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Article

Synthesis and Electrochemical Characterization of Bimetallic Ruthenium Complexes with the Bridging $\eta^2(\sigma,\sigma)$-1,3-Butadiyne-1,4-Diyl Ligand

Edison Stein*[*], *Sergio Y. Oki and Eduardo J. S. Vichi

Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13083-970, Campinas - SP, Brazil

O complexo [*cis*-{RuCl(bpy)$_2$(μ-C≡C-)}]$_2$ (**1**) foi obtido pelo tratamento de 1 equiv de 1,4-bis(trimetilsilil)-1,3-butadiino ou bis(trimetilsilil)acetileno com 2 equiv do complexo *cis*-[RuCl$_2$(bpy)$_2$]·2H$_2$O, NaF e NaBF$_4$ na mistura de solventes metanol/CH$_2$Cl$_2$ (10/1) com rendimentos de 52% e 35%, respectivamente. Análises de RMN de ^{1}H, ^{13}C{H} e principalmente eletroquímica, confirmaram que o mesmo produto foi obtido dos dois métodos. Análise de (**1**) através de voltametria cíclica, no intervalo de potencial de 0 a 1,20 V mostrou dois picos de oxidação quasi-reversíveis referentes ao par redox Ru(II)/Ru(III). Os dois processos redox são separados por 520V, indicando comunicação eletrônica significante entre os dois centros metálicos

The bis(ruthenium)alkyne complex [*cis*-{RuCl (bpy)$_2$(μ-C≡C-)}]$_2$ (**1**) was obtained by treatment of 1 equiv of either 1,4-bis(trimethylsilyl)-1,3-butadiyne or bis(trimetylsilyl)acetylene with 2 equiv of *cis*-[RuCl$_2$(bpy)$_2$]·2H$_2$O, NaF and NaBF$_4$ salts in methanol/CH$_2$Cl$_2$ mixture (10/1) in 52% and 35% yields, respectively. ^{1}H, ^{13}C{H} NMR and principally electrochemical analyses confirmed that the same product was obtained from the two reactions. Cyclic voltammetric analyses of (**1**) from 0 to 1.20 V displays two one-electron quasi-reversible oxidation peaks attributed to the Ru(II)/Ru(III) couple. The redox processes are separated by 520 mV, indicating a significant electronic communication between the two metallic centers.

Keywords: electrochemistry, ruthenium complex, bimetallic complexes

Introduction

Organometallic polymers whose metal centers are joined by organic ligands with delocalized π-systems have been investigated extensively over the last several years[1]. Such species are of interest due to their potential usefulness in the areas of electronics and materials science[2]. Organometallic polymers, with transition metals linked by a polyynediyl ligand, M-(C≡C)$_n$-M, have attracted increasing attention from various viewpoints[3]. The π-conjugated polycarbon system is extended to the two terminal metal units and such systems are expected to display attractive properties resulting from i) π-conjugation along the rodlike linkage, ii) stabilization of odd-electron (mixed-valent) species formed by oxidation and reduction, and iii) hyperpolarizability. One particular type of organometallic polymer, with transition metals linked by a 1,3-butadiyne-1,4-diyl ligand, is known to have a rigid, rodlike structure and exhibits unusual properties both in solution and in the solid state[4]. Here we report the synthesis and characterization of a complex containing the $\eta^2(\sigma,\sigma)$-1,3-butadiyne-1,4-diyl ligand, synthesized from the reactions of *cis*-[RuCl$_2$(bpy)$_2$]·2H$_2$O (bpy = bipyridine) with 1,4-bis(trimethylsilyl)-1,3-butadiyne or bis(trimethylsilyl)acetylene.

Experimental details

Materials and methods

Ruthenium trichloride hydrate, DBU (1,8-diazabicyclo [5.4.0]undec-7-ene), 1,4-bis(trimethylsilyl) 1,3-butadiyne, bis(trimethylsilyl)acetylene, trimethylsilylacetylene and acetonitrile-d$_3$ were purchased from Aldrich and used as received. Acetonitrile was treated with the appropriate drying agent, distilled and stored under argon. Other solvents were used without further purification. The complex *cis*-[RuCl$_2$(bpy)$_2$]·2H$_2$O was prepared according to the published method.[5]

Infrared spectra were recorded on a Bomem FTIR spectrophotometer, ^{1}H and ^{13}C{H} spectra were obtained on a Bruker Model AC300/P spectrometer operating at 300 and 75.45 MHz, respectively, using tetramethylsilane as internal standard. Elemental analyses were performed on a Perkin-Elmer Model 2400 CHN apparatus.

Electrochemical measurements were performed on an EG&G Princeton Applied Research (PAR) M273A electrochemical analyzer interfaced to an IBM computer employing PAR 270 electrochemical software. A standard three-electrode cell was designed to allow the tip of the reference electrode to closely approach the working electrode. Positive feedback IR compensation was applied routinely. All measurements were carried out under dry argon, in anhydrous deoxygenated acetonitrile; solution were *ca*. 1×10^{-3} mol dm^{-3} with respect to the compounds under study and *ca*. 1×10^{-1} mol dm^{-3} with respect to the supporting electrolyte, $[Bu_4N][ClO_4]$. A platinum disk working electrode, a platinum wire auxiliary electrode and a saturated Ag/AgCl reference electrode were used in these experiments.

Synthesis of [cis-{RuCl (bpy)$_2$(μ-C≡C-)}]$_2$ (**1**)

A modification of the existing procedure[6] was used for the synthesis of this complex. To a suspension of 1,4-bis(trimethylsilyl)1,3-butadiyne (0.035 g, 0.18 mmol), or bis(trimethylsilyl)acetylene (0.033 g, 0.19 mmol), $NaBF_4$ (0.052 g, 0.48 mmol) and NaF (0.020 g, 0.48 mmol) in 50 cm^3 of a $MeOH/CH_2Cl_2$ mixture (10:1), *cis*-$[RuCl_2(bpy)_2]\cdot 2H_2O$ (0.19 g, 0.36 mmol) was added as a solid. The mixture was heated at 45°C overnight. The solution was filtered on a filter paper and the solvent evaporated under vacuum to ¼ of the original volume and the complex precipitated with addition of diethyl ether. The solid was dissolved in CH_2Cl_2 and passed through an alumina plug to remove salts. Addition of hexane gave **1** (0.18 g, 0.19 mmol, 52% yield) (or 0.13 g, 0.14 mmol, 35% yield), respectively, as black crystals. (Anal. Calcd. for $C_{44}H_{32}N_8Ru_2Cl_2$: C, 55.87; H, 3.41; N, 11.85. Found: C, 55.63; H, 3.36; N, 11.92%), (or C, 55.87; H, 3.41; N, 11.85. Found: C, 55.79; H, 3.39; N, 11.75%), respectively.

Synthesis of cis-[RuCl(bpy)$_2$]-C≡C-SiMe$_3$ (**2**)

Degassed acetone (30 cm^3), *cis*-$[RuCl_2(bpy)_2]\cdot 2H_2O$ (0.200 g, 0.38 mmol) and $AgBF_4$ (0.075 g, 0.38 mmol), were stirred magnetically for 1.5 h under argon. After this period, the reaction mixture was filtered through a filter paper by gravity and degassed by bleeding argon through the solution for *ca*. 15 min and 55 mm^3 of H-C≡C-SiMe$_3$ (0.38 mmol) was added. The reaction mixture was stirred for 6 h at room temperature and 70 mm^3 of DBU, was added and stirred for further 1h. The solution was then filtered by gravity and the solvent removed by rotatory evaporator to ¼ of the original volume and precipitated with addition of diethyl ether. The solid obtained was dissolved in CH_2Cl_2 and passed through an alumina plug to remove salts. Addition of hexane gave **2** (0.178 g, 0.33 mmol, 85% yield) as black crystals. (Anal. Calcd. for $C_{25}H_{25}N_4RuClSi$: C, 54.98; H, 4.61; N, 10.26. Found: C, 54.52; H, 4,55; N, 10.20%). IR ($\nu_{C\equiv C}$/cm^{-1}): 1972 (KBr). $^{13}C\{H\}$ NMR (CD_3CN): δ -6.14 (s, $SiMe_3$). ^1H NMR (CD_3CN): δ -0.11 (s, $SiMe_3$).

Results and Discussion

*Syntheses of complex [*cis*-{RuCl (bpy)$_2$(μ-C≡C-)}]$_2$* (**1**)

Treatment of 1 equiv of 1,4-bis(trimethylsilyl)-1,3-butadyine with 2 equiv of the *cis*-$[RuCl_2(bpy)_2]\cdot 2H_2O$ in a methanol/CH_2Cl_2 mixture (10:1) in the presence of NaF and $NaBF_4$ salts produced, after heating overnight at 45°C, a red-purple solution. The bis(ruthenium) alkyne complex **1** [*cis*-{RuCl (bpy)$_2$(μ-C≡C-)}]$_2$ (**1**) was isolated from this solution as a black powder in 52% yield. In this one-step procedure, the 1,4-butadienyl bridging ligand is generated *in situ* by the fluoride-induced cleavage of the terminal trimethylsilyl groups (eq 1).

$$Me_3Si\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}SiMe_3 + 2NaF \xrightarrow{MeOH} H\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}H + 2\,Me_3Si\text{-}F + 2\,MeONa \quad (1)$$

$$2\ cis\text{-}[RuCl_2(bpy)_2] + 2NaBF_4 \longrightarrow 2\ cis\text{-}[RuCl(bpy)_2][BF_4] + 2NaCl \quad (2)$$

As described, the BF_4^- anion acts as a halide abstractor[7] (eq 2) to promote the complexation of the terminal alkyne at the ruthenium center, giving the vinylidene complex isolated in many cases as the final product of the reaction (eq 3).

$$2\ cis\text{-}[RuCl(bpy)_2][BF_4] + H\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}H \longrightarrow cis\text{-}[RuCl(bpy)_2\}_2({=}C{=}C{=}C{=}CH_2)][BF_4]_2 \quad (3)$$

However, under these conditions, the cleavage of the trimethylsilyl group is associated with the formation of a stoichiometric amount of a strong base. This base *in situ* deprotonates the vinylidene intermediate, allowing the formation of the bis-(ruthenium alkynyl) complex **1** as the final product of the reaction (eq 4).

$$\{cis\text{-}[RuCl(bpy)_2\}_2({=}C{=}C{=}C{=}CH_2)][BF_4]_2 + 2MeONa \longrightarrow [cis\text{-}\{RuCl\ (bpy)_2(\mu\text{-}C{\equiv}C\text{-})\}]_2 + 2MeOH + 2NaBF_4 \quad (4)$$

To our knowledge, this is the first example reported so far of a diynediyl complex bearing the RuCl(bpy)$_2$ fragment. Because of the complexity of the ^1H and ^{13}C spectra it is not possible to use it to characterize the complex. The complex was characterized by elemental analysis and, mainly, by electrochemical studies. The absence of the absorption of the C≡C stretching in the IR spectrum and the presence of the two quasi-reversible oxidation peaks in the cyclic voltammogram revealed by the electrochemical studies, attributed to the couple Ru(II)/Ru(III), suggest that compounds **1** is a dimer (see discussion below).

Attempts to obtain [*cis*-{RuCl(bpy)$_2$}$_2$(μ-C≡C-)] by reacting *cis*-[RuCl$_2$(bpy)$_2$]·2H$_2$O with bis(trimethylsilyl) acetylene under the same conditions used for the reaction with 1,4-bis(trimethylsilyl)-1,3-butadiyne, surprisingly, afforded the same complex **1** whose elemental analyses, ^{1}H NMR and ^{13}C NMR data are very close to that of complex synthesized using 1,4-bis(trimethylsilyl)-1,3-butadiyne as the ligand. Dimerization of the bis(trimethylsilyl)acetylene ligand probably occurred due to the temperature used, considering that the dimerization of the bis(trimethylsilyl) acetylene ligand does not occur at room temperature. All attempts to obtain complex [*cis*{RuCl(bpy)$_2$}$_2$(μ-C≡C-)] using other methods were unsuccessful.

Complex **2** was prepared by reaction of the free ligand, H-C≡C-SiMe$_3$ with *cis*-[RuCl (bpy)$_2$(CH$_3$COCH$_3$)]$^+$ (eq 5, 6)

$$cis\text{-}[\mathrm{RuCl_2(bpy)_2}] + \mathrm{AgBF_4} \xrightarrow{\text{acetone}} cis\text{-}[\mathrm{RuCl(bpy)_2\,(acetone)}]^+ + \mathrm{BF_4^-} + \mathrm{AgCl} \quad (5)$$

$$cis\text{-}[\mathrm{RuCl(bpy)_2\,(CH_3COCH_3)}]^+ + \mathrm{H\text{-}C{\equiv}C\text{-}SiMe_3} \xrightarrow{\text{DBU}} cis\text{-}[\mathrm{RuCl(bpy)_2\,(C{\equiv}C\text{-}SiMe_3)}] + \mathrm{CH_3COCH_3} \quad (6)$$

The monoacetone complex[8] is known to be a valuable synthetic intermediate. The preparation of the monoacetone complex must be carefully timed[5]. After short reaction times (<1.5 h) the complex is not completely formed, the limiting factor being the rate of dissolution of cis-[RuCl$_2$(bpy)$_2$]·2H$_2$O in acetone. After long reaction times (>1.5 h) a dark, red-brown precipitate begins to form. Isolation of this complex showed it to be identical with dimer *cis*-[RuCl(bpy)$_2$]$_2$[BF$_4$]$_2$ by cyclic voltametry[9]. Isolation of complex **2** was achieved by precipitation from an acetone solution by adding diethyl ether, after filtration through an alumina plug to remove salts.

^{1}H and ^{13}C{^{1}H} NMR spectra.

The of ^{1}H NMR spectrum of [RuCl$_2$(bipy)$_2$], in (DMSO-d$_6$) has been discussed in the literature[10] and shown to be more complex than expected for the *cis* or *trans* configurations. The reason for the complexity of the spectrum is that a mixture of *cis* and *trans* compounds were present in solution, with possible solvent interation[10]. In the *cis* configuration, the molecule has no symmetry so that the 16 bipyridine hydrogens are expected to be unique. A first-order coupling scheme predicts eight doublets and eight triplets for the ^{1}H NMR spectrum assigned to the aromatic hydrogens of bipyridine[5]. In fact, complexes **1** – **2** showed a more complicated pattern of ^{1}H and ^{13}C{^{1}H}NMR spectra in the aromatic region, which would be expected for a *cis* or *trans* compounds. The ^{13}C{^{1}H}NMR spectra of the complexes studied are similar in the aromatic region and display five sets of resonances, concentrated at δ 160.4 – 158.2, 155.2 – 149.5, 139.0 – 136.9, 127.6 – 126.7 and 124.7 – 123.7. Each set of resonance exhibits more peaks than would be expected for the *cis* configuration. This is in agreement with the fact that the pyridine groups of each ligand are not magnetically equivalent and both *cis* and *trans* configurations probably would be present. Moreover, in these complexes, the ^{13}C NMR signals of the Ru-C≡C- carbons are masked by the signals of pyridyl carbons.

Cyclic voltammetric analysis of [cis-{RuCl(bpy)$_2$(m-C≡C-)}]$_2$ (**1**) *and cis-[RuCl(bpy)$_2$]-C≡C-SiMe$_3$* (**2**)

The results of cyclic voltammetry experiments in CH$_3$CN solution for the compounds **1**–**2** and the starting complex *cis*-[RuCl$_2$(bpy$_2$] are given in Table 1.

Table 1. Cyclic Voltammetry Results for Complexes [*cis*-{RuCl(bpy)$_2$ (-C≡C)}]$_2$ (**1**), *cis*-[RuCl(bpy)$_2$]-C≡C-SiMe$_3$ (**2**), and *cis*-[RuCl$_2$(bpy)$_2$].

Complex	$E_{1/2}$ V[a]	K_C[c]
1[d]	+2.47[b], +2.05[b], +0.871, +0.351, -1.42, -1.61	6.13 x 10^8
2	+1.53, +0.410, -1.25[b], -1.39, -1.56	
1[e]	+2.46[b], +2.02[b], +0.874, +0.354, -1.42, -1.62	6.13 x 10^8
[RuCl$_2$(bpy)$_2$]	+2.07[b], +0.410, -1.48, -1.61	

[a] In CH$_3$CN solution at room temperature, 200 mV s^{-1}. E$_{1/2}$ values were calculated from the average of the anodic and cathodic peak potentials, $E_{1/2}=(E_{pa} + E_{pc})/2$. [b] Irreversible peak. [c] $\ln K_C = (n_1E_1^0 - n_2E_2^0)\,F/RT$ with $n_1 = n_2 = 1$. [d] Synthesized from complex *cis*-[RuCl$_2$(bpy)$_2$]·2H$_2$O and 1,4-bis(trimethylsilyl)1,3 butadiyne. [e] Synthesized from complex *cis*-[RuCl$_2$(bpy)$_2$]·2H$_2$O and bis(trimethylsilyl)acetylene.

The results of the cyclic voltammetric experiments on *cis*-[RuCl$_2$(bpy)$_2$] in CH$_3$CN at room temperature are shown in Figure 1.

This compound exhibited two quasi-reversible oxidation peaks at E$_{1/2}$ +2.07 and +0.410V vs Ag/AgCl and two quasi-reversible reduction peaks at E$_{1/2}$ –1.48 and –1.61 V vs Ag/AgCl. The peaks at +2.07 and +0.410 V were attributed to the Ru(III)/Ru(IV) and Ru(II)/Ru(III) couples, respectively. The two reduction peaks at –1.48 and -1.61V were ascribed to the bpy ligand. These results are consistent with the previous study on this complex[9]. The same electrochemical behavior was shown by compound **2** (see Figure 2). This compound shows two quasi-reversible oxidation peaks at E$_{1/2}$ +1.53 and +0.410 V vs Ag/AgCl, owing to the Ru(III)/Ru(IV) and Ru(II)/Ru(III) couples, respectively, and a irreversible reduction process at –1.25 V and two quasi-reversible peaks at –1.39 and –1.56 V vs Ag/AgCl, due to the bpy ligand. Table 1 shows that the potential of the Ru(II)/Ru(III) couple in complex *cis*-[RuCl$_2$(bpy)$_2$] and **2** is the same as in compound **1**, which implies that the Ru(II) orbital energy is unchanged in the complex **2** when of the substitution of the trimethyl(silyl) acetylide by one chloride on *cis*-[RuCl$_2$(bpy)$_2$] complex.

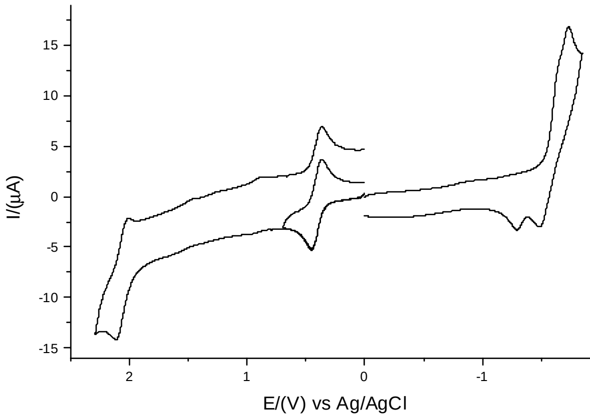

Figure 1. Cyclic voltammetric response for the complex *cis*-[RuCl$_2$(bpy)$_2$] at scan rate 200 mV s^{-1}, at room temperature.

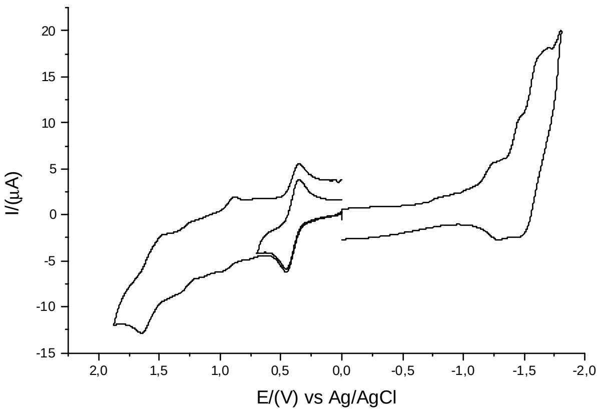

Figure 2. Cyclic voltammetric response for the complex *cis*-[RuCl(bpy)$_2$]-C≡C-SiMe$_3$ (**2**) at 200 mV s^{-1}, at room temperature.

The cyclic voltammetric response for dimeric complex **1** is shown in Figure 3. This complex displays one irreversible oxidation peak at +2.05 V. vs Ag/AgCl, ascribed to the Ru(III)/Ru(IV) couple and two quasi-reversible reduction peaks at –1.42 and –1.61 V vs Ag/AgCl, due to the reduction of the bpy ligand. Two oxidation peaks at +0.351 and +0.871 V vs Ag/AgCl with the i$_{pc}$/i$_{pa}$ current ratio of unity were attributed to the Ru(II)/Ru(III) couple. This means that the neutral dimer undergoes two successive one-electron oxidations to yield the mono- and the dications, respectively (eq 7).

$$\underset{\mathbf{1}}{\text{Ru(II)-Ru(II)}} \underset{}{\overset{-e}{\rightleftharpoons}} \underset{\mathbf{1}^{+}}{[\text{Ru(II)-R(III)}]^{+}} \overset{-e}{\rightleftharpoons} \underset{\mathbf{1}^{2+}}{[\text{Ru(III)-Ru(III)}]^{2+}} \qquad (7)$$

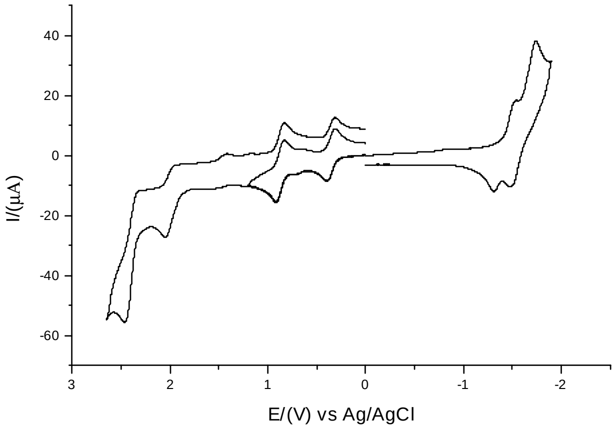

Figure 3. Cyclic voltammetric response for the complex [*cis*-{RuCl(bpy)$_2$](-C≡C-)}]$_2$ (**1**) at 200 mV s^{-1}, at room temperature, synthesized from complex *cis*-[RuCl$_2$(bpy)$_2$]·2H$_2$O and 1,4 bis(trimethylsilyl)1,3-butadiyne.

The ΔE_p value for the two redox processes is 520 mV, clearly indicates a strong communication between the two ruthenium centers propagated throughout the orbitals of the -C≡C-C≡C-bridge. This reflects the extent of the delocalization between metal centers in the ground state. The important stabilization of the mixed-valence Ru(II)/Ru(III) state is shown by the large value of the comproportionation constant, K_C = 6.13 x 10^8. The one-dimensional- C$_4$- bridge acts as a molecular wire to convey the odd electron from one metal center to the other. The high value of ΔE_p = 720V, corresponding to a K_C = 1.60 x 10^{12}, reported for complex ([FeCp*(dppe)]-C≡C-C≡C-[FeCp*(dppe)])[11], shows that the delocalization, greatly favored by the - C$_x$- bridge, strongly depends on the electronic structure of the metal unit.

Figure 4 shows the cyclic voltammetric response for complex **1**, synthesized using bis(trimethylsilyl) acetylene as the ligand. The one irreversible oxidation peak observed at +2.02V vs Ag/AgCl was ascribed to the Ru(III)/Ru(IV) couple, the two quasi-reversible peaks at –1.42 and –1.62 V vs Ag/AgCl were assigned to the reduction of the bpy ligand and the two reversible peaks (i$_{pc}$/i$_{pa}$ = 1) at +0.354 and +0.874 V vs Ag/AgCl were ascribed to the dimer Ru(II)/Ru(III) couple that undergoes two successive one-electron oxidations (DE$_p$ = 520 mV) to yield the mono- and the dications, respectively.

The data on Table 1 and the electrochemical behavior presented in Figures 3 and 4 for compound **1** obtained from 1,4-bis(trimethylsilyl)1,3-butadiyne or bis(trimethylsilyl) acetylene are very similar. We therefore, suggest that these compounds are the same. As stated above, dimerization of the ligand may occur, owing of the mechanism of the

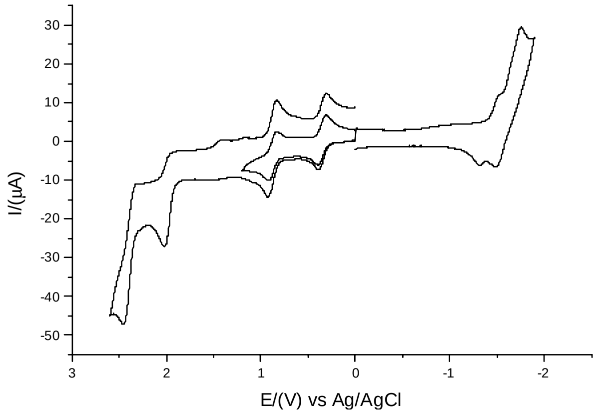

Figure 4. Cyclic voltammetric response for the complex [*cis*-{RuCl(bpy)$_2$](-C≡C-)}]$_2$ (**1**) at 200 mV s^{-1}, at room temperature, synthesized from complex *cis*-[RuCl$_2$(bpy)$_2$]·2H$_2$O and bis(trimethylsilyl) acetylene.

reaction and the temperature used, since the reaction does not occur at room temperature. Moreover, it was expected that the communication between the two metallic centers of dimer complexes having a bridged acetylenic linkage would be greater than that between metallic centers linked by a bridging butadiyne. Indeed, biferrocenyl derivatives bridged by acetylenic linkages Fc-C≡C-Fc and Fc-C≡C-C≡C-Fc have already been described and showed similar cyclic voltammograms with ΔE_p 130 and 100 mV, respectively[12,13]. Since ΔE values for the two compounds reported herein are the same, 520mV, these compounds should be the same.

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