re^{I} orbital as compared to the non-polypyridine ligands Cl$^-$ and TfO$^-$. This is a direct effect of the electron-donating ligands, which enhance the electron density on the metal, making it more susceptible to oxidation. Nevertheless, for L = pptz, the Re^{II}/Re^{I} oxidation potential was markedly displaced to more-positive values (*ca.* 400 mV) compared to the other cationic com-

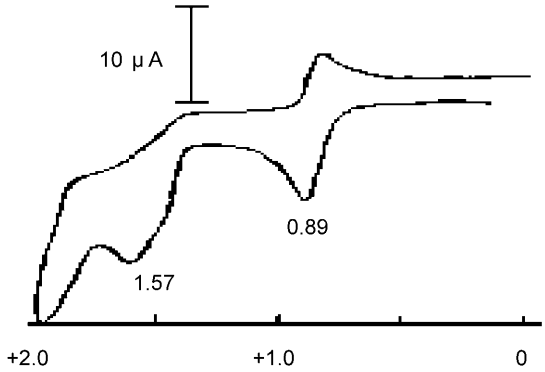


Fig. 4. *Cyclic voltammogram of* fac-*[Re(CO)$_3$(ppl)(pptz)]PF$_6$*. Potentials (in V) were determined with the Ag/AgCl system relative to SCE.

plexes. Specifically, the (pptz)$^+$ cation, generated at 0.89 V, reduces the electronic density on the metal, making its oxidation difficult. Again, this behavior reflects a certain degree of metal-mediated interaction between donor (pptz) and acceptor (ppl).

In *Table 6*, the electrochemical behavior of *fac*-[Re(CO)$_3$(ppl)(pptz)]PF$_6$ is compared with that of the analogous complex *fac*-[Re(CO)$_3$(dppz)(pptz)]PF$_6$. The only difference between ppl and dppz is that the latter has an additional fused benzene ring on the polypyridine ligand. As can be seen, coordinated dppz is the better acceptor than ppl, as expected due to its more-extended aromatic system [15]. The excited state of *fac*-[Re(CO)$_3$(dppz)(pptz)]PF$_6$ has been studied extensively [7a][13d][14c][16], and it was observed that a charge-separated, positively charged excited state of the type {*fac*-[Re^I(CO)$_3$(dppz)$^-$(pptz)$^+$]$^+$}* is formed upon photo-excitation ($\tau = 110 \pm 10$ ns) [7a]. Due to the structural and electrochemical similarities between the above two complexes, a similar excited-state behavior can be expected for *fac*-[Re(CO)$_3$(ppl)(pptz)]PF$_6$. Moreover, the greater ΔE value for *fac*-[Re(CO)$_3$(ppl)(pptz)]$^+$ relative to *fac*-[Re(CO)$_3$(dppz)(pptz)]$^+$ should hinder charge recombination to a greater extent, generating an excited state with an enhanced lifetime. Photophysical work to corroborate this hypothesis is currently in progress.

Table 6. *Electrochemical Data for two Structurally Related Rhenium Complexes*

Complex	$E_{1/2}$ [V]		E_p [V]	ΔE[a])
	(N,N)$^{0/-}$	(pptz)$^{+/0}$	Re^{II}/Re^I	
fac-[Re(CO)$_3$(ppl)(pptz)]PF$_6$	−0.99	+0.89	+1.57	1.88
fac-[Re(CO)$_3$(dppz)(pptz)]PF$_6$	−0.89	+0.84	+1.60	1.73

[a]) $\Delta E = E_{pptz} - E_{(N,N)}$.

Conclusions. – The electron-acceptor properties of the ppl ligand **2** are enhanced when coordinated to Re^I. For complexes *fac*-[Re(CO)$_3$(ppl)L], with L = Cl$^-$ or TfO$^-$, the electrochemical properties of ppl are only slightly affected. However, for pyridine-type ligands, its donor properties are notably enhanced, especially in the case of pptz. The *fac*-[Re^I(CO)$_3$(ppl)(pptz)]PF$_6$ complex is a promising candidate for obtaining long-lived charge-separated excited states.

Financial support from *Fondecyt* (Líneas Complementarias 8980007, grant No. 1020517), is gratefully acknowledged.

Experimental Part

1. *General.* Reagents (anal. grade) were obtained from *Aldrich* and used without further purification. Solvents for electrochemical measurements were of spectroscopic grade. The precursor 1,10-phenanthroline-5,6-dione was prepared according to [17]. 10-(picolin-4-yl)phenothiazine (pptz) was prepared according to published procedures [16a], with some modifications. [Re(CO)$_5$Cl] was kindly provided by Dr. *H. Klahn* [18]. UV/VIS Spectra: *Shimadzu UV3101PC* apparatus; λ_{max}. IR Spectra: *Bruker Vector-22* FT-IR spectrometer, as KBr discs; in cm^{-1}. ^{1}H-NMR Spectra: *Bruker AC-200* spectrometer, at 200 MHz; δ in ppm rel. to Me$_4$Si, J in Hz. Cyclic voltammetry (CV): *Bas CV-50W 2.3 MF-9093* equipment, in MeCN or 1,2-dichloroethane soln., with Bu$_4$N$^+$PF (*Aldrich*) as electrolyte.

2. *ESR Measurements.* ESR Spectra were recorded at r.t. in the X-band modus (9.85 GHz) with a *Bruker ECS-106* spectrometer using a rectangular cavity and a 50-KHz field modulation. Calibration was done with the α,α'-diphenyl-β-picrylhydrazyl (DPPH) radical. The radical anions were generated *in situ* by electrolytic reduction at r.t. Simulated ESR spectra were generated with the software WINEPR Simfonia (vers. 1.25); radio *Lorentzian/Gaussian* = 0.4.

3. *Synthesis of Pyrazino[2,3-*f*][1,10]phenanthroline* (ppl; **2**). This compound was prepared by a slight modification of the published procedures [8a]. UV (MeCN): 254 (IL, $\pi \rightarrow \pi^*$), 326–341 (IL, n $\rightarrow \pi^*$). ^{1}H-NMR (CDCl$_3$): 9.29 (*dd*, H$_a$); 7.79 (*dd*, H$_b$); 9.47 (*dd*, H$_c$); 8.96 (*s*, H$_d$). Anal. calc. for $C_{14}H_8N_4$ (268.28): C 76.11, H 3.00, N 20.88; found: C 76.89, H 3.16, N 19.92.

4. *Syntheses of Precursor Complexes.* The *fac*-[Re(CO)$_3$(ppl)Cl] and *fac*-[Re(CO)$_3$(ppl)(TfO)] complexes were prepared in analogy to literature procedures for analogous compounds [3][6].

4.1. *fac*-[Re(CO)$_3$(ppl)Cl]. A suspension of ppl (**2**; 200 mg, 0.87 mmol) and [Re(CO)$_5$Cl] (316 mg, 0.87 mmol) in anh. toluene (40 ml) was heated at reflux for 2 h under an inert atmosphere. The solvent was evaporated to dryness, the yellow solid was dissolved in a minimum of MeCN, and the crude product was precipitated by addition of Et$_2$O. The product was filtered off, washed with Et$_2$O (3 × 5 ml), and dried under high vacuum. Yield: 390 mg (82%). Anal. calc. for $C_{17}H_8ClN_4O_3Re$ (537.94): C 37.96, H 1.49, N 10.41; found: C 37.93, H 1.39, N 10.04.

4.2. *fac*-[Re(CO)$_3$(ppl)(TfO)]. A suspension of *fac*-[Re(CO)$_3$(ppl)Cl] (0.34 g, 0.64 mmol) and TfOAg (0.165g, 0.64 mmol) in anh. THF (40 ml) was heated at reflux for 2 h under an inert atmosphere in the dark, and then cooled to r.t. The precipitated AgCl was removed by filtration, and the filtrate was evaporated to dryness. The resulting yellow solid was dissolved in MeCN, and the product was precipitated by addition of Et$_2$O, filtered, and dried under high vacuum. Yield: 360 mg (87%). Anal. calc. for $C_{18}H_8ClF_3N_4O_6ReS$ (651.55): C 33.18, H 1.28, N 8.60, S 4.92; found: C 33.53, H 1.37, N 8.88, S 5.15.

5. *Synthesis of Cationic Complexes.* Complexes of the type *fac*-[Re(CO)$_3$(ppl)(L)]PF$_6$, with L = bpy, ^{t}Bu-py, MeO-py, and pptz[1]), were obtained from the above [Re(CO)$_3$(ppl)(TfO)] precursor complex by the following procedure [3][7]. To a soln. of *fac*-[Re(CO)$_3$(ppl)(TfO)] (0.1 g, 0.15 mmol) in anh. MeOH (20 ml), the appropriate reagent was added: 24 mg (1 equiv.) of bpy; *ca.* 0.5 ml (> 1 equiv.) of ^{t}Bu-py or MeO-py; 50 mg (1.13 equiv) of pptz. The mixture was heated at reflux for 2 h under an inert atmosphere. The soln. was cooled to r.t., excess NH$_4$PF$_6$ was added, and the mixture was stirred for 12 h. The resulting yellow precipitate was isolated by decantation, and purified by column chromatography (Al$_2$O$_3$; petroleum ether and MeCN/CHCl$_3$), followed by precipitated from Et$_2$O.

Data of fac-*[Re(CO)$_3$(ppl)(bpy)]PF$_6$.* Yield: 94 mg (76%). Anal. calc. for $C_{27}H_{16}N_6O_3Re \cdot PF_6$ (803.63): C 40.35, H 2.00, N 10.46; found: C 41.54, H 2.12, N 11.08.

Data of fac-*[Re(CO)$_3$(ppl)(^{t}Bu-py)]PF$_6$.* Yield: 1.12 g (95%). Anal. calc. for $C_{26}H_{21}N_5O_3Re \cdot PF_6$ (782.66): C 39.90, H 2.70, N 8.95; found: C 39.12, H 2.79, N 9.32.

Data of fac-*[Re(CO)$_3$(ppl)(MeO-py)]PF$_6$*. Yield: 102 mg (89%). Anal. calc. for $C_{23}H_{15}N_5O_4Re \cdot PF_6$ (756.57): C 36.51, H 2.00, N 9.25; found: C 36.12, H 1.94, N 10.05.

Data of fac-*[Re(CO)$_3$(ppl)(pptz)]PF$_6$*. Yield: 113 mg (77%). Anal. calc. for $C_{35}H_{22}N_6O_3ReS \cdot PF_6$ (937.84): C 44.82, H 2.36, N 8.96, S 3.42; found: C 44.21, H 1.99, N 9.15, S 3.50.

REFERENCES

[1] M. S. Wrighton, D. L. Morse, *J. Am. Chem. Soc.* **1974**, *96*, 998; D. L. Morse, M. S. Wrighton. *J. Am. Chem. Soc.* **1976**, *98*, 3931.

[2] E. Ioachim, E. A. Medlycott, G. S. Hanan, *Inorg. Chim. Acta* **2006**, in press; R. Ziessel, A. Juris, M. Venturim, *Chem. Commun.* **1997**, 1593; J. R. Schoonover, G. F. Strouse, R. B. Dyer, W. D. Bates, P. Chen, T. J. Meyer, *Inorg. Chem.* **1996**, *35*, 273.

[3] L. A. Worl, R. Duesing, P. Y. Chen, L. Della-Ciana, T. J. Meyer, *J. Chem. Soc., Dalton. Trans.* **1991**, 849.

[4] A. S. Polo, M. K. Itokazu, N. Y. M. Iha, *J. Phochem. Photobiol. A* **2006**, in press; C. G. Garcia, J. F. de Lima, N. Y. Iha, *Coord. Chem. Rev.* **2000**, *196*, 219; M. K. Itokazu, A. S. Polo, N. Y. M. Iha, *J. Phochem. Photobiol. A* **2005**, *160*, 27.

[5] A. Juris, V. Balzani, *Coord. Chem. Rev.* **1998**, *101*, 105; D. J. Stufkenes, A. Vlcek Jr., *Coord. Chem. Rev.* **1998**, *177*, 127; V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serrini, *Chem. Rev.* **1996**, *96*, 759.

[6] a) K. K.-W. Lo, K. H.-K. Tsang, K.-S. Sze, *Inorg. Chem.* **2006**, *45*, 1714; b) K. K.-W. Lo, W.-K. Hui, *Inorg. Chem.* **2005**, *44*, 1992; c) K. K.-W. Lo, K. H.-K. Tsang, W.-K. Hui, N. Zhu, *Inorg. Chem.* **2005**, *44*, 6100; d) K. K.-W. Lo, K. H.-K. Tsang, *Organometallics* **2004**, *23*, 3062; e) J. Guerrero, E. Piro, E. Wolcan, M. R. Feliz, G. Ferraudi, S. A. Moya, *Organometallics* **2002**, *20*, 2842; f) S.-S. Sun, A. J. Lees, *Organometallics* **2001**, *20*, 2353.

[7] a) W. D. Bates, P. Chen, D. M. Dattelbaum, W. E. Jones Jr., T. J. Meyer, *J. Phys. Chem.* **1999**, *103*, 5227; b) R. López, A. M. Leiva, F. Zuloaga, B. Loeb, E. Norambuena, K. M. Omberg, J. R. Schoonover, D. Striplin, M. Devenney, T. J. Meyer, *Inorg. Chem.* **1999**, *38*, 2924; c) H. D. Stoeffler, N. B. Thornton, S. L. Temkin, K. S. Schanze, *J. Am. Chem. Soc.* **1995**, *117*, 7121.

[8] a) A. Delgadillo, P. Romo, A. M. Leiva, B. Loeb, *Helv. Chim. Acta* **2003**, *86*, 2110; b) K.-C. Zheng, J.-P. Wang, W.-L. Peng, Y. Shen, F.-C. Yun, *Inorg. Chim. Acta* **2002**, *328*, 247; c) A. M. S. Garas, R. S. Vagg, *J. Heterocycl. Chem.* **2000**, *37*, 151; d) I. Greguric, J. R. Aldrich-Wright, J. G. Collins, *J. Am. Chem. Soc.* **1997**, *119*, 3621.

[9] D. C. Harris, M. D. Bertolucci, 'Symmetry and Spectroscopy', Dover Publications, New York, 1989; R. W. Balk, D. J. Stufkens, A. Oskam, *J. Chem. Soc., Dalton Trans.* **1981**, 1124.

[10] A. Arancibia, J. Concepción, N. Daire, G. Leiva, A. M. Leiva, B. Loeb, R. Del Río, R. Díaz, A. Francois, M. Saldivia, *J. Coord. Chem.* **2001**, *54*, 323; R. Díaz, O. Reyes, A. Francois, A. M. Leiva, B. Loeb, *Tetrahedron Lett.* **2001**, *42*, 6463.

[11] a) I. E. Pamestchenco, D. E. Polyansky, F. N. Castellano, *Inorg. Chem.* **2005**, *44*, 3412; b) M. K. Itokazu, A. S. Polo, D. L. Araújo de Feria, C. A. Bignozzi, N. Y. M. Iha, *Inorg. Chim. Acta* **2001**, *313*, 149.

[12] R. López, B. Loeb, D. Striplin, M. Devenney, K. Omberg, T. J. Meyer, *J. Chil. Chem. Soc.* **2004**, *49*, 83.

[13] a) K. K.-W. Lo, J. S.-Y. Lau, V. W.-Y. Fong, *Organometallics* **2004**, *23*, 1098; b) L. Wallace, D. P. Rillema, *Inorg. Chem.* **1993**, *32*, 3836; c) J. K. Hino, L. Della Ciana, W. J. Dessick, B. P. Sullivan, *Inorg. Chem.* **1992**, *31*, 1072; d) P. Chen, R. Duesing, D. K. Graff, T. J. Meyer, *J. Phys. Chem.* **1991**, *95*, 5850.

[14] a) K. Yoshihara, S. Kumazaki, *J. Photochem. Photobiol. C* **2000**, 22; b) G. F. Strousse, J. R. Schoonover, R. Duesing, T. J. Meyer, *Inorg. Chem.* **1995**, *34*, 2725; c) R. Duesing, G. Tapolsky, T. J. Meyer, *J. Am. Chem. Soc.* **1990**, *112*, 5378.

[15] J. A. Treadway, B. Loeb, R. López, P. A. Anderson, F. R. Kenne, T. J. Meyer, *Inorg. Chem.* **1996**, *35*, 2242.

[16] a) P. Chen, T. D. Westmoreland, E. Danielson, K. S. Schanze, D. P. Anthon, E. Neveux, T. J. Meyer, *Inorg. Chem.* **1987**, *26*, 1117; b) T. D. Westmoreland, K. S. Schanze, P. E. Neveux, E. Danielson, B. P. Sullivan, P. Chen, T. J. Meyer, *Inorg. Chem.* **1985**, *24*, 2596.

[17] M. Yamada, Y. Tanaka, Y. Yoshimoto, S. Kuroda, I. Shimao, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1006; C. J. Mooddy, C. W. Rees, R. Thomas, *Tetrahedron* **1992**, *48*, 3589.

[18] A. H. Klahn, B. Oelckers, A. Toro, A. Godoy, *J. Organomet. Chem.* **1997**, *548*, 12.

Received March 21, 2006