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

The bis(ruthenium)alkyne complex $\text{cis-}[\text{RuCl(bpy)}_2(\mu-\text{C}≡\text{C})]_2$ (I) was obtained by treatment of 1 equiv of either 1,4-bis(trimethylsilyl)-1,3-butadiyne or bis(trimethylsilyl)acetylene with 2 equiv of the complex $\text{cis-}[\text{RuCl}_2(\text{bpy})_2]2\text{H}_2\text{O}$, NaF and NaBF$_4$ salts in methanol/CH$_2$Cl$_2$ mixture (10/1) in 52% and 35% yields, respectively. $\text{H}$, $\text{C}[\text{H}]$ NMR and principally electrochemical analyses confirmed that the same product was obtained from the two reactions. Cyclic voltammetric analyses of (I) 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 $\pi$-systems have been investigated extensively over the last several years. Such species are of interest due to their potential usefulness in the areas of electronics and materials science. Organometallic polymers, with transition metals linked by a polyynediyl ligand, M-(C≡C)$_n$-M, have attracted increasing attention from various viewpoints. The $\pi$-conjugated polycarbon system is extended to the two terminal metal units and such systems are expected to display attractive properties resulting from i) $\pi$-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-diyd ligand, is known to have a rigid, rodlike structure and exhibits unusual properties both in solution and in the solid state. Here we report the synthesis and characterization of a complex containing the $\eta^2(\sigma, \sigma)$-1,3-butadiyne-1,4-diyd ligand, synthesized from the reactions of $\text{cis-}[\text{RuCl}_2(\text{bpy})_2]2\text{H}_2\text{O}$ (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 $\text{cis-}[\text{RuCl}_2(\text{bpy})_2]2\text{H}_2\text{O}$ was prepared according to the published method.

Infrared spectra were recorded on a Bomem FTIR spectrophotometer. $\text{H}$ and $\text{C}[\text{H}]$ 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. 1x10^{-3} mol dm^{-3} with respect to the compounds under study and ca. 1x10^{-4} mol dm^{-3} with respect to the supporting electrolyte, [Bu₄N][ClO₄]. 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]₂ (1)

A modification of the existing procedure 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), NaBF₄ (0.052 g, 0.48 mmol) and NaF (0.020 g, 0.48 mmol) in 50 cm³ of a MeOH/CH₂Cl₂ mixture (10:1), cis-[RuCl₂(bpy)₂]₂H₂O (0.19 g, 0.36 mmol) was added as a solid. The mixture was heated at 45°C overnight. The solution was filtered through a filter paper by gravity and degassed by bleeding argon through a three-electrode cell was designed to allow the tip of the reference electrode to closely approach the working electrode. Results and Discussion

Syntheses of complex [cis-[RuCl(bpy)₂(μ-C≡C-)]²]₂ (1)

Treatment of 1 equiv of 1,4-bis(trimethylsilyl)-1,3-butadiyne with 2 equiv of the cis-[RuCl₂(bpy)₂]²H₂O in a methanol/CH₂Cl₂ mixture (10:1) in the presence of NaF and NaBF₄ salts produced, after heating overnight at 45°C, a red-purple solution. The bis(ruthenium) alkylene complex I [cis-[RuCl(bpy)₂(μ-C≡C-)]₁] (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).

Me₃Si-C≡C≡C-SiMe₃ + 2NaF → H-C≡C≡C-H + 2Me₃Si-F + 2MeONa (1)

As described, the BF₄⁻ anion acts as a halide abstractor (eq 2) to promote the complexation of the terminal alkylene at the ruthenium center, giving the vinylidene complex isolated in many cases as the final product of the reaction (eq 3).

2 cis-[RuCl₂(bpy)₂]²BF₄⁻ + H-C≡C-C≡C-H → cis-[RuCl(bpy)₂]²(C≡C=C≡C=CH₂)[BF₄]₂ (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 I as the final product of the reaction (eq 4).

[cis-[RuCl(bpy)₂]²(C≡C=C≡C=CH₂)][BF₄]₂ + 2MeONa → cis-[RuCl(bpy)₂(μ-C≡C-)]² + 2MeOH + 2NaBF₄ (4)

To our knowledge, this is the first example reported so far of a diyne-diyne complex bearing the RuCl(bpy)₂ fragment. Because of the complexity of the H¹ and ¹³C 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 \([\text{cis-}[\text{RuCl}(_2\text{(bpy)}_2)]_2\mu-[\text{C}_2\text{SiMe}_3]}\) by reacting \([\text{cis-}[\text{RuCl}(_2\text{(bpy)}_2)]_2\text{H}_2\text{O}\) 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 1 whose elemental analyses, \(^1\text{H}\) NMR and \(^{13}\text{C}\{^1\text{H}\}\) NMR data are very close to that of complex 1. The \(^1\text{H}\) NMR and \(^{13}\text{C}\{^1\text{H}\}\) NMR spectra of the complexes studied are similar in the aromatic region and display five sets of resonances, concentrated at \(\delta 160.4 - 158.2\), \(155.2 - 149.5\), \(139.0 - 136.9\), \(127.6 - 126.7\) 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 \(^{13}\text{C}\) NMR signals of the Ru-C carbons are masked by the signals of pyridyl carbons.

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

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>(E_{pa}^{1/2})</th>
<th>(E_{pc}^{1/2})</th>
<th>(K^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{RuCl}(_2\text{(bpy)}_2)]_2)</td>
<td>+2.46$^{a, b}$</td>
<td>+2.02$^{b}$</td>
<td>+0.874</td>
</tr>
<tr>
<td>([\text{RuCl}(_2\text{(bpy)}_2)]_2\text{C}_2\text{SiMe}_3)</td>
<td>+2.46$^{a, b}$</td>
<td>+0.354, +1.42, +1.62</td>
<td></td>
</tr>
<tr>
<td>([\text{cis-}<a href="m-%5Ctext%7BC%7D_2%5Ctext%7BSiMe%7D_3">\text{RuCl}(_2\text{(bpy)}_2)</a>]_2)</td>
<td>+0.351, +1.42, +1.61</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) In CH$_3$CN solution at room temperature, 200 mV s$^{-1}$. \(E_{pa}^{1/2}\) values were calculated from the average of the anodic and cathodic peak potentials, \(E_{pa}^{1/2}=(E_{pa}+E_{pc})/2\). $^{b}$ Irreversible peak. \(K^e\) values were calculated from the average of the anodic and cathodic peak potentials, \(K^e=(E_{pa}-E_{pc})/2\).

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

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

This compound exhibited two quasi-reversible oxidation peaks at \(E_{pa}^{1/2}+2.07\) and +0.410 V vs Ag/AgCl and two quasi-reversible reduction peaks at \(E_{pc}^{1/2}-1.48\) 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 -1.61 V were ascribed to the bpy ligand. These results are consistent with the previous study on this complex. The same electrochemical behavior was shown by compound 2 (see Figure 2). This compound shows two quasi-reversible oxidation peaks at \(E_{pa}^{1/2}+1.53\) 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-[RuCl₂(bpy)₂] and 2 is the same as in compound 1, which implies that the Ru(II) orbital energy is unchanged in the complex when of the substitution of the trimethyl(silyl) acetylide by one chloride on cis-[RuCl₂(bpy)₂] complex.

\[
\text{Ru(II)-Ru(II)} \rightleftharpoons \text{[Ru(II)-R(III)]}^+ \rightleftharpoons \text{[Ru(III)-Ru(III)]}^{2+} \quad (7)
\]

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, \(K_C = 6.13 \times 10^8\). The one-dimensional- C≡C- bridge acts as a molecular wire to convey the odd electron from one metal center to the other. The high value of \(\Delta E_p = 720\) V, corresponding to a \(K_C = 1.60 \times 10^{12}\), reported for complex \([\text{FeCp}*(\text{dppe})-\text{C≡C-C≡C-}[\text{FeCp}*(\text{dppe})])\]¹, shows that the delocalization, greatly favored by the -C≡C- bridge, strongly depends on the electronic structure of the metal unit.

The data on Table 1 and the electrochemical behavior presented in Figures 3 and 4 for compound 1 obtained from 1,4-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 3. Cyclic voltammetric response for the complex \([\text{cis}-\{\text{RuCl(bpy)}_2\}_{1,4}(\text{C≡C-})_2]\) at 200 mV s⁻¹, at room temperature, synthesized from complex cis-[RuCl₂(bpy)₂] 2H₂O and 1,4 bis(trimethylsilyl)1,3-butadiyne.

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 +2.02 V 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 (\(i_{pa}/i_{pa} = 1\)) 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.
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 \( \text{Fc-C}≡\text{C-Fc} \) and \( \text{Fc-C}≡\text{C}≡\text{C-Fc} \) have already been described and showed similar cyclic voltammograms with \( \Delta E_p \) 130 and 100 mV, respectively\(^{12,13}\). Since \( \Delta E \) values for the two compounds reported herein are the same, 520 mV, these compounds should be the same.

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References


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