

Mixed-valent Complexes of Rhodium with Acetylinic Ligands: Their Electrochemical Studies

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Abstract

Two acetylinic mixed-valent rhodium(II, III) complexes: $[\text{cis}\{-\text{Rh}_2(\text{II,III})\text{Cl}(\text{bpy})_2(\mu\text{-C}\equiv\text{C-})\}]_2$, (A) and $\text{cis}\{-\text{Rh}(\text{II,III})\text{Cl}(\text{bpy})_2\}\text{-C}\equiv\text{C-SiMe}_3$, (B) (where bpy = bipyridine) have been prepared. (A) was accomplished through two pathways. The two complexes were characterized by ^1H , ^{13}C NMR, elemental, magnetic, electrochemical analyses and mass spectrophotometry. Cyclic voltametric analyses of the products from 0.00 -1.20 V display two one-electron quasi-reversible oxidation peaks which were attributed to the Rh(II), Rh(III) couple. The redox processes were separated by 528 mV, indicating a significant electronic communication between the two metallic centres. The yields of (A) and (B) were found to be 37 and 32 % respectively.

Keywords: Acetylinic, Mixed-valent rhodium, Electrochemical, Cyclic voltametric analyses

1. Introduction

Several researchers have extensively investigated organometallic polymers whose metal centres are joined by organic ligands with delocalized π -systems (Rusjan, et al., 2004; Kellogg, et al., 2005; Phimpaka, et al., 2010; Eweis, et al., 2006). Such species are of interest due to their potential usefulness in the areas of electronics and material science. From an inorganic chemistry point of view, the main interest is related to the multiple metal bonds and paramagnetic ground states that characterized the species (Zing, et al., 2008). Organometallic polymers, with transition metals linked by a polynediyl ligand, $\text{M}-(\text{C}\equiv\text{C})_n\text{-M}$, have attracted increasing attention from various viewpoints (Serrano, et al., 1998; Estiu, et al., 1999; Fabiyi, et al., 2005).

The π -conjugated poly-carbon system is extended to the two terminal metal units.

Such systems are expected to display attractive properties resulting from π -conjugation along the rod-like linkage, stabilization of odd-electron (mixed-valent) species formed by hyper-polarizability, oxidation and reduction. Here we report the synthesis and characterization of complexes containing a bridging acetylinic ligand,

synthesized from the reactions of *cis*-[RhCl₂(bpy)₂] \cdot 2H₂O with 1,4-bis(trimethylsilyl)-1,3-butadiyne or bis(trimethylsilyl)acetylene and [RhCl₂(bpy)₂] \cdot 2H₂O with bis(trimethylsilyl)acetylene. The complexes have been characterized by ¹H, ¹³C NMR, MS and electrochemical analyses.

2. Experimental

Infrared spectra were recorded on a Beckman IR 4250 spectrophotometer. Samples were prepared as pressed pellets of KBr. ¹H and ¹³C spectra were obtained on a Bruker Model AC300/P spectrophotometer 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. Melting points (m. p.) were recorded on digital melting point apparatus WRS-IB and uncorrected. Mass spectra were measured with Finnigan trace DSQ spectrometer. 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. All measurements were carried out under dry argon, in anhydrous deoxygenated acetonitrile; solution were *ca.* 1 \times 10⁻³ mol \cdot dm⁻³ with respect to the compounds under study and *ca.* 0.1 mol \cdot dm⁻³ with respect to the supporting electrolyte, [Bu₄N][ClO₄].

A platinum disk working electrode, platinum wire auxiliary electrode and a saturated Ag/AgCl reference electrode were used in these experiments.

All chemical used were analytical reagent grade purchased from Aldrich and were used without further purification. Rhodium trichloride hydrate, 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), 1,4-bis(trimethylsilyl) 1,3-butadiyne, bis(trimethylsilyl)acetylene, trimethylsilylacetylene and acetonitrile-d₃ were 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*-[RhCl₂(bpy)₂] \cdot 2H₂O was prepared according to the published method (Abied, et al., 1978).

2.1 Preparation of Complexes: Synthesis of *cis*-[Rh₂(II,III)Cl(bpy)₂(-μ-C≡C-)]₂, (A)

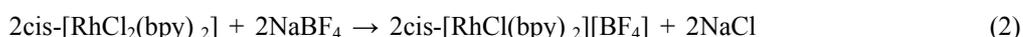
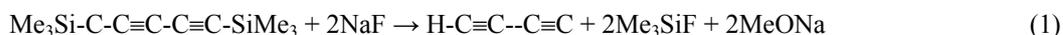
50.00 mL of a mixture (8:1) of MeOH/CH₂Cl₂, 8.00 mL of 0.33 mmol of NaBF₄, 5 mL of 0.6 mmol of NaF were all added to 0.35 g of *cis*-[RhCl₂(bpy)₂] \cdot 2H₂O in a conical flask. The content of the flask were emptied into another flask containing 15 mL of 0.18 mmol suspension of 1,4-bis(trimethyl)1,3-butadiyne (pathway A) or 10.00 ml of 0.20 mmol of bis(trimethylsilyl)acetylene (pathway B). The mixture was then thoroughly mixed and refluxed for about 48 hrs at a constant temperature of 62 °C on a heater fitted with magnetic stirrer. The solution was allowed to cool to room temperature (about 295 °K) and then filtered on a 4 fritte grade filter paper. The filtrate was allowed to evaporate under vacuum to about ¼ of the original volume in order to remove the solvent. The complex precipitated on the addition of about 6 mL diethyl ether. The precipitate was dissolved in CH₂Cl₂ and passed through an alumina plug to remove salts. Black crystals of the complex, (A) were obtained on addition of n-hexane. The crystals were then washed and re-crystallized from methanol, dried in desiccators over CaCl₂, then, in vacuum.

2.2 Synthesis of *cis*-[Rh₂Cl(bpy)₂]₂-C≡C-SiMe, B

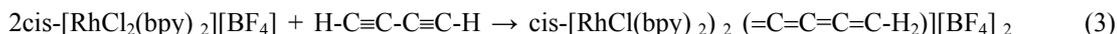
25 mL of 90% degassed acetone, 5 mL of 0.43 mmol of AgBF₄ and 5 mL of 0.40 mmol of solution of *cis*-[RhCl₂(bpy)₂] \cdot 2H₂O were mixed together in a flask and stirred magnetically for about 6 h under argon. The reaction mixture was then filtered through a 4 fritte grade filter paper and degassed by bleeding argon through the solution for 30 mins. Then 5 mL of 0.45 mmol of H-C≡C-SiMe₃ was added and the reaction mixture was heated at a constant temperature of 338 °K on a heater supplied with magnetic stirrer for 48 h. The resulting solution was filtered and the solvent removed by rotatory evaporator to a quarter of the original volume and precipitated with addition of diethylether. The crystals obtained were dissolved in CH₂Cl₂ and passed through an alumina to remove salts. The complex B was precipitated on addition of hexane. It was re-crystallized as in the case of A.

3. Results and Discussion

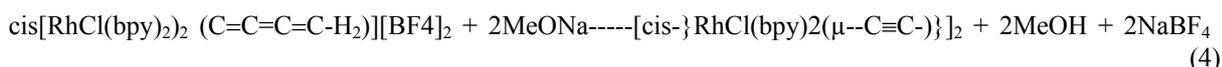
The yields, elemental analyses, molar conductivities and other parameters of the complexes are shown in Table 1. The proposed synthetic route of A is shown in equations (1-4). The 1, 4-butadiyne bridging ligand is generated *in situ* by the fluoride-induced⁶ cleavage of the terminal trimethylsilyl groups (equation 1).



As described,^{7,8} the BF_4^- anion acts as a halide abstractor (equation 2) to promote the complexation of the terminal alkyne at the rhodium center, giving the vinylidene complex isolated in many cases as the final product of the reaction (eq. 3).

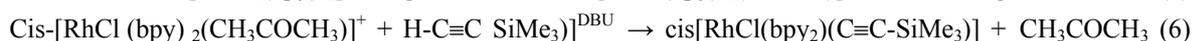
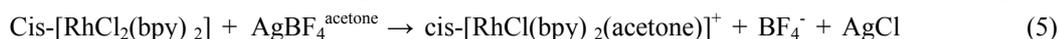


However, under these conditions, the cleavage of the trimethylsilyl group is associated with the formation of a stoichiometric amount of a strong base. This base *in situ* deprotonates the vinylidene intermediate, allowed the formation of the bis-(rhodium alkynyl) complex **1** as the final product of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



This is the first example reported so far of a di-ynediyl complex bearing the $\text{RhCl}(\text{bpy})_2$ fragment. Because of the complexity of the ^1H and ^{13}C spectra it is not possible to use it to characterize the complex. The absence of the absorption of the $-\text{C}\equiv\text{C}-$ 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 Rh(II)/Rh(III) , suggest that compound **A** is a dimer. Attempts to obtain $[\text{cis}\{-\text{Rh}_2\text{Cl}(\text{bpy})_2\}_2(\text{C}\equiv\text{C}-)]$ by reacting $\text{cis}[\text{RhCl}_2(\text{bpy})_2]_2 \cdot 2\text{H}_2\text{O}$ 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 **A** whose elemental analyses, ^1H 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 $[\text{cis}\{\text{Rh}_2\text{Cl}(\text{bpy})_2\}_2(\text{C}\equiv\text{C}-)]$ using other methods were unsuccessful.

Complex **B** was prepared by reaction of the free ligand, $\text{H}-\text{C}\equiv\text{C}-\text{SiMe}_3$ with $\text{cis}[\text{RhCl}(\text{bpy})_2(\text{CH}_3\text{COCH}_3)]^+$ (eq 5, 6)



The monoacetone complex is known to be a valuable synthetic intermediate (Tian, et al., 2005). The preparation of the monoacetone complex must be carefully timed (Banford, et al., 2002; Heinrich, et al., 2002; Fabiyi, et al., 2005). After short reaction times (< 2h), the complex is not completely formed, the limiting factor being the rate of dissolution of $\text{cis}[\text{RhCl}_2(\text{bpy})_2]_2 \cdot 2\text{H}_2\text{O}$ in acetone. After long reaction times (> 2h), a dark, red-brown precipitate begins to form. Isolation of this complex showed it to be identical with dimer $\text{cis}[\text{RhCl}(\text{bpy})_2]_2[\text{BF}_4]_2$ as revealed by cyclic voltametry. Isolation of complex **B** was achieved by precipitation from an acetone solution by adding diethyl ether, after filtration through an alumina plug to remove salts.

The characteristic IR bands of the complexes are listed in Table 2. The assignments of the spectra bands have been carried out with references to related studies (Banford, et al., 2002; Kahn, et al., 1975).

The ^1H NMR spectrum of $[\text{Rh}_2\text{Cl}_2(\text{bipy})_2]$, in ($\text{DMSO}-d_6$) has been discussed in the literature and shown to be more complex than expected for the *cis* or *trans* configurations (Kellogg, et al., 2005; Heinrich, et al., 2002). The reason for the complexity of the spectrum is that a mixture of *cis* and *trans* compounds were present in solution, with possible solvent interaction (Fabiyi, et al., 2005; Hench, et al., 1984). 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 ^1H NMR spectrum assigned to the aromatic hydrogens of bipyridine. In fact, complexes **A** and **B** showed a more complicated pattern of ^1H and ^{13}C NMR spectra in the aromatic region, which would be expected for a *cis* or *trans* compounds.

The ^{13}C NMR spectra of the complexes studied are similar in the aromatic region and display five sets of resonances, concentrated at δ : 160.4-158.6, 154.3-149.5, 139.0-136.9, 127.2-126.7 and 123.7-122.7. 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 $\text{Rh}-\text{C}\equiv\text{C}-$ carbons are masked by the signals of pyridyl carbons. The mass spectrum for **A** shows sets of peaks at m/z 102, 921, 993, 1017.5 and the maximum 1053.5. There are many peaks just below the expected masses of the parent ion, $m/z = 1053.5$. The presence of lower-mass peaks suggests that fragmentation occurred. They are dominated by single intense peaks but accompanied by a number of weaker ones. The separation between each set can be explained as follows: 1053.5-1017.5 = 35.5, 1053.5-921, 1053-993, 1053.5-983 and 1053.5-206 are attributed to losses of Cl^- , 2 bipyrimidyl ions, acetylinic ligand and 2 Rh ions respectively. For compound **B** the following m/z were observed: 567, 552, 537, 501.5, 470, and 273, 206, and 103. These correspond to losses of Me, 2 Me, $-\text{C}\equiv\text{C}-\text{SiMe}$, Cl^- , 2 bipyridyl, 2 Rh, and one Rh ions respectively.

Cyclic voltammetric analysis of $[\text{cis-}\{\text{RhCl}(\text{bpy})_2(-\text{C}\equiv\text{C}-)\}_2]$ and $\text{cis-}[\text{RhCl}(\text{bpy})_2]-\text{C}\equiv\text{C}-\text{SiMe}_3$.

The results of cyclic voltammetry experiments in CH_3CN solution for the compounds **A** and **B** and the starting complex $\text{cis-}[\text{Ru}_2\text{Cl}_2(\text{bpy})_2]$ are given in Table 3. The results of the cyclic voltammetric experiments on $\text{cis-}[\text{Rh}_2\text{Cl}_2(\text{bpy})_2]$ in CH_3CN at room temperature are shown in Figure 1. This compound exhibited two quasi-reversible oxidation peaks at $E_{1/2} + 2.07$ and $+0.410$ V 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 Rh(III)/Rh(IV) and Rh(II)/Rh(III) couples, respectively. The two reduction peaks at -1.48 and -1.61 V were ascribed to the bpy ligand. These results are consistent with the previous study on similar complex (Rusjan, et al., 2005; Kahn, et al., 1975; Carraher, et al., 1985). The same electrochemical behavior was shown by compound **B** (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 Rh(III)/Rh(IV) and Rh(II)/Rh(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 3 shows that the potential of the Rh(II)/Rh(III) couple in complex $\text{cis-}[\text{RhCl}_2(\text{bpy})_2]$ and **B** is the same as in compound **A**, which implies that the Rh(II) orbital energy is unchanged in the complex **B** when of the substitution of the trimethyl(silyl) acetylide by one chloride on $\text{cis-}[\text{RhCl}_2(\text{bpy})_2]$ complex. The cyclic voltammetric response for dimeric complex (**A**) is shown in Figure 3. This complex displays one irreversible oxidation peak at $+2.05$ V vs Ag/AgCl, ascribed to the Rh(III)/Rh(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 Rh(II)/Rh(III) couple.

This means that the neutral dimer undergoes two successive one-electron oxidations to yield the mono- and the di-cations, respectively (eq 7).



The ΔE_p value for the two redox processes is 528 mV, clearly indicates a strong communication between the two rhodium centers propagated throughout the orbitals of the $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ bridge. This reflects the extent of the delocalization between metal centers in the ground state. The important stabilization of the mixed-valence Rh(II)/Rh(III) state is shown by the large value of the comproportionation constant, $K_C = 6.13 \times 10^8$. The one-dimensional $-\text{C}_4-$ bridge acts as a molecular wire to convey the odd electron from one metal center to the other. Figure 4 shows the cyclic voltammetric response for complex **A**, synthesized using bis(trimethylsilyl) acetylene as the ligand. The one irreversible oxidation peak observed at $+2.02$ V vs Ag/AgCl was ascribed to the Rh(III)/Rh(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 Rh(II)/Rh(III) couple that undergoes two successive one-electron oxidations ($\Delta E_p = 520$ mV) to yield the mono- and the di-cations, respectively.

The data on Table III and the electrochemical behavior presented in Figures 3 and 4 for compound **A** 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 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. Since ΔE_p values for the two compounds reported herein are the same, 520mV, these compounds should be the same.

Hence two new complexes of rhodium with bridging acetylinic ligands have been successfully prepared and characterized. Possibilities of their mesomorphic properties are being studied.

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Table 1. Physical properties and elemental analyses of complexes

Empirical Formula (Formula Weight)	Analysis % Found (Calculated)							
	Colour	Yield (%)	M.Pt(°C)	N	C	H	μ_{eff} (B.M.)	Λ_{max} ($\Omega^{-1} \text{ cm}^2 \text{ Mol}^{-1}$)
$\text{C}_{34}\text{H}_{33}\text{N}_4\text{Cl}_2\text{Rh}_2$ (1053.04)	black	37.33	267-9	11.87(11.91)	55.87(55.86)	3.34(3.36)	4.4	7.4
$\text{C}_{16}\text{H}_{22}\text{N}_4\text{Rh}_2\text{ClSi}$ (567)	black	32.65	259-61	10.36(10.26)	54.58(54.55)	4.59(4.61)	3.66.3	7.4

Table 2. Selected infrared bands (cm^{-1}) of the complexes ^b

Compound	$\nu(\text{C}=\text{C})$	$\nu\text{C}=\text{Ar}$	$\nu(\text{Rh}-\text{C})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{Rh}-\text{N})$	$\nu(\text{Si}-\text{C})$	$\nu(\text{C}-\text{H})$
$\text{C}_{34}\text{H}_{33}\text{N}_4\text{Cl}_2\text{Rh}_2$	3117 m	1596 m	726 s	1634 m	1675 s	676 s	-	2955 m
$\text{C}_{16}\text{H}_{22}\text{N}_4\text{Rh}_2\text{ClSi}$	1973 m	3115 s	728 s	1629 s	1673 m	674 s	701 m	2952 s

^bs = strong, m = medium, s = sharp, br = broad.

Table 3. Cyclic voltammetry results for complexes (A) and (B) and $\text{RhCl}_2(\text{bpy})_2$

Complex	^a $E_{1/2}(\text{V})$	^b Kc
A ^c	+ 2.47 ^e , +2.05 ^e , 0.870	6.14×10^8
	+ 0.349, -1.40, -1.63	
A ^d	+ 2.45 ^e , +2.02 ^e , +0.874	6.14×10^8
	0.350, -1.41, -1.62	
B	+ 1.53, +0.412, -1.24 ^e	
	- 1.39, -1.56	
[$\text{RhCl}_2(\text{bpy})_2$]	+ 2.06 ^e , +0.411	
	-1.48, -1.63	

^aIn CH_3CN solution at 293 °K, 200mV s^{-1} . $E_{1/2}$ values were obtained from the average of the anodic and cathodic peak potentials ^b $L_n Kc = (n_1 E_1^0 - n_2 E_2^0) F/RT$ with $n_1 = n_2 = 1$.

^csynthesized complex from pathway A. ^dsynthesized complex from pathway B and

^eirreversible peaks.

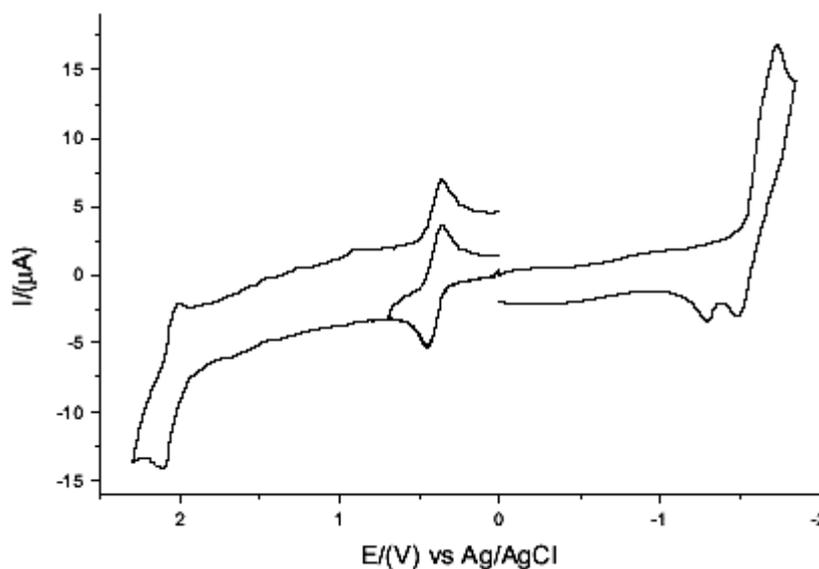


Figure 1. Cyclic voltammetric response for complex A at 200mV s^{-1} , at room temperature (two scans)

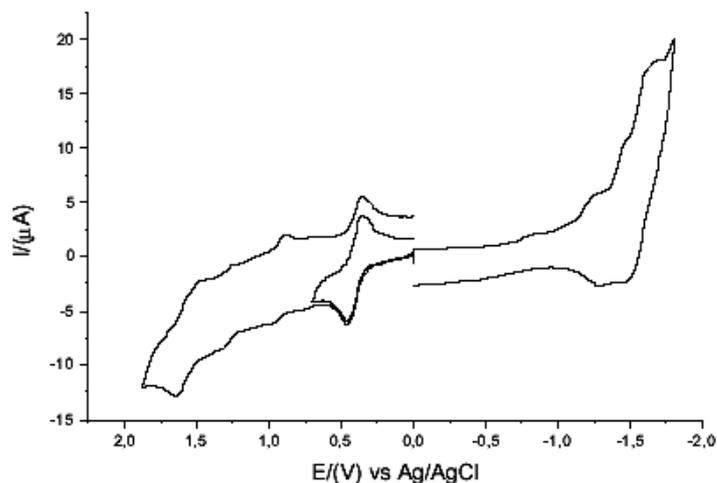


Figure 2. Cyclic voltammetric response for complex **B** at 200 mV s^{-1} , at room temperature (two scans)

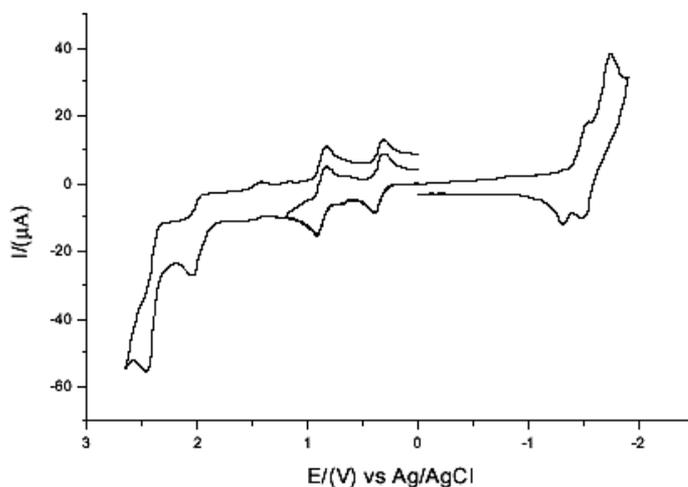


Figure 3. Cyclic voltammetric response for the A at 200 mV s^{-1} , at room temperature, synthesized form complex $\text{cis-}[\text{RuCl}(\text{bpy})_2]\cdot 2\text{H}_2\text{O}$ and 1, 4-bis(trimethyl-silyl) 1,3-butadiyne (two scans)

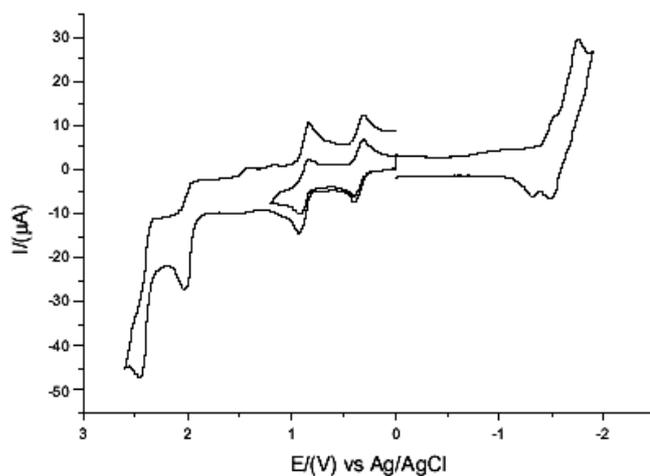


Figure 4. Cyclic voltammetric response for the A at 200 mV s^{-1} , at room temperature, synthesized form complex $\text{cis-}[\text{RuCl}(\text{bpy})_2]\cdot 2\text{H}_2\text{O}$ and bis(trimethylsilyl)acetylene (two scans).