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Mode of formation of polymeric [$\{Ru(bipy)(CO)_2\}_n$] (bipy = 2,2′-bipyridine) films

Sylvie Chardon-Noblat,[a] Alain Deronzier,*[,a] Daniela Zsoldos, Raymond Ziessel,*[,b] Matti Haukka,[c] Tapani Pakkanen*[,c] and Tapani Venäläinen[c]

[a] *Laboratoire d'Electrochimie Organique et de Photochimie Rédox, URA CNRS 1210, Université Joseph Fourier Grenoble 1, BP 53, 38041 Grenoble Cédex 9, France*
[b] *Laboratoire de Chimie, d'Electronique et de Photonique Moléculaires, Ecole Européenne Chimie, Matériaux, Polymères de Strasbourg, UMR CNRS 46, 1 rue Blaise Pascal, BP 296F, 67008 Strasbourg Cedex, France*
[c] *Department of Chemistry, University of Joensuu, PO Box 111, FIN-80101 Joensuu, Finland*

Electrochemical generation of the organometallic polymer [$\{Ru^0(bipy)(CO)_2\}_n$] by reduction of [Ru^{II}(*trans*-Cl_2)(bipy)-$(CO)_2$] proceeded *via* the formation of the corresponding dimer [$\{Ru^I$(*trans*-Cl)(bipy)$(CO)_2\}_2$] and a tetrameric species; only dimers were formed by electroreduction of the [Ru^{II}(*cis*-Cl_2)(bipy)$(CO)_2$] isomer or [Ru^{II}Cl(bipy)$\{$*cis*-$(CO)_2\}$-(CO_2Me)].

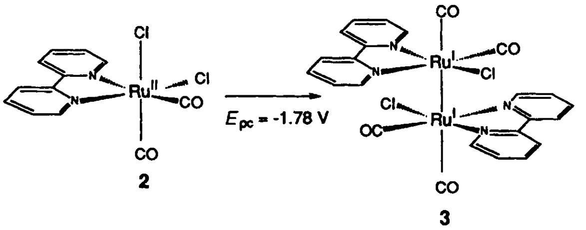
Carbon dioxide is an abundant substance of primary importance as a natural source of carbon and as a major atmospheric pollutant. Consequently, there has been an ever increasing number of studies concerned with thermal and electrolytic transformation of CO_2, supposedly into valuable C_1 and C_2 feedstocks.[1] Although highly attractive, electroreduction of CO_2 at solid metal electrodes involves several major problems, including large overpotentials, poor selectivity and limited stability of the electrodes.[2,3] Recently, a new type of modified electrode demonstrating outstanding catalytic activity for the reduction of CO_2 in aqueous media was introduced in an effort to overcome the above limitations.[4–6] These electrodes are highly selective for reduction of CO_2 and capable of extended usage. The active material is generated by electrolysis of monomeric ruthenium(II) complexes bearing two *trans* leaving groups (*e.g.* chloride anions) and adheres strongly to the electrode surface in the form of a blue film [equation (1)

$$n[Ru^{II}Cl_2(bipy)(CO)_2] + 2ne^- \longrightarrow [\{Ru^0(bipy)(CO)_2\}_n] + 2nCl^- \quad (1)$$

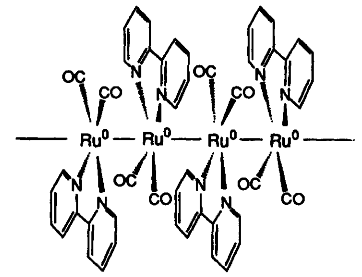
summarizes the overall process (bipy = 2,2′-bipyridine)]. The bulk material has been characterized and identified as an organometallic polymer consisting of [$Ru^0(bipy)(CO)_2$] repeating units. However, its mode of formation remains unknown. The polymer comprises an extended Ru–Ru backbone having a staggered arrangement somewhat similar to a [$\{Ru(CO)_4\}_n$] oligomer.[7,8]

We now describe the electrochemical behaviour of some potential precursors, in order to establish the mechanism involved in the electrochemical formation of [$\{Ru^0$(bipy)-$(CO)_2\}_n$] polymeric films. On the other hand since chemical treatment of the same catalyst precursors with strong bases has recently been shown to yield highly active catalyst systems for the water–gas shift reaction (WGSR),[9] the similarities of both catalytic systems will be discussed.

It has recently been shown that the mononuclear precursor [$Ru^{II}Cl_2(bipy)(CO)_2$] exists in two stereoisomeric forms having *trans*-(Cl)/*cis*-(CO) **1** and *cis*-(Cl)/*cis*-(CO) **2** configurations.[10,11] Interestingly, whereas electroreduction of the *trans* complex results in facile formation of the required polymeric film the corresponding *cis* isomer does not polymerize. Thus isomer **2** undergoes irreversible one-electron reduction (E_{pc} = −1.78 V) to form dimer **3** having a direct Ru^I–Ru^I bond resulting from the leaving of the axial chloro ligand (Scheme 1). This dimer has been isolated and characterized,† and undergoes a quasi-reversible one-electron reduction ($E_{\frac{1}{2}}$ = −1.94 V) but does not form a polymeric film [Fig. 1(*a*)]. Similarly the corresponding mononuclear complex **4** bearing an axial C(O)OMe group, known to be a poor leaving group, undergoes



Scheme 1



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† The dimers **3** and **5** were obtained by an exhaustive one electron reduction at −1.80 and −1.75 V respectively of a solution of 10^{-2} mol dm^{-3} of complexes **2** and **4** in MeCN + 0.1 mol dm^{-3} $[NBu^n{}_4]ClO_4$ at a platinum cylinder. After standing for one night in the glove box the resulting precipitate was filtered off, washed with a few cm^3 of MeCN and dried under vacuum (respective yields: 90 and 65%). The structures of the dimers were confirmed by spectroscopic and elemental analysis. [$\{RuCl(bipy)(CO)_2\}_2$]·MeCN **3** (Found: C, 42.00; H, 2.25; N, 9.35. Calc. for $C_{26}H_{19}Cl_2N_5O_4Ru_2$: C, 42.30; H, 2.60; N, 9.50%). Desorption chemical ionization mass spectrum (electron capture mode): 696 [*M* − H]. IR: (KBr pellet) ν_{CO} 1994.9, 1951.5, 1932.3, 1922.2 and 1901.8 cm^{-1}; (polyethylene pellet) ν_{Ru-Cl} 346 and ν_{Ru-Ru} 171 cm^{-1}. λ_{max}(MeCN) 472, 630 and 792 nm. [$\{Ru(bipy)(CO)_2$-$(CO_2Me)\}_2$]·MeCN **5** (Found: C, 45.70; H, 3.05; N, 8.65. Calc. for $C_{30}H_{25}N_5O_8Ru_2$: C, 45.90; H, 3.20; N, 8.90%). IR: (KBr pellet) ν_{CO} 1992.2, 1951.6, 1931.5, 1923.1 and 1902.5, ν_{CO_2Me} 1634.6 cm^{-1}; (polyethylene pellet) ν_{Ru-Ru} 170 cm^{-1}. λ_{max}(MeCN) 476, 626 and 790 nm.

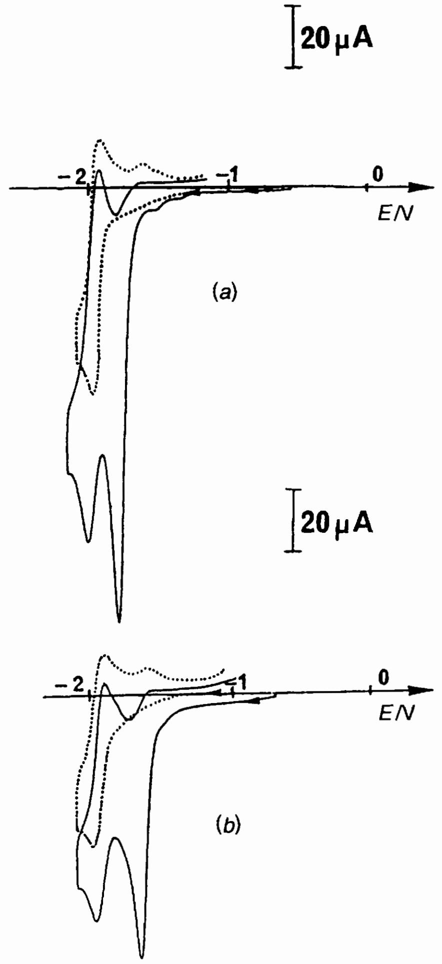
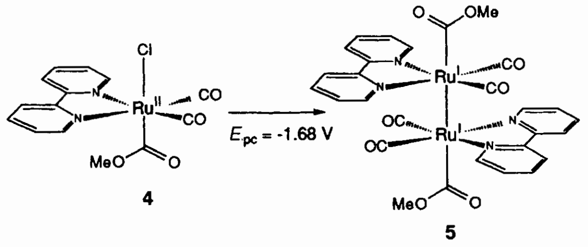


Fig. 1 Cyclic voltammograms of MeCN containing 0.1 mol dm^{-3} [NBu$^n_4$]ClO$_4$ under an argon atmosphere at a scan rate of 100 mV s^{-1} at a carbon electrode (19.6 mm^2) showing (——) initial and (· · ·) final solution after exhaustive electrolysis at −1.80 V; (*a*) 1.6 × 10^{-3} mol dm^{-3} solution of complex **2**; (*b*) 1.3 × 10^{-3} mol dm^{-3} solution of complex **4**



Scheme 2

one-electron electrochemical dimerization to form **5** which again contains a direct Ru^{I}–Ru^{I} bond (Scheme 2). This dimer, like **3**, was isolated and characterized, but does not polymerize and exhibits a quasi-reversible one-electron reduction at $E_{\frac{1}{2}}$ = −1.98 V [Fig. 1(*b*)].

In marked contrast is the electrochemical behaviour of [Ru^{II}(*trans*-Cl$_2$)(bipy)(CO)$_2$] **1** (Scheme 3). A polymeric [{Ru^0(bipy)(CO)$_2$}$_n$] film, with electrochemical and spectroscopic characteristics identical to those described previously,[4,5] is obtained by cycling the potential between −0.9 and −2.0 V or by potentiostatting the electrode at −1.60 V in dimethyl sulfoxide (dmso) electrolyte.† The first scan of the cyclic voltammogram exhibits an intense irreversible two-electron cathodic peak at −1.60 V associated with an anodic peak at −0.84 V, typical of an electrodeposition–redissolution phenomenon. Fig. 2(*a*) shows the growth of the electroactive film. Two distinct quasi-reversible peak systems appear ($E_{\frac{1}{2}}$ = −1.0 and −1.65 V; ΔE_p = 30 mV) whose size increases continuously. Similar electrochemistry persists after removal of the modified electrode and immersion in fresh electrolyte. The first system, associated with an intense anodic desorption peak at a less negative potential (not shown here), is attributed to the reoxidation of Ru^0 to Ru^{I}. The second reduction step corresponds to ligand reduction to the bipy$^{\bullet -}$ level.

Growth of [{Ru^0(bipy)(CO)$_2$}$_n$] films can also be accomplished from a solution of the chemically prepared dimeric [{Ru^{I}(*trans*-Cl$_2$)(bipy)(CO)$_2$}$_2$] complex **6**.[10] Fig. 2(*b*) shows evolution of the cyclic voltammogram by continuously cycling the potential between −0.9 and −2.0 V. The initial cathodic scan shows irreversible peaks at E_{pc} = −1.45 and −1.60 V (the first being associated with a shoulder at −1.36 V). If the cycling potential range is limited to −1.50 V, growth of the film is inefficient. Exhaustive electrolysis at E_p = −1.40 V, after consumption of one electron per mol of **6**, produces a red-brown solution (λ_{max} = 514, 714 and 835 nm). Although this compound was not isolated it is believed to be the soluble tetramer **7**. The resulting solution exhibits one irreversible peak at E_{pc} = −1.60 V and growth of the [{Ru^0(bipy)(CO)$_2$}$_n$] film is ensured by continuous cycling of the potential between −0.9 and −2.0 V (Fig. 2). Moreover, exhaustive electrolysis at −1.60 V of a solution of **6** or **7** leads to deposition of a deep blue, strongly adherent [{Ru^0(bipy)(CO)$_2$}$_n$] film on the working electrode, after exchange of two electrons per mol of complex. The reaction results in quantitative conversion into polymeric film upon exhaustive electrolyses.

These results clearly show that polymerization occurs directly upon reduction of **1** by an electrochemical propagation process [equations (2)–(4) and Scheme 3]. This is a consequence of the

$$[\mathrm{Ru^{II}Cl_2(bipy)(CO)_2}] + e^- \longrightarrow [\mathrm{Ru^{II}Cl_2(bipy^{\bullet -})(CO)_2}]^- \quad (2)$$

$$[\mathrm{Ru^{II}Cl_2(bipy^{\bullet -})(CO)_2}]^- \longrightarrow [\mathrm{Ru^{I}Cl(bipy)(CO)_2}] + \mathrm{Cl^-} \quad (3)$$

$$[\mathrm{Ru^{I}Cl(bipy)(CO)_2}] \longrightarrow \mathbf{6} \longrightarrow \mathbf{7} \longrightarrow \text{polymer} \quad (4)$$

easier or similar reducibility of dimer **6** and parent oligomer **7**. In terms of mechanism it means that the polymerization proceeds *via* the initial formation of an Ru^{I} species [equations (2) and (3)] which dimerizes into compound **6**, rather than a direct two-electron reduction of **1** into an Ru^0 species [equations (2), (3), (5) and (6)] followed by an aggregation

$$[\mathrm{Ru^{I}Cl(bipy)(CO)_2}] + e^- \longrightarrow [\mathrm{Ru^{I}Cl(bipy^{\bullet -})(CO)_2}]^- \quad (5)$$

$$[\mathrm{Ru^{I}Cl(bipy^{\bullet -})(CO)_2}]^- \longrightarrow [\mathrm{Ru^{0}(bipy)(CO)_2}] + \mathrm{Cl^-} \quad (6)$$

$$[\mathrm{Ru^{0}(bipy)(CO)_2}] \longrightarrow \text{polymer} \quad (7)$$

process [equation (7)].

A crucial point for the formation of the polymeric structure is a *trans* stereochemistry of the two leaving groups. The overall process is somewhat analogous to the well established formation of organic polymers by electroreduction of metallic complexes containing halogenated ligands,[12] but has never been applied so far to the generation of organometallic counterparts.

It has previously been shown that [Ru$_3$(CO)$_{12}$] and several monometallic ruthenium carbonyl complexes with 2,2′-bipyridine yield catalytically-active heterogeneous systems on solid supports.[9,13] Characteristic to these catalysts has been the formation of a deep blue, air-sensitive compound having high

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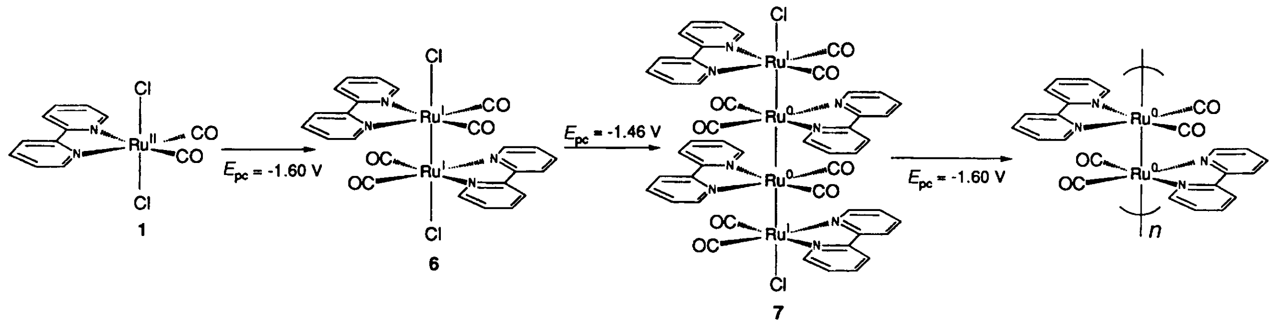
† Here electropolymerisation was accomplished in dmso instead of in MeCN since the dimer **6** is not soluble in the latter solvent.



Scheme 3

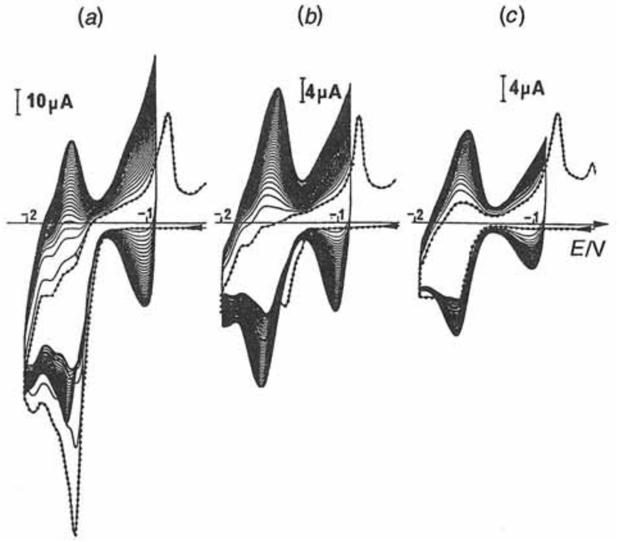


Fig. 2 Cyclic voltammograms of dmso containing 0.1 mol dm^{-3} [NBu$^n_4$]ClO$_4$ under an argon atmosphere at a scan rate of 100 mV s^{-1} at a platinum electrode (19.6 mm^2) showing in each case (–•–•–) initial sweep and (——) second to thirtieth successive scans between −0.9 and 2.0 V of (*a*) 2 × 10^{-3} mol dm^{-3} solution of complex **1**, (*b*) a 10^{-3} mol dm^{-3} solution of dimer **6**, (*c*) solution obtained by exhaustive reduction at −1.40 V of solution obtained in (*b*) (formally compound **7**)

activity in the WGSR and for hydroformylation of olefins.[14] The highest activity and selectivity have been found for a catalyst where the dimeric precursor [{Ru^I(*trans*-Cl)(bipy)(CO)$_2$}$_2$] **6** was treated with NaOH. The spectroscopic characterization of the catalyst prepared under these conditions exhibits IR spectra (ν_{CO} 1969.3, 1906.6 and 1882.8 cm^{-1}) superimposable on the spectra of electrochemically prepared polymers described herein. This observation indicates that the [{Ru^0(bipy)(CO)$_2$}$_n$] polymer can be prepared both electrochemically and chemically. It also rationalizes the activities of the catalyst in the electrochemical CO$_2$ reduction process and the WGSR process since these reactions are mechanistically related. The WGSR experiments conducted with the electropolymerized material are currently under investigation in order to confirm this point and will be reported in due course.

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