Photophysical and electrochemical properties of novel pyridyl-ethylene Re-complexes

Rubén A. Machado[1], Franklin Vargas[1]*, Alejandro J. Arce[1], David Rivillo[1],
Ysaura De Sanctis[1], Gilberto Jorge[2], José D. Martinez[2] and Lindora D'Ornelas[3]

[1]*Centro de Química, Instituto Venezolano de Investigaciones Científicas (Ivic), Apartado 21827, Caracas 1020-A, Venezuela.* [2]*Laboratorio de Electroquímica.* [3]*Laboratorio de Síntesis Organometálica. Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, apartado postal 47102, Caracas, Venezuela.*

Abstract

The absorption and fluorescence spectra at different excitation wavelengths of the recently reported rhenium carbonyl complexes [$Re_2(\mu:\eta^3$-$C_{12}H_{10}N_2)(CO)_8$ **(1)**, [$Re_2(\mu$-H)$(\mu:\eta^3$-$C_{12}H_9N_2)(CO)_7$ **(2)** and [$Re_2(\mu$-H)$(\mu:\eta^5$-$C_{12}H_9N_2)(CO)_6$ **(3)** have been studied and compared between them with the aim to evaluate their potential as molecular switches and charge transfer species. Their photostability in dichloromethane solutions (aerobic conditions) under UV-A and UV-B light irradiation, and photoinduced charge transfer reactions with tetrazolium blue were analyzed. The redox properties of complexes **1-3** have been examined by cyclic voltammetry: the behavior of complexes **1** and **3** is very similar, giving quasi-reversible oxidation-reduction processes, while for **2** a totally irreversible oxidation-reduction process was observed.

Key words: rhenium carbonyl complexes, charge transfer, photoactivity, fluorescence, photostability.

Propiedades fotofísicas y electroquímicas de nuevos complejos piridiletilénicos de renio

Resumen

Se estudiaron los espectros de absorción y fluorescencia a diferentes longitudes de onda de excitación de los nuevos complejos carbonílicos de renio [$Re_2(\mu:\eta^3$-$C_{12}H_{10}N_2)(CO)_8$ **(1)**, [$Re_2(\mu$-H)$(\mu:\eta^3$-$C_{12}H_9N_2)(CO)_7$ **(2)** y [$Re_2(\mu$-H)$(\mu:\eta^5$-$C_{12}H_9N_2)(CO)_6$ **(3)**, y fueron comparados entre ellos con el interés de evaluar su potencial como interruptores moleculares y especies de transferencia de carga. Además, se estudió la fotoestabilidad de estos complejos en soluciones del diclorometano bajo condiciones aeróbicas e irradiación UV-A y UV-B, y se analizaron los procesos de transferencia de carga fotoinducida en presencia de azul de tetrazolium. Las propiedades redox de los complejos **1**-**3** se examinaron mediante voltametría cíclica: el comportamiento de los complejos **1** y **3** fue similar, mostrando procesos de oxidación-reducción cuasi-reversibles; el complejo **2** mostró un proceso de oxidación-reducción totalmente irreversible.

Palabras claves: complejos carbonílicos, renio, transferencia de carga, fotoactividad, fluorescencia, fotoestabilidad.

*   Autor para la correspondencia. E-mail: fvargas@ivic.ve.

Introduction

Photochemical and photophysical properties of N-heterocyclic rhenium carbonyl complexes have been the subject of extensive investigation in the last 20 years because of the outstanding interest on photocatalytic reactions, theoretical studies and many potential applications. Information on photophysical properties obtained *via* optical studies, such as electronic absorption and fluorescence spectra, is of great importance to understand charge-transfer reactions (1, 2). Mechanistic studies in the field of organometallic photochemistry have been mainly confined to transition-metal carbonyls. This also holds for the photochemical reactions of metal-metal-bonded complexes, for which most mechanistic information is available for the carbonyl dimers $M_2(CO)_{10}$ (M= Mn, Re), $CpFe_2(CO)_4$, $Cp_2M_2(CO)_6$ (M= Mo, W), and their derivatives (3). Both hemolytic splitting of the metal-metal bond and loss of CO appeared to be primary photoprocesses for these dimers.

We recently reported the interaction of 1,2-bis(2-pyridyl)ethene with the labile compound $[Re_2(CO)_8(CH_3CN)_2]$ to give the dinuclear complexes $[Re_2(\mu:\eta^3\text{-}C_{12}H_{10}N_2)(CO)_8$ **(1)**, $[Re_2(\mu\text{-}H)(\mu:\eta^3\text{-}C_{12}H_9N_2)(CO)_7$ **(2)** and $[Re_2(\mu\text{-}H)(\mu:\eta^{\eta5}\text{-}C_{12}H_9N_2)(CO)_6$ **(3)**, among others (4) (figure 1). Fluorescence was observed for the interconversion between **2** and **3**: decarbonylation of **2** in refluxing cyclohexane gives **3**, which easily reverts to **2** under CO atmosphere.

In order to understand the photochemical behaviour of these metal-metal bonded complexes (**1**-**3**), we carried out studies on their photochemical and electrochemical properties as fluorescence, UV absorption and cyclic voltammetry (CV). The effect of tetrazolium-blue salt (NBT, reduction potential = -0.08 volt) on the optical spectra of these Re compounds was explored to give some clues on photoinduced charge-transfer processes.

Experimental

Chemicals

All analytical or HPLC grade solvents were obtained from Merck (Darmstadt, Germany). The tetraethyl ammonium bromide was purchased from Aldrich and used as provided. Complexes $[Re_2(\mu:\eta^3\text{-}C_{12}H_{10}N_2)(CO)_8$ **(1)**, $[Re_2(\mu\text{-}H)\text{-}(\mu:\eta^3\text{-}C_{12}H_9N_2)(CO)_7$ **(2)** and $[Re_2(\mu\text{-}H)\text{-}(\mu:\eta^5\text{-}C_{12}H_9N_2)(CO)_6$ **(3)** were prepared as reported (4). UV-Vis spectrophotometry of compounds **1**, **2**, **3** and ligand solutions was followed using a Milton-Roy Spectronic 3000 array instrument (Milton Roy Company-USA). The fluorescence spectra were registered with a Shimadzu RF 1501 spectrofluorophotometer. Electrochemical data (CV) were recorded on a PAR 273A potentiostat/galvanostat. The airtight CV cell was based on a three-electrode design, using as working electrodes a sphere (0.2827 cm^2) and a platinum disc (0.0707 cm^2), and as counter-electrode a platinum sheet (1 cm^2); silver wire was used as pseudo-reference. Solutions were prepared at 1×10^{-3} mol/L in the electrolytic media (0.1 mol/L tetraethyl am-
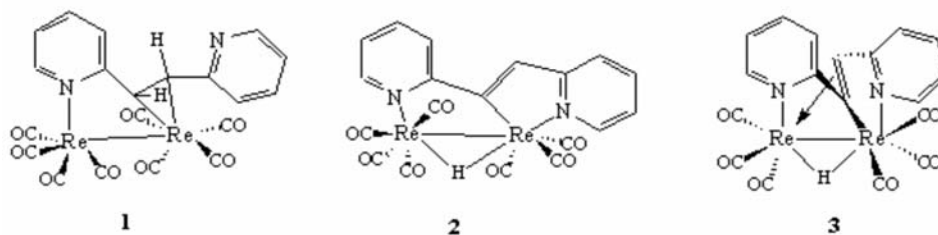

Figure 1. Structures for the Re complexes **1-3**.

monium bromide, TEAB/dichloromethane). All experiments were carried out under nitrogen atmosphere. The potential of the pseudo-reference electrode was determined from two half-wave potentials for the couple $Fe(Cp)_2^{0/+}$ using a solution 1×10^{-3} M $Fe(Cp)_2$ in dichloromethane.

Thermal treatment of $[Re_2(\mu\text{-}H)(\mu\text{:}\eta^3\text{-}C_{12}H_9N_2) (CO)_7$ (2)

Compound **2** (0.010 g, 0.0133 mmol) was dissolved in cyclohexane (30 mL). The solution was heated under reflux for 4 h. The solvent was evaporated under reduced pressure and TLC (SiO_2) of the residue (eluant: dichloromethane/n-hexane, 3:7, v/v) gave $[Re_2(\mu\text{-}H)(\mu\text{:}\eta^5\text{-}C_{12}H_9N_2)(CO)_6]$ (**3**) as a green solid (0.007 g, 73%).

Carbonylation of $[Re_2(\mu\text{-}H)(\mu\text{:}\eta^5\text{-}C_{12}H_9N_2)(CO)_6$ (3) at room temperature

Compound **3** (0.010 g, 0.0138 mmol) was dissolved in $[CO(CD_3)_2]$ (1 mL) in a NMR tube and sealed under 1 atm. CO. After 17 days at room temperature, cluster **3** was completely converted to $[Re_2(\mu\text{-}H)(\mu\text{:}\eta^3\text{-}C_{12}H_9N_2)(CO)_7$ (**2**).

Photochemical reactions

Solutions of **1**, **2** and **3** in CH_2Cl_2 were irradiated under aerobic conditions at room temperature, with an Osram HQL 250 W medium pressure Hg lamp placed inside a Pyrex immersion-well photoreactor (Applied Photophysics parts No. 3230 + 3307) for UV-A irradiation (output spectral 320-400 nm) with a maximum at 370 nm and a total irradiance of 17 mW/cm^2 as measured with a UVX Digital Radiometer after 1 h continued illumination. The distance between the light source and the test aliquots was 10 cm. The temperatures detected in the cuvette during a standard 1 h irradiation were no higher than 27 °C. Irradiation was also carried out under the same conditions with a Rayonet photochemical reactor equipped with 16 phosphorus lamps with an emission maximum of 300 nm for UV-B experiments (23 mW/cm^2 of irradiance).

Quantum yields

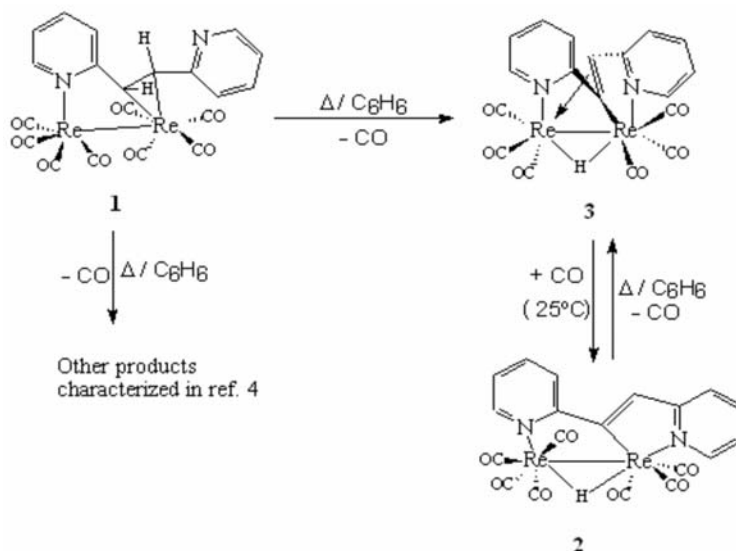Fluorescence quantum yields for compounds **1**, **2** and **3** were determined at room

Figure 2. Interconversion of compounds **1-3**.

temperature either by comparing the corrected fluorescence intensity of compounds **1**-**3** in CH_2Cl_2 to that of rhodamine B (1.0 x 10^{-6} M in CH_2Cl_2; fluorescence quantum yield = 0.69) or to that of quinine bisulfate (0.05 M in H_2SO_4; fluorescence quantum yield, 0.55) (5,6).

In the product quantum yields determination, photolysis was allowed to proceed to less than 10% product formation to minimize light absorption by the photoproducts and additional products from side reactions. The photon flux incident on 3 ml of solution in quartz cuvettes (1 cm optical path) was measured by means of a ferric oxalate actinometer giving about 10^{15}- 10^{16} quanta s^{-1}.

Electron transfer mechanism detection by reduction of NBT

Under the same conditions for the photolysis of compounds **1, 2** and **3** (5.1 x 10^{-5} M), the photoreduction of nitro blue tetrazolium ([NBT]= 5.1 x 10^{-5} M) was followed in the presence of the 3 Re-complexes, both in the presence and absence of oxygen as a function of irradiation time, by determining the increase in absorbance at 560 nm due to the formation of diformazan product (7-9).

Results and discussion

Photolability of compounds **1**-**3**, ligand 1,2-bis(2-pyridyl)-ethylene (L) and the binuclear metal complex [$Re_2(CO)_8(CH_3CN)_2$] (MC) in CH_2Cl_2 were studied. Data for the absorption spectra before and after irradiation is shown in table 1.

Solutions of compounds **1**, **2** and **3** in dichloromethane were stable under UV-A irradiation (320-400 nm) for 8 hours, so these conditions were used for the studies on electron and energy transfer. On the contrary, the same solutions were unstable (photolabile) under UV-B light (290-320 nm) for 4 hours, where non-identified decomposition products were obtained.

Compounds **1**, **2** and **3** were able to photosensitize the reduction of nitro blue tetrazolium (NBT) to formazan in ethanol solution (30 °C). This reaction was more efficient for compound **2** than the others (figure 3). The ligand (L) also showed an efficient electron-transfer reaction with NBT.

Complexes **1** and **3** showed to be less efficient than the ligand for the photochemically induced transfer of electrons in the presence of NBT. It seems that structural differences in **2** make it particularly a more efficient photosensitizer for the NBT reduction. The efficiency for the energy transfer (possibly due to its more structural rigidity) diminishes from its singlet excited state (lower fluorescence quantum yield), winning efficiency for the electronic transfer.

The photoinduced electron transfer from the complexes to NBT was always effective in the absence of oxygen. In its presence, the electron transfer to NBT was quenched, superoxide anion being generally formed. The studies of the photoreduction of NBT for the complexes **1**-**3** predict that the electron-transfer process is mainly caused through the ligands connected in the complex and not to an increase in the connections Re-Re.

The Cyclic voltammetry (CV) of the electrolyte, ligand and precursor metal salt solutions used for the synthesis of the complexes were previously examined to discard the presence of pollutants. The CV curves for these solutions do not show any peaks reveling the absence of oxidative-reductive processes, ruling out the possibility that the metal or the carbonylic groups show electro-activity in the sweeping area.

The cyclic voltagramm of the complex **1** (figure 4) shows a wide reduction peak at -0.537 V/(Fe(Cp)$_2^{0/+}$) and a second peak at -1.062 V/(Fe(Cp)$_2^{0/+}$) which are attributed to the coordinated ligand to the metallic centers, since the binuclear labile of rhenium did not show electroactivity in this area. In

Table 1
Position (nm) of principal bands in the absorption and fluorescence spectra for different
excitation wavelengths

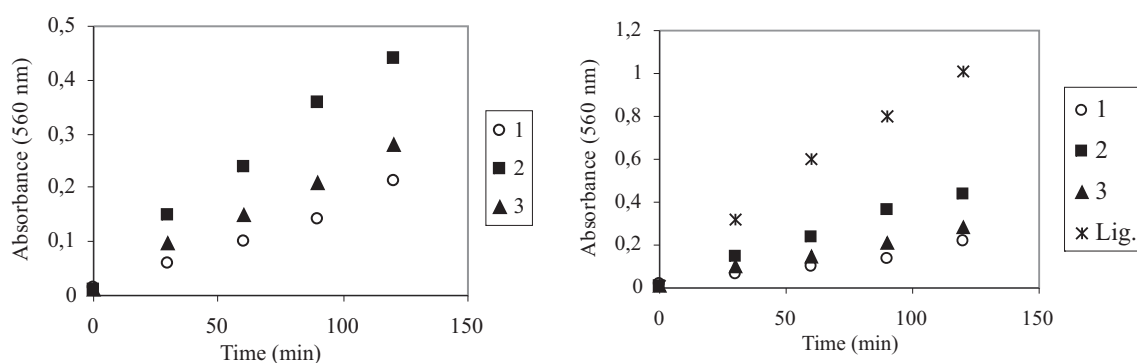| Compound (ΦF_F)	Absorbance, nm (Intensity)	Fluorescence, nm (Intensity)		
		λ_{exc} = **256**	**380**	**415**
1 (5x10^{-2})	229 (0.70) 260 (0.55) 415 (0.13)	358 (195) 516 (554) 767 (167)	761 (4)	829 (2)
2 (2x10^{-4})	229 (0.90) 376 (0.29)	517 (10)	760 (4)	829 (2)
3 (4x10^{-3})	229 (0.89)	355 (190) 518 (10) 705 (50)	762 (4)	830 (3)
L	266 (0.06) 318 (0.14)	353 (2) 516 (3) 769 (1)	760 (5)	828 (3)
MC	229 (0.60) 318 (0.19)	327 (15) 357 (18) 520λ (1) 638 (5) 705 (4)	760 (6)	828 (4)

Figure 3.   Photoreduction of NBT (5.1 x 10^{-5} M) sensitized by compounds **1**, **2** and **3** (5.1 x 10^{-5} M) in ethanolic solutions. Comparison with the ligand (L) 1,2-bis(2-pyridyl)-ethylene (left graphic).

the anodic scanning appears two peaks: (ox1) at 0.435 V/$(Fe(Cp)_2^{0/+})$ and (ox 2) at 0.744 V/$(Fe(Cp)_2^{0/+})$ that would correspond to the oxidation of the reduction products obtained in the cathodic scanning. The oxidation-reduction processes of these complexes are quasi-reversible with $\Delta E1= 0.972$ V and $\Delta E2= 1.806$ V respectively.

We want to highlight that after a second cycle, a third peak (red3) appears at -1.359 V/$(Fe(Cp)_2^{0/+})$ and the (ox 1) peak disappears, which seems to indicate the formation of a non electro-active chemical species in the first sweeping.

The same study for complex **1** was carried out for complex **2**, (the voltagram of complex **2** is shown in figure 5). Oxidation peaks are not observed for the anodic scanning, but the cathodic scanning showed a reduction peak at -0.503 V/$(Fe(Cp)_2^{0/+})$ that corresponds to a totally irreversible reaction, since peaks of oxidation do not appear when it is carried out a scanning toward oxidations potentials. This fact indicates the formation of a non electroactive chemical species in the range of studied potentials.

The voltammetric behavior of complex **3** (figure 6) was similar to that of complex **1** (used for figure 6, in the first cycle solid line, and second cycle line + symbol, this to differentiate). Peaks of oxidation are not observed for the anodic scanning, but the cathodic scanning showed a reduction peak at -0.500 V/$(Fe(Cp)_2^{0/+})$, which is oxidized to a potential of 0.944 V/$(Fe(Cp)_2^{0/+})$. Amplifying the area where the oxidation peak appears, it was found (as for complex **1**) another oxidation peak at 0.689 V/$(Fe(Cp)_2^{0/+})$, analogous to complex **1,** these peaks are shifted to more positive potentials.

Furthermore the conjugated double bond for the complex **2** can stabilize charge by resonance, which translates into an increased current reduction and the absence
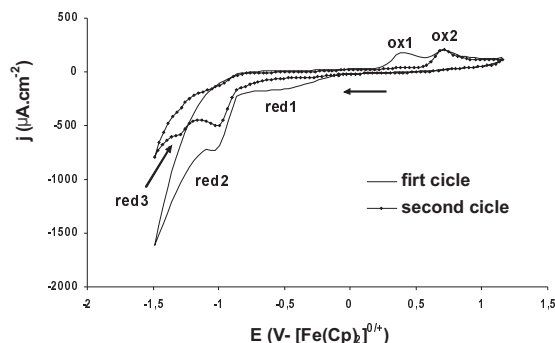

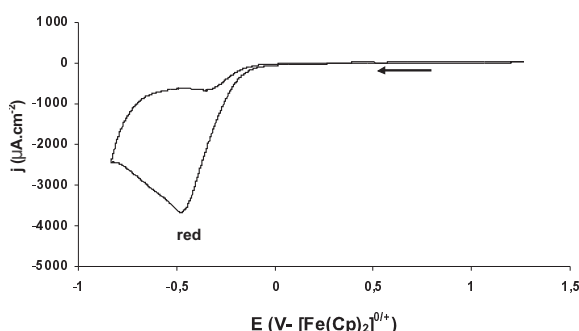Figure 4.   Voltagram of complex **1**, $1x10^{-3}$ mol/L in 0.1 M (TEAB)/CH_2Cl_2, scan rate 0.2 Vs^{-1}.

Figure 5.   Voltagram of complex **2**, $1x10^{-3}$ mol/L in 0.1 M (TEAB)/CH_2Cl_2, scan rate 0.2 Vs^{-1}.
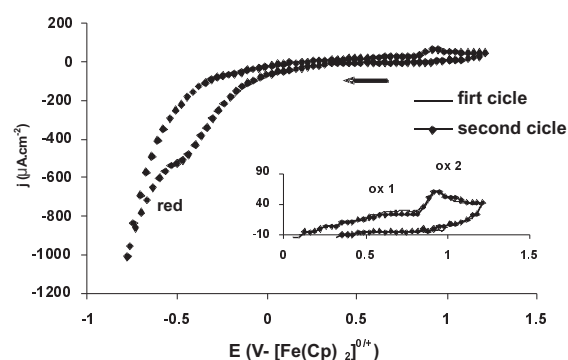

Figure 6.   Voltagram of complex **3**, $1x10^{-3}$ mol/L in 0.1 M (TEAB)/CH_2Cl_2, scan rate 0.2 Vs^{-1}.

of oxidation peaks. However in the complexes **1** and **3** this stabilization is not possible.

Conclusions

The substitution of CO groups by a more basic ligand (L) in $[Re_2(CO)_{10}]$, should move the reduction process of the rhenium core to a more cathodic potential as is observed in other complexes (10). The less negative reduction potential and the change from an irreversible to a quasi-reversible process, in comparing **2** to **1** and **3**, is already indicative of a more delocalized system, and so, of a communication between the two metallic centers through of the 1,2-bis(2-pyridyl)ethene in **2** and **3**. The rhenium complexes **1**-**3** have been shown to photosensitize the reduction of nitro blue tetrazolium (NBT) under UV-A irradiation. Among these three metallic complexes, compound **2** stood out to produce a higher photoinduced reduction of NBT. This compound presents a lower fluorescence quantum yield and consequently deficiency for the process of energy transfer from its singlet state. These results indicate that direct electron transfer may occur from the excited state, possibly from the triplet state of these complexes to the substrate, especially to the oxygen. Naturally, superoxide could be involved as an intermediate when oxygen is present. This was evidenced by the generation of superoxide anion by the irradiation of the complexes and the quenching of the observed reduction of NBT. The electron transfer process observed from the ligand alone is also remarkable. Compounds **2** and **3** can serve as a CO detection probe by means of UV-Vis or fluorescence spectroscopy, since both show absorption and fluorescence bands that can be precisely differentiated among them.

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