RESEARCH ARTICLE

FTIR Spectroelectrochemical Studies on [Ru$_3$(CO)$_{12}$] and *fac*-[Re(Cl)(CO)$_3$(4bzpy)$_2$] (4bzpy = 4-benzoylpyridine)

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Abstract

Incorporation of wire mesh platinum electrodes into a standard infrared solution cell yielded an inexpensive and easy to maintain optically transparent thin layer electrochemical (OTTLE) cell, well suited for IR analysis of species with half-lives of seconds to minutes. As test bed, two reactions were investigated, which are discussed in the literature: (i) for [Ru$_3$(CO)$_{12}$] evidence was found for at least partial reversibility in the two-electron reduction process to [Ru$_3$(CO)$_{11}$]$^{2-}$, and (ii) for fac-[Re(Cl)(CO)$_3$(4bzpy)$_2$] (4bzpy = 4-benzoylpyridine) additional information concerning the two-step electron reduction of the two benzoylpyridine ligands (again partially reversible) could be obtained.

Keywords   FTIR, OTTLE, thin layer electrochemical cell, carbonyl complexes.

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1. Introduction

Electrochemical methods have been used for some forty years[1] to study the mechanism of electron transfer to obtain thermodynamic data, and, to synthesize novel organometallic complexes. Among the most frequently used methods are cyclic voltammetry, polarography, chronoamperometry and coulometry, all well reviewed[2-5] in a number of papers. In recent years spectroscopic techniques have been added [6-8] as tools for the detection and identification of reaction intermediates produced by electrochemical reactions.

In the last ten years, it became possible to perform such studies on a micro scale by direct reaction and observation in optically transparent thin layer electrochemical[9-11] (OTTLE) cells, which were first introduced by Murray et al.[12] in 1967. The technique consists of a noble metal minigrid sandwich between two glass plates entrapping electrolyte in the light path. OTTLE cells are small enough to fit into a conventional IR or UV-vis spectrophotometer, and complete electrolysis can be achieved in a very short time. By controlling the electrode potential, very reactive intermediates can be isolated and identified spectroscopically, free from residual details of redox chemical reagents.

Thus, flow OTTLE cells were used in combination with UV/visible as well as ESR spectroscopies by Compton and co-workers[13,14], while Mann and co-workers[15] studied the IR spectroelectrochemistry of substituted phosphine complexes. Kaim and co-workers[16] used a combination of cyclovoltammetry, IR and ESR spectroscopies in their study of $[M(PR_3)_2(CO)_3(L)]$ (M = Mo, W; R = isopropyl, cyclohexyl; L = THF, η^2-H$_2$) and $[M(PR_3)_2(CO)_3]_2(\mu$-L)] (μ-L = pyrazine (pz), 4,4′-bipyridine (bp), 3,6-bis(4-pyri-dyl)-1,2,4,5-tetrazine (4,4′–bptz)) complexes. Similarly, Roth and Weaver[17] also explored infrared spectroelectrochemical properties of several high nuclearity Pt carbonyl clusters in CH_2Cl_2.

Over the years, a variety of OTTLE cells have been developed; first for room temperature, but recently for low temperature studies as well[11]. The best design of OTTLE cells combines the effects of rapid electrolysis in a small volume at a relatively large semi-transparent electrode (like Pt or Au minigrid) with advantages of facile dismantling and cleaning. Other advantages include elimination of leakages, high resistance against organic solvents and easy mounting and alignment in the optical path

of various instruments. Especially the design of Krejicik et al.[18], in which a complete three-electrode set is melted in a polyethylene spacer of a standard commercial cuvette, can be used for a variety of techniques. The cell applied in this current study is based on this idea.

Metal carbonyl complexes have been favourite targets in spectroelectrochemical investigations due to their strong absorptions in the infrared spectroscopic region. Two prominent examples, $[Ru_3(CO)_{12}]$ and *fac*-$[Re(Cl)(CO)_3(4bzpy)_2]$ (4bzpy = 4-benzoyl-pyridine), were studied by several groups in the eighties. We re-investigated the electrochemical behaviour of these two complexes using a modern OTTLE cell, which permits infrared spectra to be collected on micro volumes. The former complex is known to display metal center reduction while in the latter the ligands are reduced.

$[Ru_3(CO)_{12}]$ has been shown to undergo electron-transfer chain (ETC) catalyzed nucleophilic substitution reactions[19-21] with high yield and product selectivity. In early work it has been assumed that radical anion stability is an essential feature of these ETC reactions, but the $[Ru_3(CO)_{12}]$ radical anion was unstable. The polarographic studies (one peak at –0.815 V) were interpreted in terms of a one-electron reduction, both chemically and electrochemically irreversible even at low temperatures[22]. Recently, detailed work of Cyr and Rieger[23,24], Robinson et al.[25] and Osella and Hanzlik[26] indicated a more complex mechanism, based on a two-electron reduction to firstly form $[Ru_3(CO)_{12}]$ and finally $[Ru_3(CO)_{11}]^{2-}$. In this work we attempted to clarify the assignment by adding vibrational spectroscopic data.

The degree of localization of electrons added to organometallic complexes is of general interest, particularly for complexes involving metal carbonyls. In a very elegant study, Shu and Wrighton[27] demonstrated that upon one-electron reduction of fac-$[Re(Cl)(CO)_3(4bzpy)_2]$, the added electron is not delocalized over the ligands, but rather centered on one of the 4bzpy ligands to form one 4bzpy anion. Furthermore, a two-electron reduction generates a dianionic complex with one electron localized on each pyridyl ketone ligand. Their detailed study can serve as an excellent benchmark for spectroscopic separation of neutral and reduced species, and in this work we attempted to repeat some of these experiments and add further information.

2. Experimental

The OTTLE cell (Fig. 1) manufactured at the *Max-Planck Institut für Strahlenchemie*, Mülheim, is based on the design of Krejicik et al.[18], with a complete three electrode set (platinum mesh and silver wire reference) melted in a polyethylene spacer of a standard commercial (Perkin-Elmer) cuvette. A Teflon holder of 10mm thickness aligns the CaF_2 salt windows, the spacer, guides the electrical wiring and holds the connection plug. The platinum electrodes are made of 0.06 mm Pt-mesh (Goodfellow, aperture 0.25 mm), which yields 65% transmittance. The spacer of 0.9 mm path length is formed by adjusting mesh strips and silver wire between pre-shaped thin polyethylene sheets, followed by baking the setup under constant pressure at 140^0 C for 20 minutes. The spacer is ready for use after cleaning and removal of excess polymer.
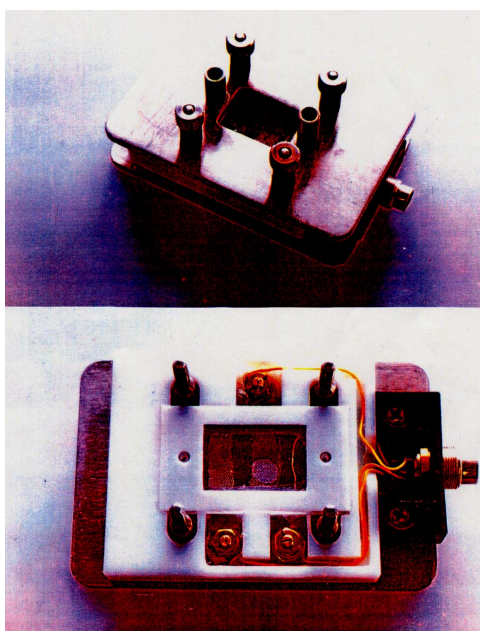

Figure 1   The OTTLE Cell. Top photo: assembled; bottom photo: top cover removed.

The room-temperature solutions, 10^{-2} mol L^{-1} [Ru$_3$(CO)$_{12}$] and 10^{-3} mol L^{-1} of *fac*-[Re(Cl)(CO)$_3$(4bzpy)$_2$], were prepared in argon-purged dry CH_2Cl_2 and CH_3CN, respectively, with 0.1 mol L^{-1} [n-Bu$_4$N]PF$_6$ as supporting electrolyte. Electrochemical measurements were made with an α Laboratorni Pristroje Praha model PA4 polarographic analyzer with 4106 XY recorder (current, 10 µA, scan rate, 5 mV/s, X,

0.2 V/cm and Y, 1.0 V/cm). IR spectra were collected on a Perkin Elmer 1720 FTIR, using the same electrochemical conditions as for the cyclic voltammetry.

3. Results and Discussion

Early electrochemical work on the reduction of $[Ru_3(CO)_{12}]$ was interpreted in terms of a chemically irreversible one-electron reduction process[22]. Recent electrochemical studies by Rieger et al. [23,24] suggest that $[Ru_3(CO)_{12}]$ undergoes a chemically irreversible two-electron reduction process, while this view was supported by Robinson et al.[25]. Our spectro-electrochemical study of the $[Ru_3(CO)_{12}]$ in dry CH_2Cl_2 with the FTIR indicates that a partial chemically reversible reaction takes place upon reduction as some IR bands (Fig. 2, a, b and c) were obtained for the starting complex upon reverse scan. The amplitude of the reverse scan bands, however, was not as large as the original ones.
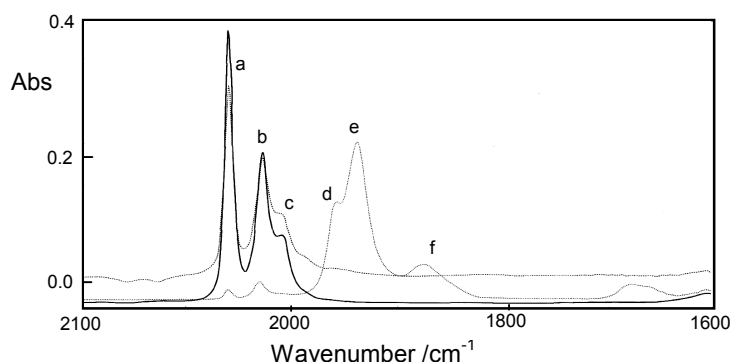

Figure 2 FTIR spectral changes observed during reduction and oxidation of $[Ru_3(CO)_{12}]$ in CH_2Cl_2 containing 0.1 mol L^{-1} $[n-Bu_4N]PF_6$ at 0, −1.4 and 0 V (scan reverse), respectively.

The cyclic voltammogram (Fig. 3) at 5 mV/sec (25 °C), with a Ag-electrode showed electrochemical reduction steps with a major peak potential (2) at −1.4 V and a small peak potential (1) at −1.05 V. The oxidation of the initially formed reduction product (2) occurred at −0.8 V (3) which is consistent with Rieger's[24] and Robinson's[25] assignments (-0.6 V to −0.8 V). Although Robinson[25] in CH_2Cl_2 did not observe peak 1 under rigorous dry conditions, Rieger's work[24] in carefully dried CH_2Cl_2 but atmosphere exposed, exhibited a small feature resembling peak 1. Robinson et al. presented evidence suggesting that this peak might be due to the product of a reaction of $[Ru_3(CO)_{12}]^{2-}$ with

water. Although our experiment was carried out in dry CH_2Cl_2, the drying was probably not rigorous enough to suppress the formation of peak 1.
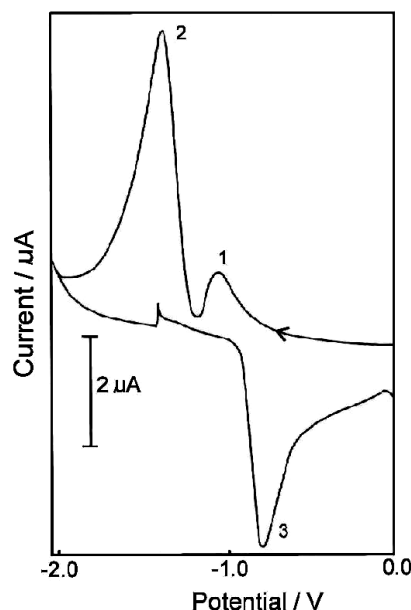

Figure 3 Cyclic voltammogram for the reduction and oxidation of $[Ru_3(CO)_{12}]$ in CH_2Cl_2 containing 0.1 mol L^{-1} $[n-Bu_4N]PF_6$, scan rate = 5 mV/s.
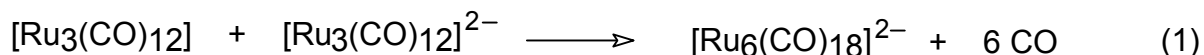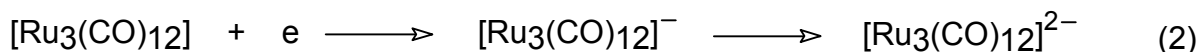
The reduction scheme proposed by Rieger et al.[23,24] from their electrochemical work was a two-electron reduction and ring opening to give $[Ru_3(CO)_{12}]^{2-}$ (via a triangular $[Ru_3(CO)_{12}]^{-}$ radical anion intermediate) which is rapidly consumed by undergoing CO loss, followed by irreversible ring closure to give the $[Ru_3(CO)_{11}]^{2-}$ dianion. From our cyclic voltammogram, $i_a/i_c = 1$, which indicates some partial chemical reversibility which agrees with the proposals of Rieger et al.[23,24] and of Robinson et al.[25] that the reaction is chemically reversible. However, since the potentials E_2 and E_3 are widely separated ($\Delta_{23} = 600$ mV), this process is electrochemically irreversible. Since diffusion is very limited in the OTTLE cell, the CO lost in the disproportionation process is not liberated but retained in the solution. Thus, the reduction product {i.e. $[Ru_3(CO)_{11}]^{2-}$} can trap some of the CO in the thin layer and reverse the process when it is oxidized and then regenerate $[Ru_3(CO)_{12}]$.

Osella and Hanzlik[26] in their study suggest a solvent dissociation of $[Ru_3(CO)_{12}]$, that in a way agrees with the previous suggestion of Rieger et al.[23,24] and of Robinson et al.[25] in which an irreversible two-electron reduction process was proposed. However,

Osella and Hanzlik[26] further mentioned that coproportionation and self-exchange reactions could occur, depending on the relative concentration of the species. They concluded that a two-electron polarographic wave should be expected under certain conditions. At concentration > 1 mmol L^{-1} the total limiting current is between a one- and two-electron stoichiometry. At higher concentration of depolarizer, the limiting current tends to favour the one-electron process, which can be explained by means of a coproportionation route, most likely the redox condensation reaction[26]:

$$[Ru_3(CO)_{12}] \; + \; [Ru_3(CO)_{12}]^{2-} \; \longrightarrow \; [Ru_6(CO)_{18}]^{2-} \; + \; 6\,CO \qquad (1)$$
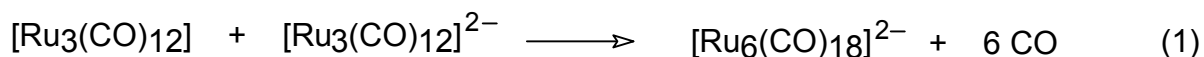
Robinson et al.[25], in their work had indicated that the oxidation of octahedral $[Ru_3(CO)_{18}]^{2-}$ is an over-all two-electron process but chemically irreversible under 'normal' conditions. They also concluded that the reaction could become chemically reversible in dilute CH_2Cl_2 solution at 293 K provided that water and oxygen are completely removed. Thus, another way of explaining the IR results is via the coproportionation route, which would be reversible at the concentration and temperature employed for this study[25,26]. The small anodic peak at −1.05 V (Fig. 2) due to the intermediate $[Ru_3(CO)_{12}]^{2-}$ (formed by two-electron reduction reaction) could be explained to have diminished as a result of the coproportionation reaction (redox condensation) the parent complex, $[Ru_3(CO)_{12}]$. The final product is then proposed to be $[Ru_6(CO)_{18}]^{2-}$, which gave the major peak of −1.4 V in the cyclic voltammogram as given in equations (2) and (1):

$$[Ru_3(CO)_{12}] \; + \; e \; \longrightarrow \; [Ru_3(CO)_{12}]^{-} \; \longrightarrow \; [Ru_3(CO)_{12}]^{2-} \qquad (2)$$

$$[Ru_3(CO)_{12}] \; + \; [Ru_3(CO)_{12}]^{2-} \; \longrightarrow \; [Ru_6(CO)_{18}]^{2-} \; + \; 6\,CO \qquad (1)$$

Earlier work of Robinson et al.[25] and of Nadjo et al.[28,] have shown that the half-life of the triangular or the opened $[Ru_3(CO)_{12}]^{-}$ moiety is < 10^{-6} s, so the monoanion radical is only being formed at the electrode surface. Since its reaction is thermodynamically favoured, it is immediately reduced to the dianion. The work of Robinson et al.[25] again showed that the voltammetric response of $[Ru_3(CO)_{12}]$ was not dependent on the scan rate. However, our IR spectral data suggests that this latter route of coproportionation would be very unlikely in the OTTLE cell. The IR data showed spectral changes in the

CO stretching region for the $[Ru_3(CO)_{12}]$ upon electrochemical reduction in CH_2Cl_2 containing 0.1 mol L^{-1} [n-Bu$_4$N]PF$_6$ (Fig 2). $[Ru_3(CO)_{12}]$ initially exhibits a characteristic three-band IR spectrum in the CO stretching region at 2060 (a), 2031 (b) and 2010 cm^{-1} (c), respectively. Upon reduction of $[Ru_3(CO)_{12}]$, the energy of the CO stretching absorptions of the complex shifts to lower energy at 1961 (d), 1943 (e) and 1880 cm^{-1} (f), respectively. These correspond with the IR absorption bands reported by Bhattacharyya et al.[29] for the $[Ru_3(CO)_{11}]^{2-}$ cluster (the three-band pattern remains). This would suggest the disproportionation route leading to the formation of the $[Ru_3(CO)_{11}]^{2-}$ as the likely route in the reduction process of $[Ru_3(CO)_{12}]$ in the OTTLE cell. When the potential is scan reversed, the new bands disappear and the original bands of $[Ru_3(CO)_{12}]$ are regenerated although not up to the same amplitude as the starting material, indicating some partial chemical reversibility of the reaction. It is also worth mentioning that no different bands appeared when the spectra were collected between 0 and -2.0 V and during the reverse scan, thus supporting the proposal of Rieger that the intermediate species are short-lived [23,24].
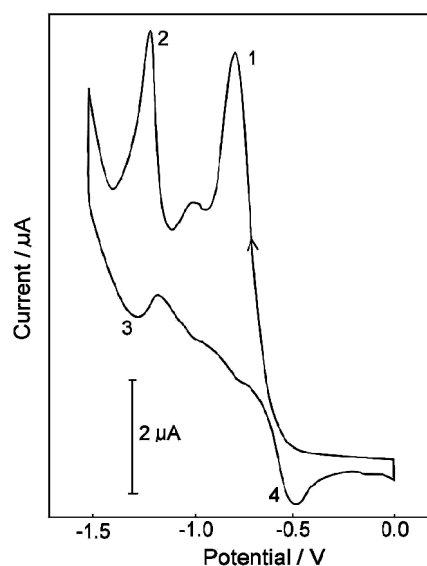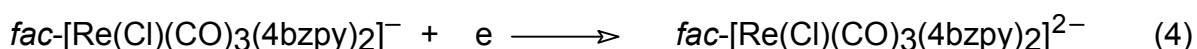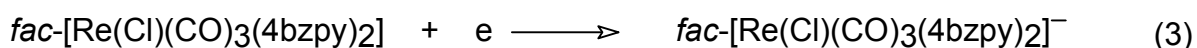

Figure 4 Cyclic voltammogram for the reduction and oxidation reaction of *fac*-[Re(Cl)(CO)$_3$(4bzpy)$_2$] in acetonitrile containing 0.1 mol L^{-1} [n-Bu$_4$N]PF$_6$, scan rate = 5 mV/s.

The cyclic voltammogram of *fac*-[Re(Cl)(CO)$_3$(4bzpy)$_2$] at 5 mV/s in CH$_3$CN containing 0.1 mol L^{-1} [n-Bu$_4$N]PF$_6$ shown in Fig. 4 exhibits one-electron reduction waves at E$_{1/2}$ −0.8 V and another at −1.2 V *vs*. the Ag-electrode (Fig.4). According to Shu and Wrighton[27] (from their IR and UV studies), the lowest unoccupied molecular orbitals of the rhenium complex are the two independent π orbitals of each of the 4bzpy ligands. In a two-electron process, the first added electron is proposed to be primarily localized on one of the 4bzpy ligands, the second electron mainly localized on the other 4bzpy ligand, while the dianion is primarily a diradical species as illustrated in equation (3) and (4):

$$\textit{fac}\text{-}[Re(Cl)(CO)_3(4bzpy)_2] \ + \ e \longrightarrow \ \textit{fac}\text{-}[Re(Cl)(CO)_3(4bzpy)_2]^{-} \qquad (3)$$

$$\textit{fac}\text{-}[Re(Cl)(CO)_3(4bzpy)_2]^{-} + \ e \longrightarrow \ \textit{fac}\text{-}[Re(Cl)(CO)_3(4bzpy)_2]^{2-} \qquad (4)$$

Our IR data also showed changes in the CO stretching region for the complex upon electrochemical reduction in CH$_3$CN containing 0.1 mol L^{-1} [n-Bu$_4$N]PF$_6$ in an OTTLE cell. The *fac*-[Re(Cl)(CO)$_3$(4bzpy)$_2$] complex exhibits a characteristic three-band IR spectrum in the CO stretching region at 2027 (a), 1923 (b) and 1895 cm^{-1} (c) respectively, as shown in Fig 5. Upon a one-electron reduction, the intensities of the IR absorption bands in the CO region decrease and new bands appear at 2013 (d), 1903 (e) and 1881 cm^{-1} (f). When the electrode potential is increased, the complex becomes two-electron reduced and the carbonyl absorptions for the mono-anionic complex disappear, concomitant with the growth of three bands at 2001 (g), 1886 (h) and 1865 cm^{-1} (i), respectively, corresponding to the dianion *fac*-[Re(Cl)(CO)$_3$(4bzpy)$_2$]$^{2-}$ (Fig. 6).
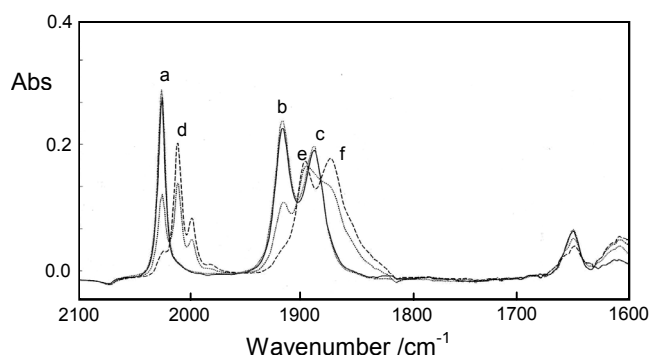

Figure 5 FTIR spectral changes observed during reduction of *fac*-[Re(Cl)(CO)$_2$(4bzpy)$_2$] in acetonitrile containing 0.1 M [n-Bu$_4$N]PF$_6$ at 0 and −0.8 V, respectively.

These results agree well with the IR data of Shu and Wrighton[27] for the mono and dianion of the rhenium complex. The two-electron reduced species can be generated and shows unique IR bands that are well resolved from both the starting complex (a, b and c) and the immediate one-electron reduced state (d, e and f). When the potential is scan reversed, the new bands of the dianion complex disappear and the original ones of *fac*-[Re(Cl)(CO)$_3$(4bzpy)$_2$] are regenerated (a, b and c), though again, not up to the same amplitude as the starting material, indicating only partial chemical reversibility of the reaction (Fig. 6).
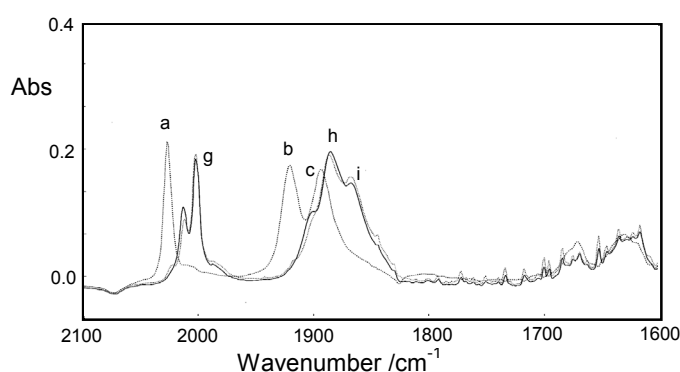

Figure 6 FTIR spectral changes observed during reduction and oxidation of *fac*-[Re(Cl)(CO)$_3$(4bzpy)$_2$] in acetonitrile containing 0.1 M [n-Bu$_4$N]PF$_6$ at −1.2 and 0 V (scan reverse), respectively.

4. Conclusion

The spectroelectrochemical data obtained from the complexes [Ru$_3$(CO)$_{12}$] and *fac*-[Re(Cl)(CO)$_3$(4bzpy)$_2$] allowed comparison of the IR spectra of the neutral and the reduced species. The spectral and electrochemical data obtained suggest partial chemically reversible two-electron reduction processes for the two complexes, respectively. The IR and electrochemical data obtained support the view that in the OTTLE cell, the reduced product - [Ru$_3$(CO)$_{11}$]$^{2-}$ from [Ru$_3$(CO)$_{12}$] - can trap the CO to regenerate some of the neutral complex. For the *fac*-[Re(Cl)(CO)$_3$(4bzpy)$_2$], the IR spectral data obtained indicated that the reduced metal complex has one electron localized on each of the 4bzpy ligands.

References

1   J. A. Page and G. Wilkinson, *J. Am. Chem. Soc.,* 1952, **74**, 6149.

2   A. J. Bard and L. Faulkner, *Electroanalytical Methods*, Wiley, New York, 1980.

3   *Laboratory Techniques in Electrochemistry: A series of Advances*, (P.T. Kinnssinger and W.R. Heineman, eds.), Vol.15, Marcel Dekker, New York, 1984.

4   P. H. Rieger, *Electrochemistry*, Chapman and Hall, New York, 1993.

5   R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.

6   R. L. McCreey, *Prog. Anal. Spectrosc.*, 1988, **11**, 141.

7   F. Battaglini, E. J. Calvo and F. J. Doctorovich, *J. Organomet. Chem.*, 1977, **547**, 1.

8   *Spectroelectrochemistry, Theory and Practice*, (R. J. Gale, ed.), Plenum Press, New York, 1988.

9   D. A. Scheson, S. Saranpagani and F. L. Urbach, *Anal. Chem.*, 1985, **57**, 1501.

10   K. Rajeshwar, R. O. Lezna and N. R. de Tacconi, *Anal. Chem.*, 1992, **64**, 429A.

11   F. Hartl, H. Luyten, H. A. Niewenhuis and G. C. Schoemaker, *Appl. Spectr.*, 1994, **48**, 1552.

12   R. W. Murray, W. R. Heinemann and G. W. O'Dom, *Anal. Chem.*, 1967, **39**, 165.

13   R. G. Compton, H. C. Filscher, R. G. Wellington and J. Winkler, *J. Phys. Chem.,* 1992, **96**, 8153.

14   R. G. Compton, J. Winkler, D. J. Riley and S. D. Bearpark, *J. Phys. Chem.* 1994, **98**, 6818.

15   C. A. Blaine, J. E. Ellis and K. R. Mann, *Inorg. Chem.*, 1995, **34**, 1552.

16   W. Bruns, W. Kaim, E. Waldhor and M. Krejcik, *Inorg. Chem.*, 1995, **34**, 663.

17   J. D. Roth, M. J. Weaver, *J. Anal. Chem.*, 1991, **63**, 1603.

18   M. Krejcik, M. Danek and F. Hartl, *J. Electroanal. Chem.*, 1991, **317**, 179.

19   G. J. Bezems, P. H. Rieger and S. J. Visco, *J. Chem. Soc., Chem. Commun.*, 1981, 265.

20   A. Darchen, C. Mahe and H. Patin, *J. Chem. Soc., Chem. Commun.,* 1982, 243.

21   M. I. Bruce, D. C. Kehoe, J. G. Matisons, B. K. Nicholson, P. H. Rieger and M. L. Williams, *J. Chem. Soc., Chem. Commun.,* 1982, 442.

22   A. M. Bond, P. A. Dawson, B. M. Peake, B. H. Robinson and J. Simpson, *Inorg. Chem.*, 1997, **16**, 2199.

23   J. E. Cyrr, J. A. de Gray, D. K. Gosser, E. S. Lee and P. H. Rieger, *Organometallics*, 1985, **4**, 950.

24   J. E. Cyrr and P. H. Rieger, *Organometallics*, 1991, **10**, 2153.

25   A. . Downard, B. H. Robinson, J. Simpson and A. M. Bond, A., *J. Organomet. Chem.*, 1987, **320**, 363.

26   D. Osella and J Hanzlik, *Inorg. Chim. Acta,* 1993, **213**, 311.

27   C. Shu and M. S. Wrighton, *Inorg. Chem.*, 1988, **27**, 4326.

28   L. Nadjo and J. M. Saveant, *Electroanal. Chem.*, 1973, **48**, 113.

29   A. A. Bhattacharyya, C. C. Nagel and S. G. Shore, *Organometallics,* 1983, **2**, 1187.