

Redox-Active Polymers Based on Nonbridged Metal–Metal Bonds. Electrochemical Formation of $[\text{Os}^{\text{II}}(\text{bpy})(\text{CO})(\text{L})]_n$ (bpy = 2,2'-bipyridine; L = CO, MeCN) and of Their Reduced Forms: A Spectroelectrochemical Study

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IR, UV–vis, and EPR spectroelectrochemistry at variable temperatures and in different solvents were applied to investigate in situ the formation of electroactive molecular chains with a nonbridged Os–Os backbone, in particular, the polymer $[\text{Os}^{\text{II}}(\text{bpy})(\text{CO})_2]_n$ (bpy = 2,2'-bipyridine), from a mononuclear Os(II) carbonyl precursor, $[\text{Os}^{\text{II}}(\text{bpy})(\text{CO})_2\text{Cl}_2]$. The one-electron-reduced form, $[\text{Os}^{\text{II}}(\text{bpy}^{\bullet-})(\text{CO})_2\text{Cl}_2]^-$, has been characterized spectroscopically at low temperatures. This radical anion is the key intermediate in the electrochemical propagation process responsible for the metal–metal bond formation. Unambiguous spectroscopic evidence has been gained also for the formation of $\{[\text{Os}^{\text{II}}(\text{bpy}^{\bullet-})(\text{CO})_2]^- \}_n$, the electron-rich electrocatalyst of CO_2 reduction. The polymer species are fairly well soluble in butyronitrile, which is important for their potential utilization in nanoscience, for example, as conducting molecular wires. We have also shown that complete solubility is accomplished for the monocarbonyl-acetonitrile derivative of the polymer, $[\text{Os}^{\text{II}}(\text{bpy})(\text{CO})(\text{MeCN})_2\text{Cl}]_n$.

Introduction

The strongly increasing demand for nanoscale molecular devices for electronic application has given rise to the renaissance of research in the area of low-dimensional molecular solids. Recently, some new one-dimensional (1D) systems have been explored. Among them, those based on linear chains of transition metal atoms appear to be very promising, in particular, those involving unsupported metal–metal interactions.¹ However, apart from oligomeric mixed-valence metal chains such as platinum blue derivatives, for example, mixed-valence tetranuclear platinum compounds

based on $[\text{Pt}_4(\text{NH}_3)_8(\text{C}_5\text{H}_6\text{NO})_4]^{4+}$ ($\text{C}_5\text{H}_6\text{NO} = \alpha$ -pyridone),² and some rhodium and iridium analogues,³ only very rare examples of infinite metal–metal-based chains have been reported so far. This kind of material is considered to be more promising as conducting molecular wires as compared to the short-chain oligomeric systems.¹ Thus far, only two different representatives, demonstrating the validity of this concept, have been introduced. The more recent type involves an infinite 1D mixed-valence rhodium chain prepared by reduction of precursor binuclear complexes. The mixed-valence compounds $\{[\text{Rh}(\text{MeCN})_4](\text{BF}_4)_{1.5}\}_n^{4-}$ and $\{[\text{Rh}_2(\mu\text{-O}_2\text{CMe})_2(\text{L})_2](\text{BX}_4) \cdot \text{H}_2\text{O}\}_n$ (L = 2,2'-bipyridine (bpy) or

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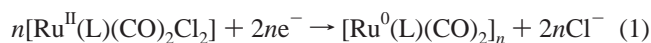
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1,10-phenanthroline (phen) derivatives; X = F, Ph)⁵ are the most relevant examples of these materials.

The second type of metal–metal-bonded materials, prepared and investigated since 1993, has been based on electroactive polymeric chains of nonbridged ruthenium or osmium atoms having the general formula $[M^0(L)(CO)_2]_n$.⁶ For instance, for M = Ru and L = 2,2'-bipyridine (bpy), the average Ru–Ru bond distance in the chain is 2.95 Å and the estimated average chain length is ca. 60 Å.^{6b} The low metal oxidation state and the two vacant coordination sites needed for the metal chain formation are achieved, for example, by electrochemical reduction of a precursor mononuclear ruthenium complex such as $[Ru^{II}(L)(CO)_2Cl_2]$. The reduction is associated with decoordination of both chloride ligands. The overall process is summarized in eq 1.



This type of polymer proved to be highly selective and efficient as catalysts for the water–gas shift reaction (WGSR)⁷ and, most importantly, for electroreduction of carbon dioxide in aqueous media.⁸ In addition, these polymers also exhibit interesting photochemical properties.⁹ It is noteworthy that photoelectrochemical systems for catalytic production of oxygen (and other species) from CO₂ currently receive attention with regard to the intended manned missions to Mars.¹⁰

Combined experimental data suggest that the polymerization occurs by an electrochemical propagation process, with the transient formation of a dimer, tetramer, and higher oligomers (eqs 2–5).¹¹ The polymerization process should involve, as the first step, the formation of an unstable radical

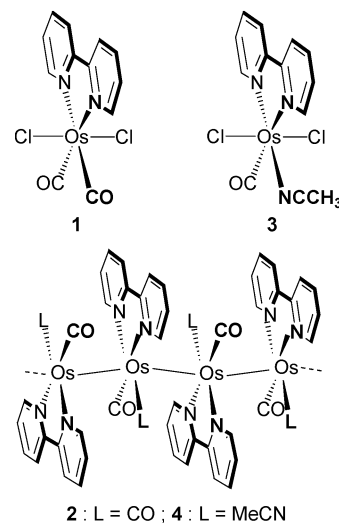
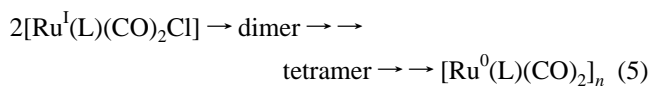
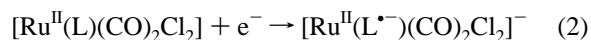


Figure 1. Schematic representation of the complexes $[Os(bpy)(CO)_2Cl_2]$ (1) and $[Os(bpy)(CO)(MeCN)Cl_2]$ (3) and the polymers $[Os(bpy)(CO)_2]_n$ (2) and $[Os(bpy)(CO)(MeCN)]_n$ (4).

anion with the singly reduced ligand $L^{\bullet-}$ (eq 2) that concomitantly loses one Cl^- ligand and transforms to a coordinatively unsaturated species (eqs 3 and 4). The reactive 17-electron transient readily dimerizes, and the resulting dimer is concomitantly rapidly reduced at the applied reduction potential of the $[Ru^{II}(L)(CO)_2Cl_2]$ precursor to promote further chain extension (eq 5; the added electrons and decoordinates Cl^- ligands have been omitted).



In this paper, we demonstrate the polymerization process for a closely related dichloride complex in which the Ru(II) center has been replaced by Os(II): *trans*-(Cl)-[Os(bpy)(CO)₂Cl₂] (1). Preliminary information on the corresponding electrogenerated Os–Os-bonded polymer $[Os(bpy)(CO)_2]_n$ (2), depicted in Figure 1, has been communicated elsewhere.^{6c}

Hereinafter, we will also show that the polymerization can be inhibited at sufficiently low temperatures, where the radical anionic intermediate $[Os^{II}(bpy^{\bullet-})(CO)_2Cl_2]^-$ (**1^{•-}**) is stable enough to be characterized by a combination of IR, UV–vis, and EPR spectroelectrochemical techniques (Tables 1 and 2). The stability of this anionic species is the consequence of the strong Cl–Os σ/π -bonding that makes the axial Os–Cl bonds in complex 1 less prone to cleavage upon reduction as compared to Ru–Cl in the corresponding Ru(II) complex (eqs 3–5). This property makes the osmium compounds convenient candidates for mechanistic and spectroscopic studies. For the first time, we have succeeded in characterizing spectroscopically the different redox states of polymer 2, in particular, its one-electron-reduced form

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Table 1. Electrochemical Data for Precursor Complexes *trans*-(Cl)-[Os(bpy)(CO)(L)Cl₂] (**1**, L = CO; **3**, L = MeCN) and Polymers [Os(bpy)(CO)(L)]_n (**2**, L = CO; **4**, L = MeCN)

redox couple	reduction potential ^a
1/1⁻	-1.57 ^b
1⁻/1²⁻	-2.16 ^c
2/2⁻	-1.75 ^b
2⁻/2²⁻	-2.48 ^c
3/3⁻	-1.79 ^b
3⁻/3²⁻	-2.55 ^c
4/4⁻	-2.06 ^b

^a Electrode potentials in volts versus Ag/Ag⁺ (10⁻² M in MeCN/10⁻¹ M TBAP); electrolyte, PrCN/10⁻¹ M TBAP for **1** and **2**, and MeCN/10⁻¹ M TBAP for **3** and **4**; working electrode, Pt disk; scan rate, 100 mV s⁻¹; temperature, 293 K. ^b Reversible system, E_{1/2}. ^c Irreversible system, E_{p,c}.

Table 2. IR CO-Stretching Frequencies for Precursor Complexes *trans*-(Cl)-[Os(bpy)(CO)(L)Cl₂] (**1**, L = CO; **3**, L = MeCN), Polymers [Os(bpy)(CO)(L)]_n (**2**, L = CO; **4**, L = MeCN), and Their One-Electron Reduction Products

complex	ν(CO)
1	2035, 1965 ^a
1⁻	2003, 1928 ^a
2	1967, 1892 ^{a,b}
2⁻	1939, 1855 ^{a,b}
3	1932 ^{a,c}
3⁻	1895 ^a
4	1889 ^c
4⁻	1858 ^{a,c}

^a In PrCN at 248 K. ^b In PrCN at 293 K. ^c In MeCN at 293 K.

that is a highly reactive electron-rich catalyst of the carbon dioxide reduction.^{6g} For comparison, a similar spectroelectrochemical study was also conducted with *trans*-(Cl)-[Os(bpy)(CO)(MeCN)Cl₂] (**3**) prepared¹² by photosubstitution of dicarbonyl complex **1** in acetonitrile.

Experimental Section

Materials and Preparations. Analytical-grade tetrahydrofuran (THF), acetonitrile (MeCN), and butyronitrile (PrCN), all purchased from Acros, were dried by conventional procedures¹³ and freshly distilled prior to use. HPLC-grade acetonitrile (Rathburn) was used as received. The supporting electrolytes Bu₄NClO₄ (TBAP; Fluka) and Bu₄NPF₆ (TBAH; Aldrich) were recrystallized from ethyl acetate and absolute ethanol, respectively, and dried under vacuum at 80 °C for 3 days. The parent complexes, *trans*-(Cl)-[Os(bpy)(CO)(X)Cl₂] (X = CO or MeCN), were prepared according to literature procedures.^{6g,12} All measurements were performed under an atmosphere of dry nitrogen or argon, in a drybox (Jaram) or using standard Schlenk techniques.

Electrochemistry. Cyclic voltammograms were recorded with EG&G PAR model 283 or 173 potentiostats, using airtight three-electrode cells. In (a) Grenoble and (b) Amsterdam, the following electrode sets were employed: working electrodes, a platinum disk with an apparent surface area of (a) 7.0 mm², and (b) 0.42 mm², polished carefully with a diamond paste containing 2 μm (Mecaprex Presi) and 0.25 μm (Oberflächentechnologien Ziesmer, Kempen, Germany) grains, respectively; auxiliary electrodes, (a) Pt wire in MeCN/10⁻¹ M TBAP, separated from the bulk solution by a frit, and (b) Pt gauze; reference electrodes, (a) Ag/Ag⁺ (10⁻² M in MeCN/10⁻¹ M TBAP), and (b) Ag wire, using the ferrocene/

ferrocenium (Fc/Fc⁺) redox couple as an internal reference system. All potentials reported here are relative to Ag/Ag⁺ (10⁻³ M in MeCN/10⁻¹ M TBAP) and can be converted to the standard¹⁴ Fc/Fc⁺ scale by adding -0.087 V, and to other reference systems.¹⁵ Bulk electrolyses were carried out in the drybox on a Pt sheet (2 cm²) placed in the cell; they were interrupted after the predetermined number of Coulombs had passed.

Spectroelectrochemistry. Electronic absorption spectra of the electrogenerated polymers were recorded in the drybox with a HP 8452A diode array spectrophotometer connected to the sample via an optical fiber.

IR and UV-vis spectral changes during spectroelectrochemical experiments at variable temperatures were monitored with optically transparent thin-layer electrochemical (OTTLE) cells¹⁶⁻¹⁸ equipped with Pt minigrid working electrodes and CaF₂ windows. IR spectroelectrochemical investigations of the polymer films were performed at room temperature exclusively in the drybox, with the OTTLE cell¹⁸ positioned in a built-in sample compartment of an FTIR spectrometer. EPR spectroelectrochemical experiments at low temperatures were conducted with an airtight three-electrode version of the Allendoerfer-type cell equipped with Au-helix working, Pt-helix auxiliary, and Ag-wire pseudoreference electrodes.¹⁹ Thin-layer cyclic voltammograms were recorded in the course of each spectroelectrochemical run for a precise potential control and for monitoring of the progress of electrolysis by the decrease of faradaic current. The spectroelectrochemical samples typically contained 10⁻⁴ M (EPR)/10⁻³ M (UV-vis)/3 × 10⁻³ M (IR) osmium complex and 3 × 10⁻¹ M supporting electrolyte. The potential of the minigrid working electrode was controlled by EG&G PAR 173 or PA4 (EKOM, Czech Republic) potentiostats. IR spectra of the electrolyzed solutions were recorded with Perkin-Elmer GX FTIR or Bio-Rad FTS 7 spectrometers, UV-vis spectra were recorded with Hewlett-Packard 8452A and 8453 diode-array or software-updated Perkin-Elmer Lambda 5 spectrophotometers, and X-band EPR spectra were recorded with a Varian Century E-104A spectrometer. The *g*-factors were determined against the polycrystalline 2,2-diphenyl-1-picrylhydrazyl (DPPH) standard (*g* = 2.0036(2)).²⁰

Results and Discussion

Electrochemical Behavior of Complex 1. In the positive potential region, the cyclic voltammogram of complex **1** shows a reversible one-electron redox system at moderate scan rates. However, it should be emphasized that the exhaustive oxidation of **1** is irreversible. The discussion of this anodic process is out of place here and has been described in detail elsewhere.¹²

In the cathodic region, the cyclic voltammogram of complex **1** in MeCN exhibits an irreversible, nearly two-electron cathodic peak at E_{p,c} = -1.61 V vs Ag/Ag⁺, associated with small anodic peaks between -0.80 and 0 V

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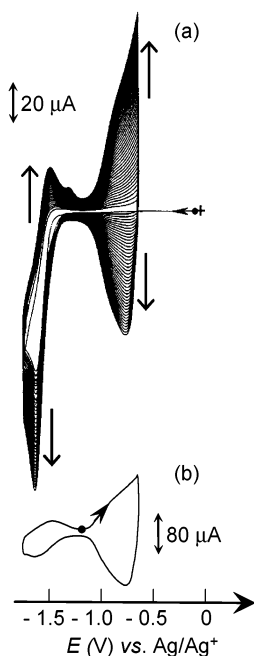
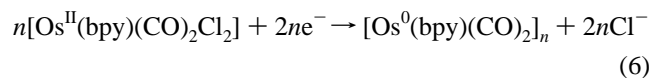


Figure 2. (a) Cyclic voltammograms of complex **1** (2.2×10^{-3} M) in MeCN. Conditions: 10^{-1} M TBAP, Pt disk electrode ($r = 2.5$ mm), 1st to 40th successive scans between -0.60 and -1.75 V, $\nu = 100$ mV s $^{-1}$. (b) Cyclic voltammogram of polymer **2** recorded with the modified Pt working electrode after the 40th reductive scan, transferred into the MeCN/ 10^{-1} M TBAP electrolyte.

observed on the reverse scan. This behavior is typical of an electrodeposition-redissolution phenomenon, as reported earlier for the corresponding mononuclear Ru(II) complex.^{6a} The negative potential shift observed for the reduction of **1** as compared to the corresponding Ru(II) complex ($E_{p,c} = -1.50$ V)²¹ under the same experimental conditions is in agreement with the stronger Cl–Os bonding reflected in the increased Os→CO π -back-donation and smaller IR $\nu(\text{CO})$ wavenumbers.^{6g}

The reductive electrochemical polymerization of **1**, monitored by iterative cyclic voltammetry (Figure 2a) or by controlled-potential electrolysis, produces a dark-blue colored electroactive polymer $[\text{Os}(\text{bpy})(\text{CO})_2]_n$ (**2**; Figure 1) adherent to the working electrode surface. Equation 6 summarizes the overall process.



The cathodic electroactivity of **1** resulting in the electropolymerization is consistent with the behavior of the corresponding *trans*-(Cl)-Ru(bpy) complex in acetonitrile (eqs 2–5). The electroreduction of **1** produces ultimately polymer **2**, most likely by a similar electrochemical propagation process. During the iterative voltammetric scans (Figure 2a), two clear reversible redox systems, characteristic of the polymer electroactivity, appear at $E_{1/2} = -0.80$ V (anodic) and $E_{1/2} = -1.55$ V (cathodic) vs Ag/Ag⁺, increasing in size continuously as the potential is repeatedly scanned from -0.60 to -1.75 V.

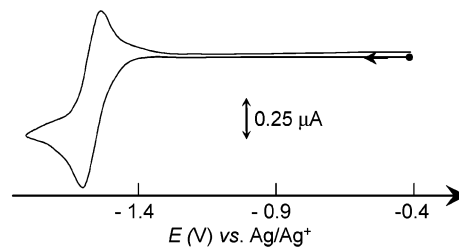
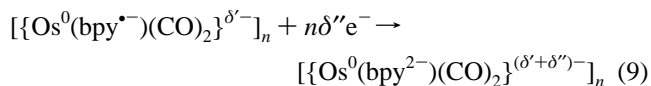
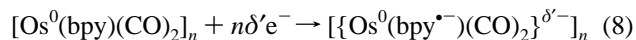
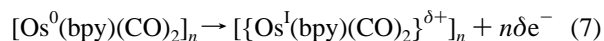


Figure 3. Cyclic voltammogram of complex **1** in MeCN. Conditions: 10^{-1} M TBAP, Pt disk electrode ($r = 0.5$ mm), $T = 253$ K, $\nu = 100$ mV s $^{-1}$.

When the modified cathode covered by the polymer layer is transferred into a fresh electrolyte solution in the absence of precursor **1**, the polymer electroactivity persists and remains unaffected, provided the potential scan is limited to -0.60 V (Figure 2b). In the CV of polymer **2**, we attribute the reversible anodic system to oxidation of the osmium centers ($2^{0/+}$; eq 7), and the reversible cathodic system to reduction of the bpy ligands ($2^{0/+}$; eq 8).^{6g} A third, less reversible cathodic step is observed at $E_{p,c} = -2.10$ V (not shown here) corresponding to the $2^{*-}/2^{2-}$ redox system (eq 9).



The doping levels (δ , δ' , and δ'') for the metal- and bpy-based redox systems, respectively, have been estimated in the film as the ratio between electrical charge recorded in the course of the oxidation (eq 7) and/or reduction (eqs 8 and 9) of the film and the charge consumed during its electrosynthesis, considering the electropolymerization yield to be quantitative. Comparable to the analogous Ru–Ru polymer,²² the doping levels are lower than 0.1 per $\{\text{Os}(\text{bpy})(\text{CO})_2\}$ polymer unit.

The complete electropolymerization of **1** (2 mM) can be achieved by exhaustive controlled-potential electrolysis of the complex at a large-surface working electrode at -1.60 V. A quantitative faradaic yield is obtained: two moles of electron per one mole of the precursor complex (eq 6). The physicochemical characterization of polymer **2**^{6g} is in line with the molecular structure presented in Figure 1.

The irreversible two-electron reduction process of **1** in acetonitrile observed by cyclic voltammetry at 293 K (Figure 2a, first scan) becomes a fully reversible one-electron system ($I_{p,a}/I_{p,c} = 1$, $E_{1/2} = -1.56$ V; $\Delta E_p = 0.06$ V) by lowering the electrolyte temperature to 253 K (Figure 3) or by using a different solvent such as less dissociating and coordinating tetrahydrofuran (THF)^{6g} or butyronitrile (PrCN; mp 161 K). The latter solvent is also more convenient than acetonitrile

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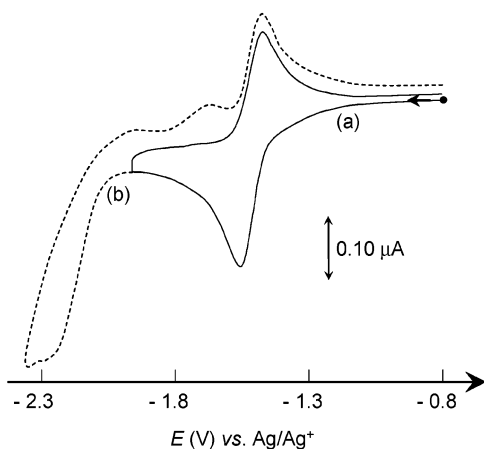
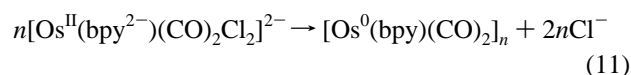
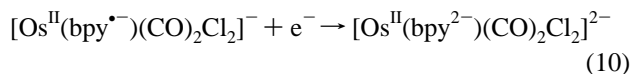


Figure 4. Cyclic voltammograms of complex **1** in PrCN. Conditions: 10^{-1} M TBAP, Pt disk electrode ($r = 0.5$ mm), scans between 0 and -2.00 V (a) and -2.35 V (b), $T = 248$ K, $\nu = 100$ mV s^{-1} .

($m_p = 227$ K) for spectroelectrochemical experiments at low temperatures (LT) with a thin-layer spectroelectrochemical cell.^{16,17}

In THF electrolyte, the cyclic voltammogram exhibits at 298 K a nearly reversible one-electron couple at $E_{1/2} = -1.64$ V ($\Delta E_p = 0.17$ V; $I_{p,a}/I_{p,c} = 0.93$) at $\nu = 100$ mV s^{-1} .^{6g} However, as the scan rate decreased to 20 mV s^{-1} , the reduction of **1** becomes almost totally irreversible. Again, the bulk electrolysis of **1** conducted in THF at room temperature results in the formation of completely insoluble Os–Os-based polymer **2** (eq 6) covering the cathode surface, with a quantitative faradaic yield of two mol of electrons consumed per one mol of **1**.

The cyclic voltammograms of complex **1** in PrCN are most informative, as in this solvent the reduction products remain fairly well soluble and clearly detectable. At 248 K, the primary cathodic step producing $\mathbf{1}^{\bullet-}$ is reversible at 100 mV s^{-1} (Figure 4, curve a; $E_{1/2} = -1.57$ V; $I_{p,a}/I_{p,c} = 1$; $\Delta E_p = 0.08$ V). Radical anion $\mathbf{1}^{\bullet-}$ is further one-electron-reduced at $E_{p,c} = -2.25$ V to dianion $\mathbf{1}^{2-}$ (eq 10; Figure 4, curve b). The irreversible nature of the latter redox reaction and the appearance of a new anodic process at $E_{p,a} = -1.68$ V on the reverse scan reveal that $\mathbf{1}^{2-}$ is highly unstable. The new anodic wave corresponds to one-electron oxidation of the reduced form of polymer **2** (see below). The shape and the current intensity of the cathodic peak of $\mathbf{1}^{\bullet-}$ are in agreement with partial electropolymerization of $\mathbf{1}^{2-}$ producing directly $\mathbf{2}^{\bullet-}$ (eqs 11 and 8) at the applied negative electrode potential.



At 293 K, the process remains reversible using a scan rate ≥ 500 mV s^{-1} ($E_{1/2} = -1.54$ V; $I_{p,a}/I_{p,c} = 1$; $\Delta E_p = 0.12$ V), whereas at $\nu = 10$ mV s^{-1} no reverse oxidation of $\mathbf{1}^{\bullet-}$ can be detected. The cyclic voltammograms recorded in PrCN at 293 K and 100 mV s^{-1} are shown in Figure 5. The formation of $\mathbf{1}^{\bullet-}$ is markedly more reversible than in acetonitrile under the same experimental conditions ($I_{p,a}/I_{p,c}$

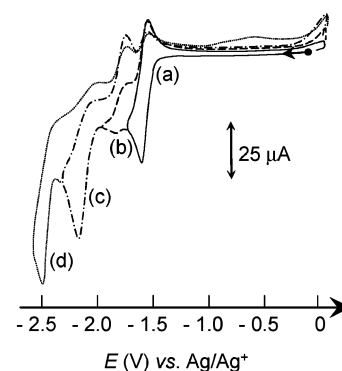


Figure 5. Cyclic voltammograms of complex **1** (1.0×10^{-3} M) in PrCN. Conditions: 10^{-1} M TBAP, Pt disk electrode ($r = 2.5$ mm), scans between 0 and -1.70 V (a), -1.90 V (b), -2.35 V (c), and -2.65 V (d), $T = 298$ K, $\nu = 100$ mV s^{-1} .

$= 0.93$; $\Delta E_p = 0.07$ V; $E_{1/2} = -1.57$ V; curve a). The subsequent cathodic step corresponding to the redox couple $\mathbf{1}^{\bullet-}/\mathbf{1}^{2-}$ is again irreversible and slightly positively shifted to $E_{p,c} = -2.16$ V as compared to 248 K (curve c). In addition, a small reversible redox couple is observed at $E_{1/2} = -1.75$ V ($\Delta E_p = 0.10$ V; curve b), which increases on the reverse scan initiated beyond the cathodic process at -2.16 V. More negatively lies the irreversible reduction at $E_{p,c} = -2.48$ V (curve d). The redox systems at -1.75 and -2.48 V correspond to the successive one-electron reductions of polymer **2**, $\mathbf{2}/\mathbf{2}^{\bullet-}$ and $\mathbf{2}^{\bullet-}/\mathbf{2}^{2-}$ (eqs 8 and 9). The negative shift of the reduction potential of polymer **2** by 0.20 V as compared to the value $E_{1/2} = -1.55$ V for the $\mathbf{2}/\mathbf{2}^{\bullet-}$ couple obtained in acetonitrile (see above and Figure 2b) has been attributed to the solubility of **2** in PrCN. In addition, Figure 5 also reveals the presence of an anodic peak at ca. 0 V corresponding to the polymer-based oxidation (eq 7). The anodic current of this oxidation increases concomitantly with that for the $\mathbf{2}^{\bullet-}/\mathbf{2}$ system when the negative potential scan limit is extended beyond the redox couple $\mathbf{1}^{\bullet-}/\mathbf{1}^{2-}$ (curve c). This series of cyclic voltammograms again confirms that two-electron-reduced $\mathbf{1}^{2-}$ converts to the singly reduced form of the Os–Os-bonded polymer ($\mathbf{2}^{\bullet-}$), following eqs 11 and 8. Differently from the scans at 248 K, the polymerization is already initiated by the formation of $\mathbf{1}^{\bullet-}$ (curve b).

At lower scan rates, the cyclic voltammograms in PrCN change in shape. At 10 mV s^{-1} , the reduction of complex **1** becomes a completely irreversible two-electron process at $E_{p,c} = -1.60$ V and the current intensity of the polymer redox couple $\mathbf{2}^0/\mathbf{2}^{\bullet-}$ at -1.75 V reaches its maximum. We may conclude the polymerization of $\mathbf{1}^{\bullet-}$ is a relatively slow process in PrCN. It should be emphasized that continuous cycling of the reduction potential between -0.85 and -1.90 V does not induce under these experimental conditions any film deposition on the cathodic surface, mainly as the consequence of the fairly good solubility of polymer **2** in PrCN (see below).

The bulk electrolysis of complex **1** at -1.60 V in PrCN at room temperature confirmed the instability of radical anion $\mathbf{1}^{\bullet-}$. The exhaustive reduction consumed two electrons per mol of the parent complex and produced a dark green solution with absorption maxima at 425 and 720 nm, which

contained a voluminous precipitate. The UV–vis spectrum resembles that of the $[\text{Ru}(\text{dmbpy})(\text{CO})_2]_n$ ($\text{dmbpy} = 4,4'$ -dimethyl-2,2'-bipyridine) polymer film strongly absorbing at ca. 790 nm.^{6a} Also in this case, no deposit was observed on the working electrode surface. A comparison of the current intensities of the $\text{Cl}^-/\text{Cl}^\bullet$ redox systems at 0.7 V vs Ag/Ag^+ in the electrolyzed and standard chloride solution²³ confirmed the overall $+2e^-/-2\text{Cl}^-$ stoichiometry of the reduction process converting complex **1** to polymer **2** (eq 6).

The cyclic voltammogram of the electrolyzed solution, recorded after the removal of the precipitate, showed that the initial cathodic peak of complex **1** was strongly suppressed. The quasi-reversible process at $E_{1/2} = -1.78$ V ($\Delta E_p = 0.11$ V) remained observable, associated with the anodic system at $E_{1/2} = -0.08$ V ($\Delta E_p = 0.16$ V) corresponding to the oxidation of the soluble polymer. By comparison of the current intensities of the redox systems, we have estimated the portion of the soluble polymer to ca. 30% of the total amount produced.

The structure of the soluble polymer has not been fully characterized yet. However, the low-lying charge-transfer absorption at 720 nm indicates the presence of $\text{Os}(\text{bpy})(\text{CO})_2$ units and metal–metal bonds in the chain structure, similar to eclipsed-to-staggered structures of dimers $[\text{Mn}(\text{CO})_3(\text{iPr-DAB})]_2$ ²⁴ and $[\text{Ru}(\text{Me})(\text{CO})_2(\text{iPr-DAB})]_2$ ^{16,25} ($\text{iPr-DAB} = N,N'$ -diisopropyl-1,4-diaza-1,3-butadiene), both strongly absorbing at 745 nm.

Spectroelectrochemical Studies of Electropolymerization of Complex 1. Spectroelectrochemistry in PrCN. As described above, the exhaustive-reduction product of complex **1** in PrCN at room temperature is obtained as a nonadherent precipitate and as a limpid solution. We have taken advantage of the fairly good solubility in PrCN to study the formation of polymer **2** in situ by spectroelectrochemical methods and to characterize its different redox states.

The electrochemical reduction of complex **1** in PrCN at room temperature was performed within an optically transparent thin-layer spectroelectrochemical (OTTLE) cell.¹⁸ Electrolysis of **1** was conducted under an argon atmosphere in a drybox, with the OTTLE cell positioned in the sample compartment of an FTIR spectrometer. In the course of the reduction, complex **1** ($\nu(\text{CO})$ at 2035 and 1965 cm^{-1}) converted into green polymer **2** absorbing at 1967 and 1892 cm^{-1} (Figure 6, spectra a and b, respectively). This fairly large wavenumber shift is in accordance with the decreased oxidation state of the metal. Importantly, the precipitate of polymer **2** obtained by the bulk electrolysis of complex **1** in PrCN at room temperature (see above) shows two $\nu(\text{CO})$ bands at 1964 and 1906/1877 cm^{-1} , the latter band being split. As expected from the corresponding cyclic voltammogram (Figure 5), the soluble polymer was obtained in the

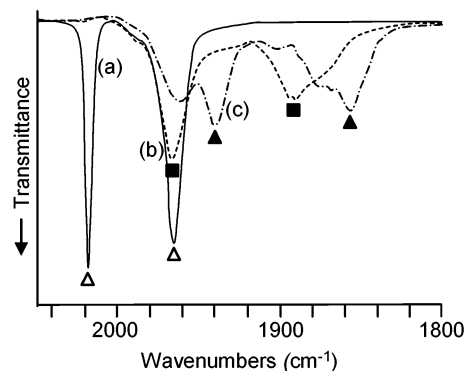


Figure 6. In-situ IR spectral changes in the CO-stretching region, accompanying the reduction of complex **1** in $\text{PrCN}/10^{-1}$ M TBAP at $T = 293$ K within an OTTLE cell:¹⁸ (a) parent complex **1** (Δ), (b) polymer **2** (\blacksquare) after two-electron reduction of **1**, and (c) partial one-electron reduction of polymer **2** into $2^{\bullet-}$ (\blacktriangle).

neutral redox state, that is, **2**, because the potential of its reduction ($E_{1/2} = -1.75$ V) is more negative than that needed for its formation from complex **1** (ca. -1.60 V). This result is different as compared to the electrolysis in THF where polymer **2** is completely insoluble and more easily reducible ($E_{1/2} = -1.55$ V). In accordance with the CV responses shown in Figure 5, the subsequent one-electron reduction of **2** produced corresponding radical anion $2^{\bullet-}$ absorbing at 1940 and 1855 cm^{-1} ($\Delta\nu$ about 30 cm^{-1} ; Figure 6, spectrum c). According to the $\nu(\text{CO})$ shift, the added electron is largely localized on the bpy ligand. Importantly, the reduction proved to be a reversible process because the back oxidation of $2^{\bullet-}$ regenerated smoothly the neutral polymer **2**.

In PrCN at 253 K, the spectroelectrochemical study of complex **1** was conducted in an airtight cryostated thin-layer cell. The reduction of complex **1** led to the appearance of new intense IR $\nu(\text{CO})$ bands at 2003 and 1928 cm^{-1} (Figure 7a). Notably, the $\nu(\text{CO})$ wavenumbers of the dicarbonyl product are smaller by about 30 cm^{-1} as compared to those of the parent complex **1**, which can be expected for one-electron reduction predominantly localized on the bpy ligand.^{12,26} They can be therefore assigned to radical anion $1^{\bullet-}$, in agreement with the reversible redox couple $1/1^{\bullet-}$ observed at this temperature by cyclic voltammetry (Figure 4). The stability of $1^{\bullet-}$ at 248 K was, however, still incomplete, and partial polymerization took place, as was indicated by the parallel growth of small $\nu(\text{CO})$ bands at ca. 1967 and 1892 cm^{-1} attributable to polymer **2**. When the thin solution layer in the spectroelectrochemical cell was warmed from 248 to 293 K while having maintained the applied reduction potential, the thermal instability of radical anion $1^{\bullet-}$ strongly increased, and its gradual conversion into largely soluble polymer **2** ($\nu(\text{CO})$ at 1967 and 1892 cm^{-1}) was observed.

The cyclic voltammogram of complex **1** shown in Figure 4 indicates that subsequent reduction of radical anion $1^{\bullet-}$ in PrCN at 248 K produces soluble negatively charged polymer $2^{\bullet-}$. Monitoring this process by IR spectroscopy revealed that the $\nu(\text{CO})$ bands of $1^{\bullet-}$ were indeed replaced by the

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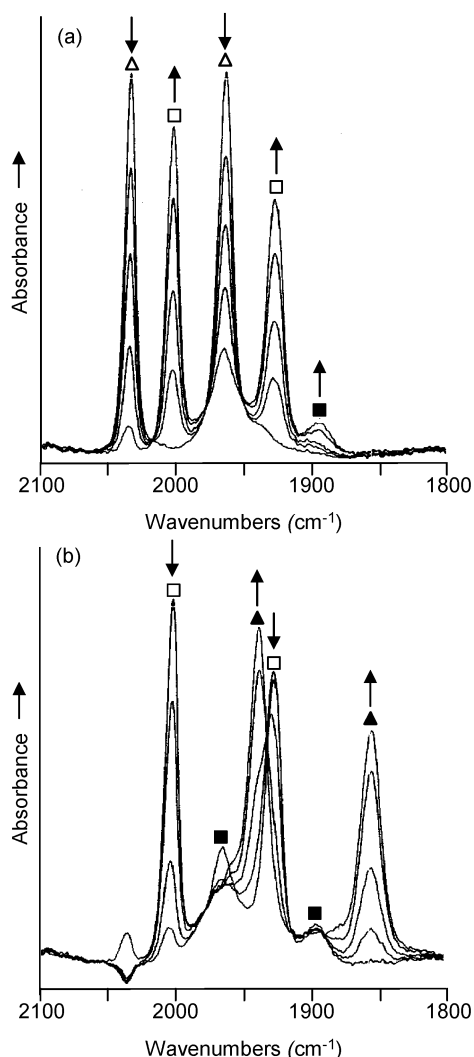


Figure 7. IR spectra in the CO-stretching region showing the changes during the exhaustive one-electron reduction of (a) complex **1** (Δ) into radical anion $1^{\bullet-}$ (\square) and (b) radical anion $1^{\bullet-}$ into reduced polymer $2^{\bullet-}$ (\blacktriangle). The symbol \blacksquare denotes a small amount of neutral polymer **2** formed during the first cathodic step. Conditions: PrCN, $T = 248$ K, electrolysis within a cryostated OTTE cell.^{16,17}

characteristic $\nu(\text{CO})$ doublet of $2^{\bullet-}$ at 1939 and 1855 cm^{-1} (Figure 7b). Importantly, oxidation of $2^{\bullet-}$ at 248 K generated exclusively neutral polymer **2** absorbing at 1967 and 1892 cm^{-1} .

To complete the description of the IR spectroelectrochemical experiments in PrCN, it is important to note that reduced polymer $2^{\bullet-}$ proved to be sensitive to temperature variation and partly converted at 293 K to another species absorbing at 1955 and 1873 cm^{-1} . These $\nu(\text{CO})$ wavenumbers are very close to 1958 and 1870 cm^{-1} , the maxima of two dominant CO-stretching bands of the solid polymer film formed by the reduction of complex **1** in THF at room temperature (see below).

UV-vis spectral changes recorded during the reversible one-electron reduction of complex **1** in PrCN at 253 K have confirmed the localization of the electron transfer on the bpy ligand. The characteristic absorptions of the $\text{bpy}^{\bullet-}$ radical

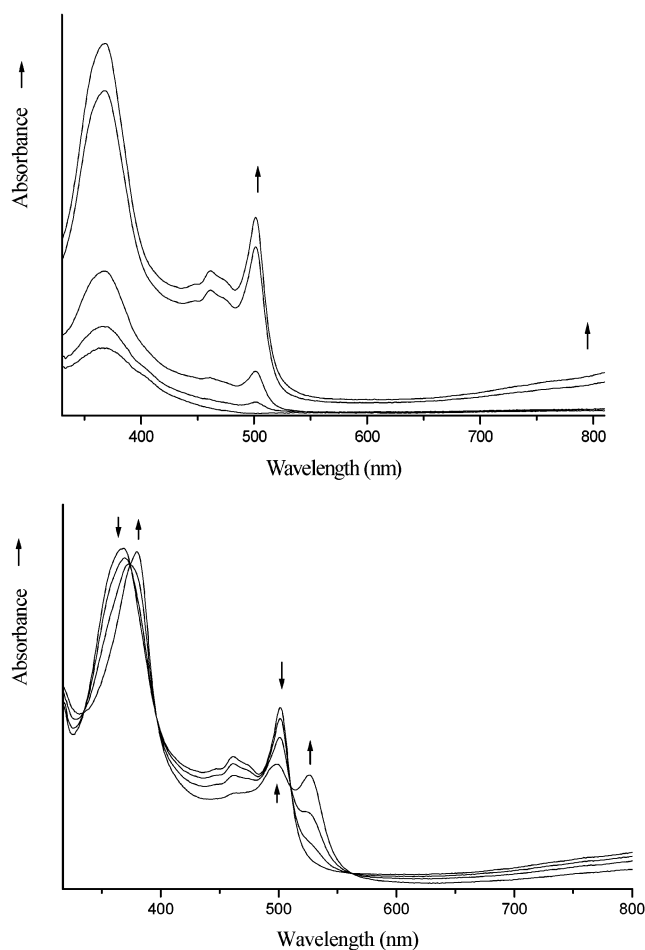


Figure 8. In-situ UV-vis spectral changes accompanying the reduction of complex **1** into $1^{\bullet-}$ (top) and of radical anion $1^{\bullet-}$ into $2^{\bullet-}$ (bottom). Conditions: PrCN/TBAH electrolyte, $T = 248$ K, within an OTTE cell.^{16,17}

anion^{27,28} arose at 369 nm (intraligand $\pi\pi^*$ transition), at 461 and 501 nm (intraligand $\pi^*\pi^*$ transitions), and between 550 and >800 nm (structured broad band extended to the NIR region; intraligand $\pi^*\pi^*$ transitions), see Figure 8a.

Importantly, the UV-vis spectra recorded in PrCN at 253 K during the second cathodic step show that all of the $\text{bpy}^{\bullet-}$ intraligand transitions have remained, merely shifting to longer wavelengths: 380 nm ($\pi\pi^*$), 499 and 527 nm ($\pi^*\pi^*$), and between 650 and >800 nm ($\pi^*\pi^*$) (Figure 8b).

The IR spectrum of this radical species shows the two $\nu(\text{CO})$ bands (1939 and 1855 cm^{-1}) attributed above to reduced polymer $2^{\bullet-}$. We can therefore conclude again that the reduction of radical anion $1^{\bullet-}$ gives rise to the formation of the reduced polymer $2^{\bullet-}$ (eq 8).

To complete the spectroelectrochemical experiments, radical anion $1^{\bullet-}$ has also been characterized by EPR spectroscopy. In this case, the electrochemical reduction of parent complex **1** was conducted in PrCN at 223 K. The EPR spectrum recorded after the electrolysis displayed an unre-

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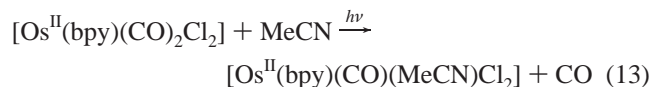
solved singlet signal ($\Delta H = 1.5$ mT) at $g = 1.9992$. The g -value also agrees with the bpy-localized unpaired electron in $\mathbf{1}^{\bullet-}$. The absence of hyperfine splitting could be attributed^{6a} to intramolecular electron-hopping between ligands. It should be noted that the same EPR spectroelectrochemical experiment conducted with complex **1** at room temperature led to a soluble EPR-silent green species corresponding to neutral polymer **2**. During this experiment, a small amount of polymer **2** precipitated at the bottom of the tubular EPR cell, similarly to the exhaustive electrolysis in the conventional electrochemical cell.

Spectroelectrochemistry in THF. In THF at 253 K, the reduction of complex **1** again produced mainly radical anion $\mathbf{1}^{\bullet-}$ with its characteristic IR $\nu(\text{CO})$ absorption at 2003 and 1926 cm^{-1} . Partial polymerization still occurred at this temperature, and a small $\nu(\text{CO})$ band belonging to polymer **2** grew up at 1895 cm^{-1} .

At room temperature, however, the $\nu(\text{CO})$ bands of parent complex **1** at 2032 and 1962 cm^{-1} were replaced progressively during the reduction by new bands at 1979(sh), 1958-(m), 1901(w), and 1870(m) cm^{-1} . As expected from cyclic voltammetry, there was no evidence for the formation of radical anion $\mathbf{1}^{\bullet-}$. Instead, a dark-blue deposit was observed on the surface of the Pt minigrad working electrode. We should recall that in the course of the electropolymerization, solid product **2** is also effectively reducible during its deposition at the applied cathodic potential of complex **1** (see Figure 2), which contributes to the complexity of the system as compared to the situation in solution.

After the electrolysis, the original electrolyte containing the liberated chloride ligands was replaced inside the drybox by a fresh solution. The IR spectrum showed again the presence of the dominant $\nu(\text{CO})$ bands at 1958 and 1870 cm^{-1} and minor bands at 1979(sh) and 1901 cm^{-1} . This observation allows us to attribute them unequivocally to polymer species forming the persistent dark-blue layer deposited at the minigrad working electrode and in its close vicinity. Interestingly, the electrochemical reduction of the washed polymer film led gradually to the appearance of two new $\nu(\text{CO})$ bands at 1930 and 1859 cm^{-1} . This shift to smaller wavenumbers is consistent with the assumed one-electron reduction of the bpy ligands in the solid material $[\text{Os}(\text{bpy})(\text{CO})_2]_n$, producing the radical species $\mathbf{2}^{\bullet-}$ (eq 8). As shown above, the latter product is fairly well soluble in PrCN, absorbing at 1939 and 1855 cm^{-1} .

Electrochemical Behavior of Complex 3. Photoirradiation of complex **1** in acetonitrile with $\lambda_{\text{exc}} \geq 320$ nm induces decoordination of a CO ligand, giving rise to the formation of the complex *trans*-(Cl)- $[\text{Os}(\text{bpy})(\text{CO})(\text{MeCN})\text{Cl}_2]$ (**3**) (eq 13; Figure 1).



This complex, in its oxidized form ($\mathbf{3}^+$), is also formed as the major product during electrochemical one-electron oxidation of the complex **1** conducted in acetonitrile at room

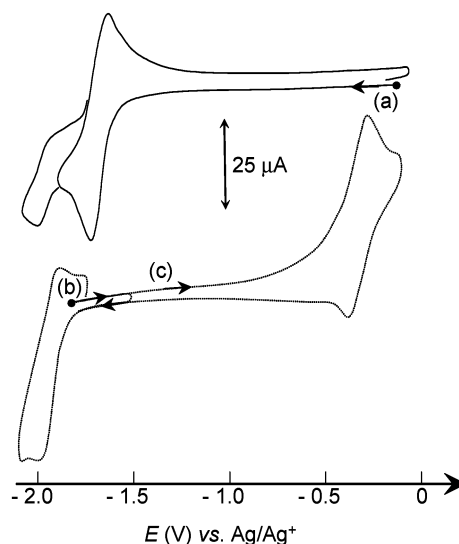
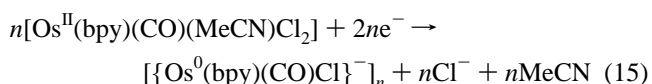
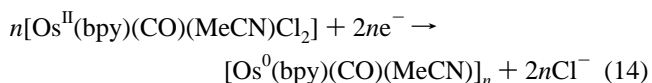


Figure 9. Cyclic voltammograms of (a) complex **3** (1.2×10^{-3} M) and (b) soluble polymer **4** after exhaustive bulk electrolysis of complex **3** at -1.9 V. Conditions: MeCN/ 10^{-1} M TBAP, $T = 293$ K, $\nu = 100$ mV/s, Pt disk working electrode ($r = 2.5$ mm).

temperature. The photo- and electrochemical syntheses, and the physicochemical and redox properties of complex **3**, have been published recently.¹²

The new monocarbonyl complex is of interest, as the preliminary electrochemical data obtained in MeCN have shown that its reduction is more reversible as compared to that of dicarbonyl complex **1** in the same electrolyte and that the reduction products are soluble. With this type of precursor complex, two different ligands may dissociate during the electropolymerization process, as shown in eqs 14 and 15. Indeed, we have previously shown that chloride^{6a} and acetonitrile²⁹ ligands in analogous Ru carbonyl complexes are good leaving groups for the electrosynthesis of Ru–Ru-bonded polymers.



Replacing one CO ligand in complex **1** by MeCN causes a significant change in the cathodic behavior. The cyclic voltammogram of complex **3** in MeCN resembles closely that of **1** recorded in PrCN at room temperature (Figure 5). Similarly, complex **3** undergoes nearly reversible one-electron reduction into corresponding radical anion $\mathbf{3}^{\bullet-}$ (Figure 9a; $E_{1/2} = -1.79$ V; $I_{p,a}/I_{p,c} = 0.85$; $\Delta E_p = 0.06$ V) followed by a small reversible redox system at $E_{1/2} = -2.06$ V ($I_{p,a}/I_{p,c} = 0.83$; $\Delta E_p = 0.08$ V). In addition, an intense irreversible wave was observed at $E_{p,c} = -2.55$ V, probably encompassing reduction of $\mathbf{3}^{\bullet-}$. The higher stability of radical anion $\mathbf{3}^{\bullet-}$ in acetonitrile as compared to $\mathbf{1}^{\bullet-}$ in this solvent (Figure 2) most likely has its origin in the delocalized

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bonding situation in parent complex **3**, as reported in our recent study.¹²

Bulk electrolysis of complex **3** at -1.90 V, conducted in MeCN at room temperature, revealed, however, that complex **3** is irreversibly reduced under these conditions and transforms to a completely soluble green species absorbing in the visible spectral region at $\lambda_{\text{max}} = 408$ and 646 nm, similar to polymer **2**. The IR spectrum of the electrolyzed solution showed in the $\nu(\text{CO})$ region a single band at 1889 cm^{-1} . The cyclic voltammogram of the reduction product displayed two reversible one-electron systems: one cathodic at $E_{1/2} = -2.06$ V ($I_{\text{p,a}}/I_{\text{p,c}} = 1$; $\Delta E_{\text{p}} = 0.12$ V) and one anodic at $E_{1/2} = -0.40$ V ($I_{\text{p,a}}/I_{\text{p,c}} = 1$; $\Delta E_{\text{p}} = 0.11$ V) (Figure 9b). The exhaustive reduction consumed two electrons and liberated slightly less than two moles of Cl^- per mole of **3**. There was no insoluble species observed as a precipitate in the electrolytic cell or as a film on the working-electrode surface. All of these results and comparison with the electrochemical reduction of complex **1** in PrCN electrolyte are in favor of the conversion of complex **3** by the exhaustive two-electron electrolysis into a polymeric structure containing Os–Os bonds, $[\text{Os}(\text{bpy})(\text{CO})(\text{MeCN})]_n$ (**4**). More details about this process have been obtained from a spectroelectrochemical investigation.

Spectroelectrochemical Studies of Electropolymerization of Complex 3. Reduction of complex **3** ($\nu(\text{CO})$ at 1932 cm^{-1}) in PrCN at 248 K in the OTTLE cell, monitored by IR spectroscopy, led to the appearance of a single product absorbing at 1895 cm^{-1} ($\Delta\nu = 35$ cm^{-1}). The EPR spectrum of this species, recorded in situ under the same conditions, showed an unresolved singlet ($\Delta H = 1.5$ mT) at $g = 1.9850$. This product can, therefore, be assigned as stable radical anion $\mathbf{3}^{\bullet-}$, in agreement with the reversible cathodic cyclic voltammetric response of the parent complex (see above). For comparison, an unresolved EPR spectrum has also been observed³⁰ for the radical complex $[\text{Os}(\text{bpy})_3]^+$, with isotropic $g = 1.989$ typical for the presence of the 5d Os center, much below the free-electron (2.0023) and free-bpy $^{\bullet-}$ (2.0030) values.

In MeCN at room temperature, reduction of complex **3** ($\nu(\text{CO})$ at 1932 cm^{-1}) resulted in the formation of EPR-silent polymer **4** ($\nu(\text{CO})$ at 1889 cm^{-1}), identical to the course of the two-electron bulk electrolysis. The subsequent cathodic step converted polymer **4** into a new species showing a single CO-stretch at 1858 cm^{-1} . The same product was obtained by reduction of radical anion $\mathbf{3}^{\bullet-}$ in PrCN at 248 K. In analogy with the reduction paths of complex **1**, the carbonyl product absorbing at 1858 cm^{-1} has been assigned as the singly reduced polymer $\mathbf{4}^{\bullet-}$, with the MeCN ligand possibly replaced by PrCN when the latter is used as the solvent.

Conclusions

The presented spectroelectrochemical data are important for the general understanding of the mechanism of the metal–metal bond formation to prepare extended metal atom chains.

The formation of polymers containing Os–Os chains, $[\text{Os}(\text{bpy})(\text{CO})_{2-m}(\text{MeCN})_m]_n$ ($m = 0$ (**2**) and 1 (**4**)), by electrochemical reduction of parent mononuclear dichloro complexes **1** and **3**, respectively, was followed conveniently by spectroelectrochemical methods (IR, UV–vis, EPR) under strictly inert conditions. For the first time, we were able to stabilize at low temperatures and spectroscopically characterize the radical anions $\mathbf{1}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$, the primary reduction products in the mechanism of the electrosynthesis of the polymers. The thermal reactivity of $\mathbf{1}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$ at elevated temperatures triggers the polymerization process, resulting in the formation of **2** and **4**, respectively, by the electrochemical propagation reactions described by eqs 2–5 for $M = \text{Os}$. Importantly, subsequent electrochemical reduction of $\mathbf{1}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$ at low temperatures produces the polymers in their reduced forms, that is, $\mathbf{2}^{\bullet-}$ and $\mathbf{4}^{\bullet-}$, respectively. This type of highly reactive electron-rich compound has been previously proposed to be the catalyst in carbon dioxide activation. Among the most important results of this study is the unambiguous spectroscopic evidence for the localization of the unpaired electrons in $\mathbf{2}^{\bullet-}$ on the bpy ligands, together with the observation of the reversible electrochemical interconversion between the neutral and reduced forms of the polymers. The conclusions can be applied for the widely studied analogous ruthenium compounds that, due to their higher reactivity, are less suited for mechanistic investigations. Valuable information has been obtained about the solubility of polymers **2** and **4**. The good solubility of **2** in butyronitrile and of the CO-substituted derivative **4** in common polar organic solvents facilitates their characterization. It also provides access to the potential utilization of this type of materials, for example, as molecular wires.³¹ In this regard, also the reversible oxidation of the metal centers to Os(I) (eq 7 and Figure 2) may be of importance. The extension of this approach to develop and characterize new 1D materials based on other metals is underway.

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