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Selective formation of *trans* and *cis*(CH_3CN) isomers of $[Ru(bpy)(CO)_2(CH_3CN)_2]^{2+}$ (bpy = 2,2′-bipyridine) from $[Ru(CO)_2(CH_3CN)_3]_2(PF_6)_2$ using an electrochemical oxidation step

Garth Cripps [a], Aymeric Pellissier [a], Sylvie Chardon-Noblat [a,*], Alain Deronzier [a,*], Raymond J. Haines [b]

[a] *Laboratoire d'Electrochimie Organique et de Photochimie Rédox, UMR CNRS 5630, Institut de Chimie Moléculaire de Grenoble FR 2607, Université Joseph Fourier, Grenoble 1, BP 53, 38041 Grenoble cedex 9, France*
[b] *Department of Chemistry, University of Natal, Private Bag X01, Scottsville, Pietermaritzburg 3209, South Africa*

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Abstract

The selective in situ synthesis of *trans* and *cis*(CH_3CN)-$[Ru(bpy)(CO)_2(CH_3CN)_2]^{2+}$ isomers from the same $[Ru(CO)_2(CH_3CN)_3]_2^{2+}$ dimer precursor but using either an electrochemical–chemical or chemical–electrochemical process is described.

Keywords: Ruthenium complexes; Carbonyl compounds; Electrosynthesis; Electrochemical oxidation

1. Introduction

Carbonyl–ruthenium(II) mono bipyridine complexes provide excellent catalysts and catalyst precursors for processes such as the reduction of CO_2 or the water gas shift reaction [1–4]. They are also versatile building blocks for making organometallic-based nanostructures such as one-dimensional Ru-wire polymeric materials e.g. $[Ru(bpy)(CO)_2]_n$ (bpy = 2,2′-bipyridine) [5]. Among these, $[Ru(bpy)(CO)_2Cl_2]$ is the main precursor complex studied and several methods for its preparation have been reported [6–11]. These are in general complicated and poorly selective, for example, a mixture of *trans* and *cis*(Cl) isomers is obtained with other by-products. $[Ru(bpy)(CO)_2(CH_3CN)_2]^{2+}$ presents an interesting alternative precursor for the preparation of metal–metal bonded polymers having selective catalytic properties towards CO_2 electroreduction [12]. The common route for its synthesis is also complicated as it involves $[Ru(bpy)(CO)_2Cl_2]$ as a starting material. Furthermore, only the *trans*(CH_3CN) equivalent complex has been described and characterized [8], the synthesis of the *cis* isomer from *cis*(Cl)-$[Ru(bpy)(CO)_2Cl_2]$ having failed [13]. However, we recently reported that electrochemical oxidation of the Ru(I) dimer [Ru (bpy) $(CO)_2$ $(CH_3CN)]_2^{2+}$ leads mainly to *cis*(CH_3CN) - [Ru (bpy) $(CO)_2$ $(CH_3CN)_2]^{2+}$ [13].

We have extended this previous work and in this paper report selective methods to produce *cis* or *trans* (CH_3CN)-$[Ru(bpy)(CO)_2(CH_3CN)_2]^{2+}$. These methods are based on a readily available binuclear ruthenium complex $[Ru(CO)_2(CH_3CN)_3]_2(PF_6)_2$ [14]. We found that the addition of the bpy ligand to an acetonitrile solution of this compound followed by electrochemical oxidation leads quantitatively to the *cis* isomer (Scheme 1, pathway A), while the electrochemical oxidation of $[Ru(CO)_2(CH_3CN)_3]_2(PF_6)_2$ in an acetonitrile solution followed by the addition of the bpy ligand leads to the formation of the *trans*(CH_3CN) isomer of $[Ru(bpy)(CO)_2(CH_3CN)_2]^{2+}$ (Scheme 1, pathway B). Attempts to replace the electrochemical oxidation by a chemical

* Corresponding authors. Fax: +33-(0)4-76-51-42-67.
E-mail address: sylvie.chardon@ujf-grenoble.fr (S. Chardon-Noblat).

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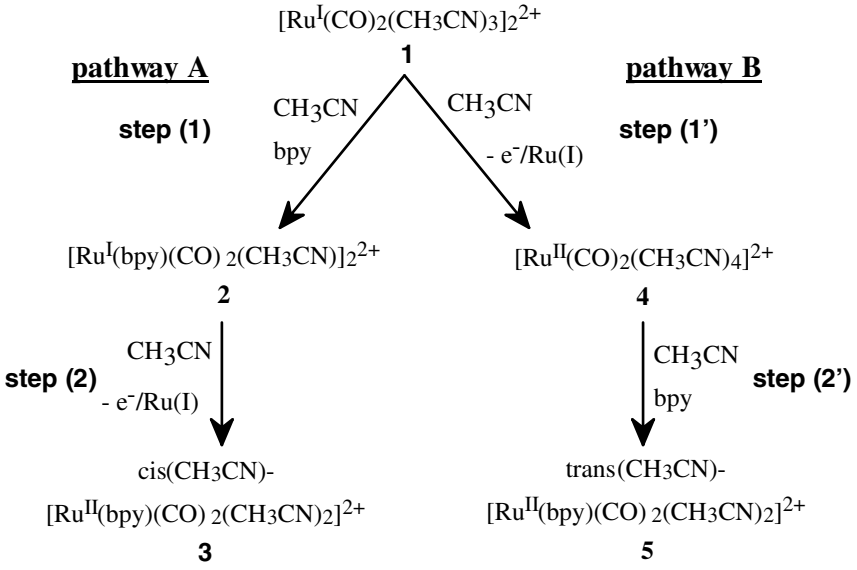

Scheme 1.

oxidation, show that only the *trans* isomer can be obtained with a good yield.

2. Results and discussion

The stable mononuclear isomers *cis* and *trans* (CH_3CN)-$[Ru(bpy)(CO)_2(CH_3CN)_2]^{2+}$ have been independently and selectively synthesized in situ from the dimer $[Ru(CO)_2(CH_3CN)_3]_2^{2+}$ (**1**) as described below.

2.1. In situ synthesis of cis(CH3CN)-[Ru(bpy)(CO)2(CH3CN)2]2+(3): pathway A

The mild experimental conditions of the synthesis of *trans*(CH_3CN)-$[Ru(bpy)(CO)_2(CH_3CN)]_2^{2+}$(**2**) [13] allowed the coordination of bpy to **1** (step (1); Scheme 1) to be followed by IR and ^1H NMR spectroscopies and cyclic voltammetry. For these experiments, monitored directly in the electrochemical cell, reagents were used in the same proportions as published [13], but at lower concentrations (ca. 1 mM). Under these experimental conditions, the coordination of the bpy was quantitative after 30 min stirring of the reaction solution.

On a Pt electrode, **1** in CH_3CN + 0.1 M TBAP is irreversibly oxidized at 1.22 V [1] and irreversibly reduced at −1.64 V (Fig. 1(a)). The addition of bpy to the electrolyte solution leads to a solution that shows a CV (Fig. 1(b)), which mirrors that of an original sample of **2** [13]. An irreversible oxidation is now seen at 1.04 V,

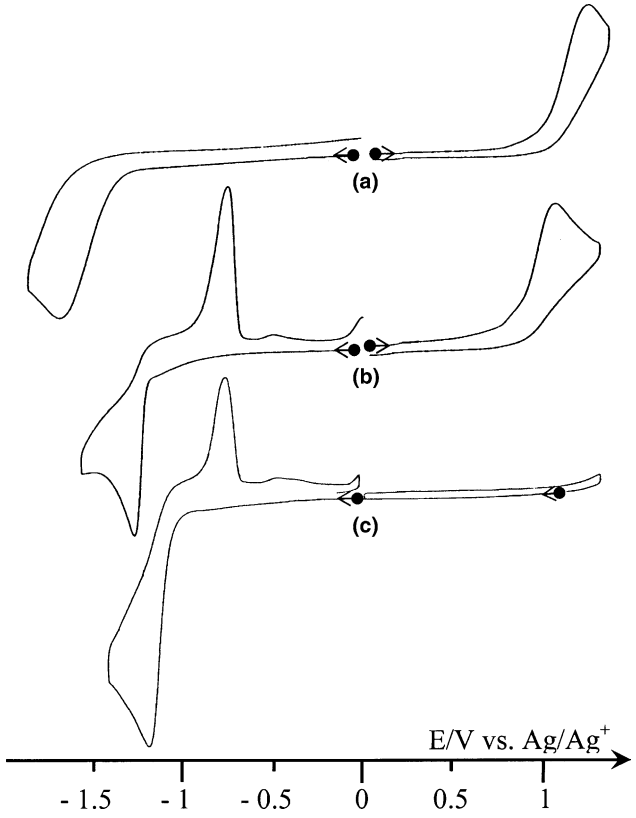

Fig. 1. CVs of **1** 1 mM in CH_3CN + 0.1 M TBAP at a Pt electrode (diam. 5 mm), $\upsilon = 100$ mV s^{-1}; (a) initial solution; (b) 30 min after addition of 2.4 M equivalents of bpy; (c) after exhaustive oxidation at 1.10 V.

while in the cathodic region of the CV an irreversible reduction at −1.24 V, with a corresponding anodic return peak at −0.74 V are evident. As expected, $[Ru(bpy)(CO)_2]_n$ polymer films can be electrosynthesized from

[1] All potentials are referenced to $Ag/AgNO_3$ 10 mM in CH_3CN containing 0.1 M TBAP and are determined by CV on a Pt electrode (diam. 5 mm) at 100 mV s^{-1}.

this solution of **2** prepared in situ, by repetitive scanning of the electrode potential between −0.9 and −1.8 V.

The IR spectrum of the Ru(I) precursor **1** recorded in situ displays in the terminal CO stretching region two strong absorption bands at 2006 and 1961 cm^{-1}, the latter being associated with a shoulder, and a weak absorption at 2031 cm^{-1}. The IR spectrum of this solution is modified by the addition of two equivalents of bpy and corresponds to that of an authentic sample of **2** (ν(CO) = 2021 (s), 1985 (sh), 1978 (w), 1944 (s) and 1927 (sh)). Likewise, the ^1H NMR spectra recorded in CD_3CN + 0.1 M $LiClO_4$ during the complexation show the disappearance of the free aromatic proton bpy signals and the growth of those of **2**.

The extension of this successful in situ methodology to synthesize Ru(I)–Ru(I) bonded dimers with functionalized bpy ligands is currently under way. For example, experiments have already shown, that the reaction of **1** with N-pyrrole substituted bpy in electrolyte solution at r.t leads to the formation of corresponding dimers, exhibiting the same electrochemical properties as those of the chemically synthesized and fully characterized ones. Through this in situ approach, different Ru(I) dimer complexes may be prepared, allowing for the rapid assessment of their electrochemical and spectroscopic properties without the necessity of a complete work-up and purification needed in a classical chemical synthesis.

During step (2) of the synthetic process (Scheme 1), the electrochemical oxidation of **2** at 1.10 V, which requires the exchange of two moles of electrons per mole of **2**, results in the formation of a mononuclear Ru(II) complex *cis*(CH_3CN)-$[Ru(bpy)(CO)_2(CH_3CN)_2]^{2+}$ (**3**) with 80% faradaic yield. The configuration of the isomer was determined by ^1H NMR spectroscopy using a CD_3CN + $LiClO_4$ electrolyte during the electrochemical oxidation of **2**. The resonances of the bpy ligand protons change from four for the initial solution of **2**, to eight well resolved signals for **3**, each integrated for one proton. This pattern reflects a non-symmetrical arrangement of ligands about the Ru(II) and is furthermore typical of asymmetry in the equatorial plane of the bpy [11]. The CV of **3** (Fig. 1(c)), shows that this Ru(II) monomer is not electroactive between 0 and 1.30 V. However, **3** is irreversibly reduced at −1.18 V and leads, by repetitive potential scans or by applied potential electrolysis, to the formation of a $[Ru(bpy)(CO)_2]_n$ adherent film on the working electrode surface.

2.2. In situ synthesis of trans(CH_3CN)-[$Ru(bpy)(CO)_2(CH_3CN)_2]^{2+}$ (**5**): pathway B

In step (1′) (Scheme 1), the exhaustive oxidation of **1** at 1.30 V in CH_3CN + 0.1 M TBAP consumes 2 equivalents of electrons per mole of dimer. This oxidation leads to a solution which shows its CV a poorly resolved, irreversible reduction peak at −1.44 V (Fig. 2(b)), while no electroactivity is observed in the anodic region of the scan. The IR spectrum of this solution exhibits two major absorption bands at 2135 and 2091 cm^{-1} in the terminal CO stretching region. In comparison, the IR spectrum of **1** recorded in the same electrolyte shows four absorption bands. The coulometry of this exhaustive oxidation, the absence of any anodic electroactivity, the shift to higher wavenumbers of the ν(CO) and the simplification of the IR absorption envelope suggested that the electrochemical oxidation affords a Ru(II) monomer complex. The breakage of the metal–metal bond would be accompanied by the coordination of the acetonitrile solvent, giving the intermediate $[Ru(CO)_2(CH_3CN)_4]^{2+}$ **4**.

In step (2′) (Scheme 1), one equivalent of bpy was added to **4** (assuming 100% faradaic yield in step 1′). This reaction goes to completion after 15 h of stirring at r.t. The IR spectrum of the final solution shows two intense absorbances at 2116 and 2069 cm^{-1}. The CV of this solution displays a reduction peak at −1.24 V with a corresponding anodic peak at −0.86 V, while the anodic CV scan shows that the resulting complex is not oxidized within the electrolyte potential limits (Fig. 2(c)). The CV and the IR spectrum of the final complex match those of the pure Ru(II) mononuclear complex *trans*(CH_3CN)$[Ru(bpy)(CO)_2(CH_3CN)_2](PF_6)_2$ (**5**) chemically synthesized [8,12]. Moreover, the irreversible system corresponding to a Ru(II)/Ru(0) redox couple, is shifted negatively (−0.06 V) compared with **3** in keeping with

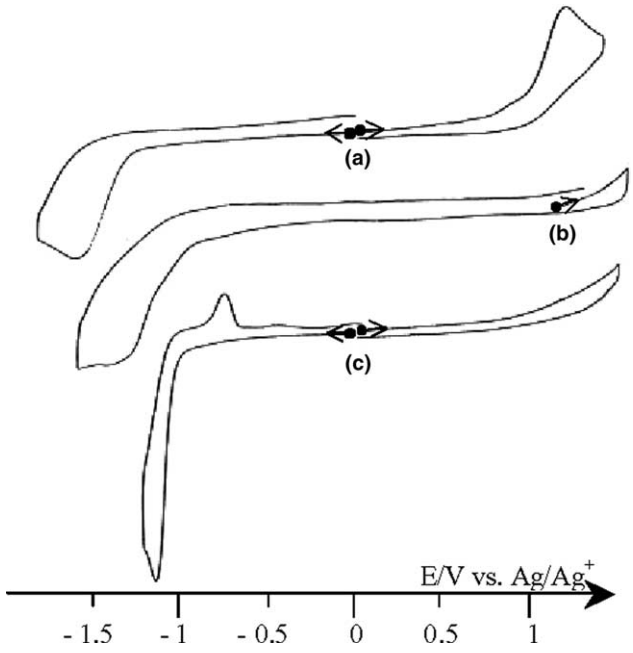

Fig. 2. CVs of **1** 1 mM in CH_3CN + 0.1 M TBAP at a Pt electrode (diam. 5 mm), υ = 100 mV s^{-1}; (a) initial solution; (b) after exhaustive oxidation at 1.30 V; (c) 15 h after addition of 1 equivalent of bpy per Ru(II) electrogenerated.

that observed between the two isomers of corresponding dichloro monomers [11]. Repetitive scanning of the electrode potential, in the range of −0.85 and −1.60 V, leads to the progressive formation of the expected Ru–Ru bonded polymer $[Ru(bpy)(CO)_2]_n$ [12].

The use of a $CD_3CN + LiClO_4$ electrolyte (pathway B) allowed for the ^1H NMR analysis confirmation of the final product and of the nature of the isomer. The spectrum of the final solution shows four aromatic proton signals due to the bpy ligand showing that the bpy ligand shares the equatorial plane with the two CO ligands.

These two in situ synthetic approaches (pathways A and B) are being extended to the synthesis of Ru(II) monomer complexes coordinated by functionalized bpy ligands.

2.3. Discussion

The origin of the difference of the stereoselectivity of the two synthetic pathways is actually unclear. However, we suggest that for pathway A, the oxidation of **2** (step (2)) may involve the formation of a bridging carbonyl dimer intermediate, implying a rearrangement of both Ru coordination spheres, instead of a direct Ru—Ru bond breaking. As a consequence, the *cis*(CH_3CN) isomer is preferably formed. For pathway B, the *trans* weakening effect of the CO in **4** could be the driving force for the replacement of CH_3CN, *trans* to CO ligands, by bpy leading to the *trans*(CH_3CN) **5** isomer.

2.4. Attempts at a purely chemical synthesis of 3 and 5

In addition, we have explored the replacement of the electrochemical steps ((2) and (1′)) by chemical oxidation using for example, $NOBF_4$ [15] or NO_2PF_6 [16]. This study has shown that only the *trans* isomer **5** can be prepared and isolated with a good yield (75%) (details are given in section 3). All attempts to chemically synthesize the *cis*(CH_3CN) isomer **3**, using either NO^+ an NO_2^+ as an oxidant, were unsuccessful. However it was possible to identify **3** in the final product mixture after workup by ^1H NMR, FT–IR and electrochemical characterizations. All these characterizations agree very well with those of the complex resulting from the in situ synthesis involving electrochemical oxidation (pathway A). The yield of this synthesis, estimated from the integrations of proton signals in the ^1H NMR spectrum, was 15%. The difference in the reactivity between both purely chemical ways may stem from the interaction between the oxidants and the aromatic bpy ligands in the dimer **2** (pathway A) [17].

3. Experimental details

NO_2PF_6 (Strem), 2,2′-bipyridine, $LiClO_4$ and TBAP (Fluka) and CH_3CN (Rathburn) were used without further purification. All other solvents were freshly distilled and dried using standard procedures [18]. Electrochemistry and synthesis were performed in a dry box (Jaram) under an inert atmosphere. The Ru(I)–Ru(I) carbonyl acetonitrile bonded dimer **1** was synthesized from the bis chloro-bridged binuclear complex $[Ru(CO)_3Cl_2]_2$ following a published procedure [14].

3.1. In situ IR and ^1H NMR characterization of complex (3)

^1H NMR (250 MHz, $CD_3CN + 0.1$ M $LiClO_4$): δ 8.95 (d, H_6), 8.80 (d, $H_{6'}$), 8.50 (m, $H_{3,3'}$), 8.40 (m, $H_{4,4'}$), 7.92 (t, H_5), 7.74 (t, $H_{5'}$). FT–IR ($CH_3CN + 0.1$ M $LiClO_4$, cm^{-1}): 2117 (s, C–O), 2063 (s, C–O).

3.2. In situ IR and ^1H NMR characterization of complex (5)

^1H NMR (250 MHz, CD_3CN+ 0.1 M $LiClO_4$): δ 8.81 (d, $2H_{66'}$), 8.48 (d, $2H_{33'}$), 8.38 (t, $2H_{44'}$), 7.85 (t, $2H_{55'}$). IR–TF ($CH_3CN + 0.1$ M $LiClO_4$, cm^{-1}): 2116 (s, C–O), 2069 (s, C–O).

3.3. Synthesis of complex (5)

$[Ru(CO)_2(CH_3CN)_3]_2(PF_6)_2$ (129 mg, 0.15 mmol) and NO_2PF_6 (65 mg, 0.34 mmol, 1.1 eq/Ru) were stirred in CH_3CN (20 mL) at r.t. for 1 h. The solvent was removed under vacuum and the residue (**4**: ν(CO) in CsI pellet = 2127(s) 2052 (s) cm^{-1}) dissolved in CH_3CN (10 mL). The bpy ligand (54 mg, 0.35 mmol) was added and the solution maintained at r.t. for 1.5 h. The volume was reduced to ca. 1 mL, an excess of Et_2O (ca. 60 mL) added and the solution stood at 0 °C for 10 min. The mixture was filtered, the precipitate washed with Et_2O (3×2 mL) and then dried under vacuum for 1 h to give an orange powder (180 mg, 75%). ^1H NMR (CH_3CN): see above. FT–IR (CsI, cm^{-1}): 2352 (m, C–N), 2337 (m, C–N), 2098 (s, C–O), 2043 (s, C–O), 842 (vs, P–F). ES^+ MS, mobile phase CH_3CN m/z 687, 646, and 317 with the calculated isotopic patterns for, respectively, $[M + H]^+$, $[M–CH_3CN + H]^+$ and $[M–CH_3CN–CO]^+$. Attempts to form X-ray quality crystals of **5** failed.

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