

Analysis of Electrolysis Reactions of Metal Complexes Using On-Line Electrospray Ionization Mass Spectrometry with a Compact Electrolytic Flow-Through Cell

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An on-line electrospray ionization mass-spectrometric analysis for an electrolysis reaction was developed by the installation of a compact, efficient flow-through cell upstream of an electrospraying needle. The electrode was designed to avoid any reduction of the oxidation products formed during electrolysis. The electrolytic oxidation reaction of a Ru and Os metal complex was carried out to examine the performance of the system. From the electrolysis of $[M(bpy)_3](PF_6)_2$ (where $M = Ru$ and Os , and $bpy = 2,2'$ -bipyridine) we detected the one-electron oxidation product, $[M(bpy)_3]^{3+}$. The electrolysis of $[Ru(bpy)_2(en)](ClO_4)_2$ ($en =$ ethylenediamine) formed two complex products along with the elimination of two and four hydrogen atoms from the en ligand. The structure of the two complex products was determined to be a monoimine and diimine complex, based on an electrolysis experiment using a deuterium-labeled complex, $[Ru(bpy)_2(ed)](ClO_4)_2$ ($ed =$ ethylene- d_4 -diamine, $H_2N-CD_2-CD_2-NH_2$). The results indicate that electrochemical oxidation occurs at the ethylenediamine ligand and that the monoimine complex is a reaction intermediate for the formation of a diimine complex.

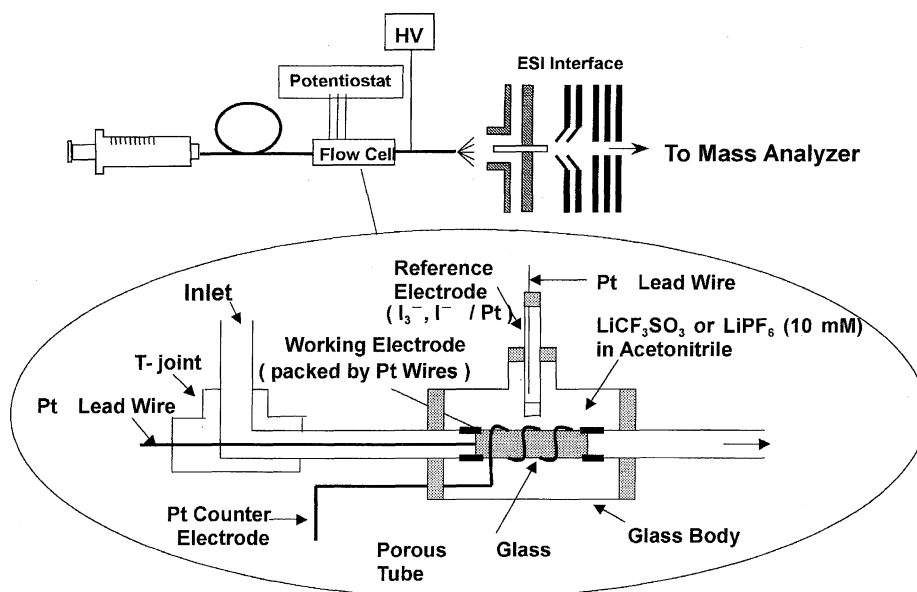
Electrospray ionization mass spectrometry (ESI-MS) can be used to analyze nonvolatile and thermally unstable compounds because of its soft ionization technique. Several reports have appeared on attempts to charge neutral molecules by a redox reaction in a electrolytic flow-through cell placed at the upstream of a ESI-MS.^{1–8} Bond and Treager reported on an on-line analysis which involved passing an electrolytic solution into the flow-through cell and interfacing to ESI-MS.² Solutions of $[NBu_4](PF_6)$ mixed with equal mole amounts of copper, nickel, and cobalt dithiocarbamate complexes were electrolyzed, and the on-line ESI-MS analysis resulted in the detection of one-electron oxidation products; however, the products were detected as weak ions among abundant interference ions, which were generated from an excess amount of the supporting electrolytes in the solution. It is anticipated that those interference ions can be avoided by using either a volatile electrolyte, such as ammonium acetate, or by using as electrolyte, such as $LiPF_6$ or $LiCF_3SO_3$, which do not form interference ions in the spectra. In fact, electrolytic cells which could perform effective electrolytic oxidation in the presence of a small amount of the supporting electrolyte have been reported.^{4–6} Xu and Cole⁴ reported on the successful detection of radical ions as one-electron oxidation products from a solution of polycyclic aromatic hydrocarbons in acetonitrile and dichloromethane, which was mixed with about ten-times $LiCF_3SO_3$.

However, there are still many unsolved problems con-

cerning the practical use of on-line ESI-MS; for example, a high potential, such as much as several hundred volts, must be applied in some cases between the electrodes of the cell, the detection is limited to easily electrolyzed compounds, and the sensitivity of detection is still very low, etc. These problems are all caused by the fact that samples are not effectively electrolyzed when flowing. We here report on our study concerning an improvement of the electrolytic cell and aim to achieve rapid, high-sensitivity on-line detection. We designed a three-pole compact flow-through cell by placing a porous glass sector between a working electrode and reference and counter electrodes. The effectiveness of the cell is shown by the successful detection of one-electron oxidation products from $[Ru(bpy)_3](PF_6)_2$ and $[Os(bpy)_3](PF_6)_2$ (where $bpy = 2,2'$ -bipyridine). We also achieved the detection and structural elucidation of unstable and short-live reaction intermediates from the reaction products of two metal complexes, $[Ru(bpy)_2(en)](ClO_4)_2$ and $[Ru(bpy)_2(ed)](ClO_4)_2$ (where $en =$ ethylenediamine, $ed =$ ethylene- d_4 -diamine, $H_2N-CD_2-CD_2-NH_2$).

Experimental

Scheme 1 shows the on-line ESI-MS in which a compact and efficient flow-through cell is installed upstream of the spraying needle. The electrolytic flow-cell used in our experiment was similar to that mentioned in the literature.^{9–11} The working electrode of the cell was made by inserting a large number of platinum wires



Scheme 1. The schematic picture of ESI-MS with the compact and efficient electrolytic flow-through cell.

in a porous glass tube, in which the electrolysis of flow through electrolyte could proceed effectively even at a low concentration. The counter electrode was placed outside of the porous glass tube so as to avoid any reduction of the oxidized products formed at the working electrode. The space between the working and reference electrode was filled with an acetonitrile solution of LiPF_6 or LiCF_3SO_3 . Instead of the commonly used alkylammonium perchlorate or hexafluorophosphate, we used LiCF_3SO_3 and LiPF_6 as the electrolyte. Purified acetonitrile was used as the solvent, and the sample concentration was about 1 mM ($1 \text{ M} = 1 \text{ mol dm}^{-3}$). The flow rate of the solution was $4 \mu\text{L min}^{-1}$. It took about 2 min for the flowing sample to pass across the working electrode in the cell, and about 1 min to arrive at the tip of the needle for spraying; therefore, electrolytic products with lifetimes of more than a few minutes could be detected by ESI-MS analysis. Ru and Os complexes were synthesized by a modification of a published method.¹²

Results and Discussion

Electrolytic Oxidation of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ and $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$ Complex. Both Ru and Os commonly exist in a divalent or trivalent state, and can be transformed between them by electrolysis in solution. We studied the electrolytic oxidation of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ and $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$ by on-line ESI-MS. The electrolysis was carried out in an acetonitrile solution by dissolving 0.3 mM of the complex together with 1.0 mM of the supporting electrolyte, LiCF_3SO_3 . Figure 1 shows the ESI spectra for the Ru complex. The complex solution before the electrolysis yielded m/z 285 ion of $[\text{Ru}(\text{II})(\text{bpy})_3]^{2+}$. The m/z values given in the text were calculated from ^{102}Ru or ^{192}Os . The isotope distribution agreed with that of the calculated values (Fig. 1a). Singly charged ions $[\text{Ru}(\text{bpy})_3](\text{PF}_6)^+$ and $[\text{Ru}(\text{bpy})_3](\text{CF}_3\text{SO}_3)^+$ were also detected. It has been reported that redox reactions occur frequently at the needle tip for some small redox potential substances.^{1,2} However, we did not detect such a reaction in the spectra. $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in acetonitrile exhibits a reversible redox wave of

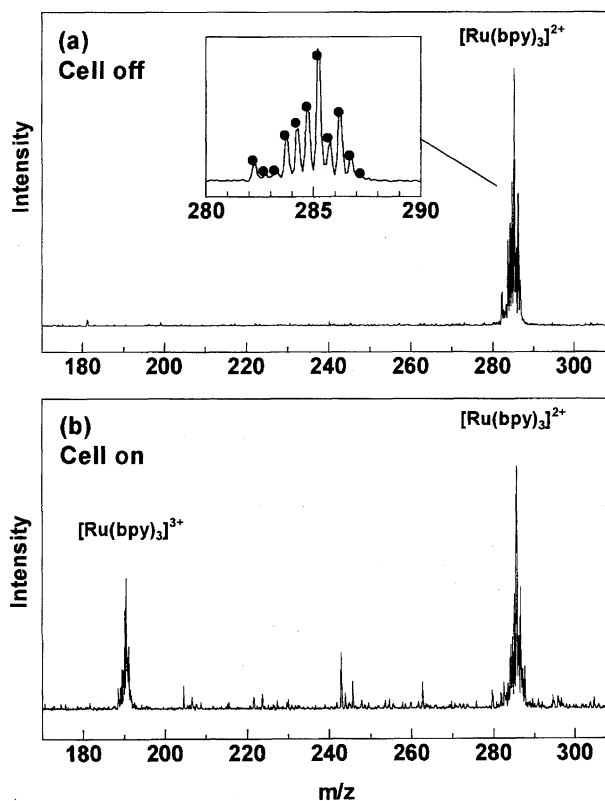


Fig. 1. Positive ion ESI spectra of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (bpy = 2,2'-bipyridine) in acetonitrile solution by dissolving 0.3 mM of the complex together with 1.0 mM of the supporting electrolyte LiCF_3SO_3 . The electrolysis reaction is (a) off and (b) on. The inset shows the isotope distribution of $[\text{Ru}(\text{II})(\text{bpy})_3]^{2+}$ in agreement with that of the calculated (•).

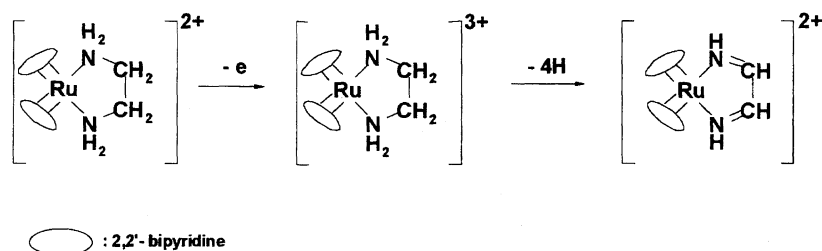
1.3 V (vs. SCE),¹² which corresponds to the potential difference between Ru(II) and Ru(III). Therefore, we carried out electrolysis by applying 1.8 V (vs. SCE) to the flow-

through cell; the ESI-MS yielded a double-charged ion at m/z 285 as well as a triple-charged ion at m/z 190, the latter being $[\text{Ru(III)(bpy)}_3]^{3+}$, resulting from the one-electron oxidation of $[\text{Ru(bpy)}_3]^{2+}$ (Fig. 1b). Neither ligand elimination ions, such as $[\text{Ru(bpy)}_2]^{2+}$ or $[\text{Ru(bpy)}]^{2+}$, nor ligand exchange ions, such as $[\text{Ru(bpy)}_2(\text{an})]^{2+}$ or $[\text{Ru(bpy)}_2(\text{an})_2]^{2+}$ (where an = acetonitrile), were observed. In acetonitrile we observed abundant peaks of lithium-solvated complex ions Li(an)^+ and Li(an)_2^+ in the spectra, and the $[\text{Ru(bpy)}_3]^{3+}$ ion decreased significantly. Therefore, we used the conditions by keeping the concentration of the electrolyte at the minimum and by increasing the overvoltage to 0.5 V above the redox potential of the complex. This resulted in the successful detection of the one-electron oxidation product. We also tried to use methanol as the solvent, which has less tendency to coordinate with lithium, and to increase the electrolyte concentration and decrease the overvoltage; however, we could not detect the one-electron oxidation ion of $[\text{Ru(bpy)}_3]^{3+}$.

The ESI spectra of a 1.2 mM solution of $[\text{Os(bpy)}_3](\text{PF}_6)_2$ in acetonitrile is shown in Fig. 2. The complex solution before electrolysis yielded the m/z 330 ion corresponding to $[\text{Os(bpy)}_3]^{2+}$ (Fig. 2a). The single-ion $[\text{Os(bpy)}_3](\text{PF}_6)^+$ was also observed. Again, we did not observe any ions resulting from the redox reaction at the needle tip. $[\text{Os(bpy)}_3](\text{PF}_6)_2$ in acetonitrile has a reversible redox wave of 0.6 V (vs. SCE) corresponding to $\text{Os(II)} \rightarrow \text{Os(III)}$. When the flow-through cell was applied with a potential 0.7 V (vs. SCE), a new ion at m/z 220 corresponding to triple charged $[\text{Os(bpy)}_3]^{3+}$ was observed (Fig. 2b). All Os experiments were carried out without any addition of a supporting electrolyte. Therefore, the observation may indicate that the electrolytic products are detectable at a relatively small overvoltage, and that the $[\text{Os(bpy)}_3](\text{PF}_6)_2$ itself must act as a supporting electrolyte. As observed in an experiment of the Ru complex, we detected no ions resulting from either the elimination or ligand exchange with the solvent acetonitrile. Despite the fact that no lithium electrolyte was added, we also detected Li(an)^+ and Li(an)_2^+ . The detection must have been due to the diffusion of the lithium ion from the external solution (50 mM of LiPF_6 in acetonitrile) through the porous glass barrier into the working electrode in the flow-through cell.

As described above, we succeeded in the on-line ESI-MS detection of one-electron oxidation products of Ru and Os metal complexes in a flow-through cell which uses only one tenth of the electrolyte concentration of the regular electrolysis experiments.

Ligand Oxidation by Electrolysis. $[\text{Ru(bpy)}_2(\text{en})]^{2+}$



Scheme 2.

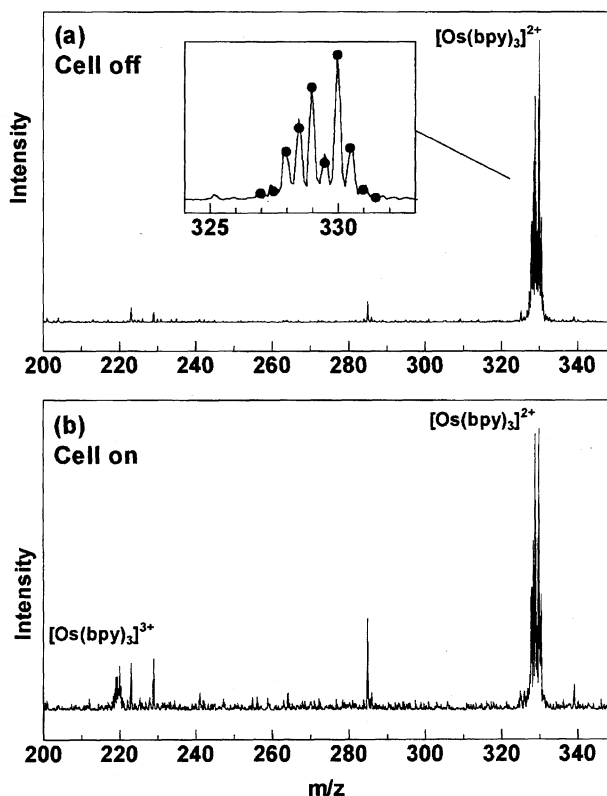


Fig. 2. ESI spectra of a 1.2 mM solution of $[\text{Os(bpy)}_3](\text{PF}_6)_2$ in acetonitrile without addition of the supporting electrolyte. The electrolysis reaction is (a) off and (b) on.

$(\text{ClO}_4)_2$ in acetonitrile has a reversible redox wave of 0.96 V (vs. SCE).¹² Meyer's group¹² reported that an oxidative dehydrogenation reaction of the diamine ligand would take place upon electrolysis at 1.15 V, and would result in the formation of a diimine complex. A reaction mechanism was proposed as Scheme 2. The $\text{Ru(II)} \rightarrow \text{Ru(III)}$ oxidation took place at the metal center, and subsequent dehydrogenation and metal reduction resulted in conversion of the diamine to diimine. They also suggested that the reaction probably proceeded through the one-electron oxidation reaction intermediate, a trivalent cation or monoimine complex. Similar reactions with $[\text{Ru(en)}_3]^{2+}$ and $[\text{Ru(phen)}_2(\text{en})]^{2+}$ (phen = 1,10-phenanthrene) have also been reported.^{13,14}

Figure 3 shows the change in the ESI spectra of a 1.0 mM solution of $[\text{Ru(bpy)}_2(\text{en})](\text{ClO}_4)_2$ caused by on and off of the electrolysis reaction. At the electrolysis off the spectra showed two ions $[\text{Ru(bpy)}_2(\text{en})]^{2+}$ ($m/z = 237$) and $[\text{Ru(bpy)}_2(\text{en})](\text{ClO}_4)^+$ ($m/z = 573$), and no ion corresponding

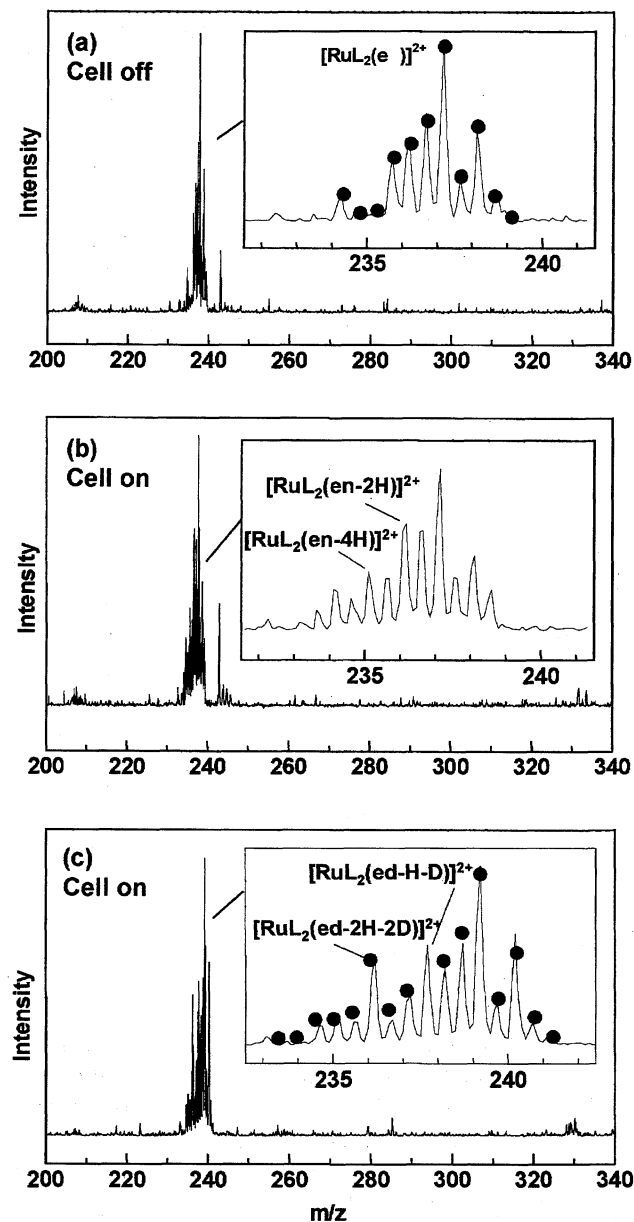


Fig. 3. ESI spectra of the 1.0 mM solution of $[\text{Ru}(\text{bpy})_2(\text{en})](\text{ClO}_4)_2$ ($L = \text{bpy}$) when the electrolysis reaction is (a) off and (b) on with the electrolysis proceeding at 0.9 V (vs. SCE). (c) the ESI spectrum of the deuterium labeled complex, $[\text{Ru}(\text{bpy})_2(\text{ed})](\text{ClO}_4)_2$ ($\text{ed} = \text{ethylene-}d_4\text{-diamine, H}_2\text{N-CD}_2\text{-CD}_2\text{-NH}_2$) during the electrolysis.

to the oxidation at the needle tip (Fig. 3a). The insert shows the isotope distribution of $[\text{Ru}(\text{bpy})_2(\text{en})]^{2+}$, which agrees with the calculated values. When the cell was turned on with the electrolysis proceeding at 1.20 V (vs. SCE), the change was observed with the ions near to m/z 237, which exhibited an isotope distribution different from that of ions before the electrolysis (Fig. 3b). The change was attributed to the formation of the electrolytic oxidation products $[\text{Ru}(\text{bpy})_2(\text{en-2H})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{en-4H})]^{2+}$, which have, respectively, two and four mass units less than $[\text{Ru}(\text{bpy})_2(\text{en})]^{2+}$. When the electrolysis of $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$ was carried out under the same conditions, no change in the ion spectra was

observed; it is therefore concluded that oxidative dehydrogenation can occur at the en, and not at the bpy, ligand. The two ions which we obtained upon electrolysis must have been the monoimine and diimine intermediate, as proposed by Meyer's group. However, we could not detect another expected intermediate, such as the one-electron oxidation product $[\text{Ru}(\text{bpy})_2(\text{en})]^{3+}$. Our previous study concerning an on-line ESI-MS of the photochemical oxidation reaction of $[\text{Ru}(\text{bpy})_2(\text{en})]^{2+}$ has shown that oxidation of the ethylenediamine complex yields the diimine via the monoimine as the reaction intermediates.¹⁵ In addition, the ligand-substitution product by acetonitrile $[\text{Ru}(\text{bpy})_2(\text{an})_2]^{2+}$, the ligand-substitution intermediate with the monodentate en ligand $[\text{Ru}(\text{bpy})_2(\text{en})(\text{an})]^{2+}$, and various kinds of oxygenated complexes, such as $[\text{Ru}(\text{bpy})_2(\text{en} + \text{O-2H})]^{2+}$, were detected. However, we did not detect any of those ions in this electrolytic oxidation reaction. In order to elucidate the structure of $[\text{Ru}(\text{bpy})_2(\text{en-2H})]^{2+}$, the deuterium-labeled ethylenediamine complex, $[\text{Ru}(\text{bpy})_2(\text{ed})](\text{ClO}_4)_2$ (where ed = ethylene- d_4 -diamine, $\text{H}_2\text{N-CD}_2\text{-CD}_2\text{-NH}_2$), was studied; the result is shown in Fig. 3c. As observed concerning an unlabeled complex, two ions of $[\text{Ru}(\text{bpy})_2(\text{ed})]^{2+}$ ($m/z = 239$) and $[\text{Ru}(\text{bpy})_2(\text{ed})](\text{ClO}_4)^+$ ($m/z = 577$) were observed with the labeled complex solution before electrolysis. Upon electrolysis, the increased intensity of the two ions $[\text{Ru}(\text{bpy})_2(\text{ed-H-D})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{ed-2H-2D})]^{2+}$, which are respectively three and six mass units less than the complex $[\text{Ru}(\text{bpy})_2(\text{ed})]^{2+}$, was observed (insert of Fig. 3c), and the increase was more significant than that observed with the unlabeled complex. It was concluded from the labeled experiment that the electrolytic oxidation products, $[\text{Ru}(\text{bpy})_2(\text{ed-H-D})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{ed-2H-2D})]^{2+}$, were the monoimine and diimin complex. Therefore, our study supports the reaction pathway proposed by Meyer et al. Furthermore, we have succeeded in the direct detection of the monoimine intermediate, which is otherwise difficult to be isolated and characterized.

In conclusion, we have developed an on-line ESI-MS for the electrolysis reaction by installing a compact and efficient flow-through cell. The cell was designed to use a porous glass tube so as to avoid any reduction of the oxidation product formed during electrolysis. The improved cell enhanced the analytical capability of ESI-MS. The system was applied to the ligand oxidation reaction of $[\text{Ru}(\text{bpy})_2(\text{en})](\text{ClO}_4)_2$. The electrolysis formed only two dehydrogenation products of $[\text{Ru}(\text{bpy})_2(\text{en-2H})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{en-4H})]^{2+}$. Their structures were determined as the monoimine and diimine complexes using the deuterium labeled complex $[\text{Ru}(\text{bpy})_2(\text{ed})](\text{ClO}_4)_2$. We have thus demonstrated ESI-MS with an electrolytic flow cell to be a useful tool for the characterization of products and for the detection of intermediates, particularly during the electrolysis of metal complexes.

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