Spectroelectrochemistry and Excited-state Absorption Spectroscopy of Rhenium(I) α,α′-Diimine Complexes

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Thin-layer electrochemistry and spectroelectrochemistry in 0.1 mol dm^{-3} NBu_4PF_6–dmf (dmf = dimethylformamide) have been used to characterize spectroscopically the sequentially reduced forms of $[Re(bipy)(CO)_3Cl]$, $[Re(dpp)(CO)_3Cl]$ and $[\{Re(CO)_3Cl\}_2(dpp)]$ [dpp = 2,3-bis(2-pyridyl)pyrazine, bipy = 2,2′-bipyridine]. Following the first reduction of each complex, the spectra exhibit similar absorption features in the near-UV region from 350 to 400 nm with a tailing absorption to *ca.* 500–600 nm. The excited-state absorption spectra of $[Re(dpp)(CO)_3Cl]$ and $[\{Re(CO)_3Cl\}_2(dpp)]$ have also been obtained and exhibit similar features as in the spectroelectrochemical measurements. The spectra are consistent with reduction of the α,α′-diimine ligand and are dominated by $\pi \longrightarrow \pi^*$ transitions of the ligand radical anion. Addition of a second electron to the monometallic complexes yields spectra that are characterized by a broad absorption band in the range 530–580 nm (ε = 10 900–12 100 dm^3 mol^{-1} cm^{-1}). In comparison, addition of a second electron to $[\{Re(CO)_3Cl\}_2(dpp)]$ also yields a broad absorption at 550 nm (ε = 8800 dm^3 mol^{-1} cm^{-1}) and loss of the absorption at 357 nm, which is analogous to the spectrum for the doubly reduced $[Re(dpp)(CO)_3Cl]$ complex. Further reduction of the bimetallic complex results in identical spectral features as the doubly reduced complex with the main difference being an increase in absorbance over the entire UV/VIS region and a red shift of the lowest energy absorption to 576 nm. The spectroelectrochemical measurements for $[\{Re(CO)_3Cl\}_2(dpp)]$ suggest the second and third reductions result in reduction of the metal centres contrary to previous reports for electron localization in the bimetallic complex, which describe the second reduction as ligand based.

Photochemical and photophysical properties of metal-to-ligand charge-transfer (m.l.c.t.) excited state(s) of transition-metal complexes with chelating heteroaromatic ligands have been the focus of extensive investigations.[1–5] The m.l.c.t. excited state(s) of d^6 transition-metal complexes have been widely studied since the first report[6] of luminescence from $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) and the demonstration by Lehn's group[7] that $[Ru(bipy)_3]^{2+}$ acts as a photosensitizer for the photoinduced generation of H_2 and O_2 from H_2O. Although not as extensive as ruthenium(II) photochemistry, the photochemistry and photophysics of m.l.c.t. excited state(s) of rhenium(I) tricarbonyl complexes with chelating α,α′-diimine ligands have evolved in a similar manner.[3,4] Initial characterization of the luminescence properties of monometallic complexes of the type $[Re(L\text{–}L)(CO)_3X]$, where L–L is a bidentate α,α′-diimine ligand and X is a halogen, MeCN, PhCN, pyridine, piperidine, $SnPh_3$ or $GePh_3$ has been reported by Wrighton and co-workers.[8] Subsequently, $[Re(bipy)(CO)_3X]$ (X = Cl or Br) complexes have been used as combination photosensitizers and catalysts for the reduction of CO_2 to CO.[9]

Recent efforts in ruthenium(II) and rhenium(I) photochemistry have been directed towards the characterization of multimetallic or supramolecular complexes as multielectron redox reagents or models for intermolecular electron transfer.[10–12] Two popular types of multimetallic complexes are the homobimetallic ruthenium(II)[13] or rhenium(I)[14] complexes derived from the combination of two fragments of either $[Ru(bipy)_2]^{2+}$ or $[Re(CO)_3Cl]$ with a chelating nitrogen bridging ligand (L^b). Optical excitation to produce m.l.c.t. excited states in these complexes formally involves the transfer of an electron from the metal to a low-lying π^* orbital of the bridging ligand. When multiple heteroaromatic ligands are present, the nature of the charge-transfer localization is not always clear. For these and other complexes with m.l.c.t. states involving heteroaromatic ligands, thin-layer transmission spectroelectrochemical methods are useful to characterize the spectral features of the reduced complexes.[15–17] The spectra generated by *in situ* outer-sphere reduction of the heteroaromatic ligand(s) can be viewed to a first approximation as the spectrum of the excited state, and in combination with emission spectroscopy, provide strong evidence for charge localization of the optical transition.[18]

Several reports have appeared that describe the synthesis and characterization of $[\{Re(CO)_3Cl\}_2L^b]$ complexes for a variety of bridging ligands.[14] The electrochemistry of these complexes is typically characterized by multiple reduction processes and a single irreversible oxidation process. Assignments of the electron localization have been made based on studies of the monometallic analogue, changes in the redox properties as a function of varying the Cl^- ligand, and by analogy to similar $[\{Re(CO)_3Cl\}_2L^b]$ complexes with different L^b ligands and to $Ru^{II}\text{–}L^b$ complexes. It is evident that subtle changes in the ligand L^b can affect the ordering of molecular orbitals and consequently the electron localization.[14h,j] Therefore, much care must be taken to utilize direct measurements on the complexes in question when assignments are made. Spectroelectrochemical measurements provide this direct comparative information and facilitate localization assignments.[15–17]

We have been interested in the electrochemical and spectroscopic properties of the bimetallic complex, $[\{Re(CO)_3Cl\}_2(dpp)]$ [dpp = 2,3-bis(2-pyridyl)pyrazine], since the synthesis and characterization were first reported in 1990.[14e,f,h] In this manuscript, we have characterized the sequentially reduced forms of $[\{Re(CO)_3Cl\}_2(dpp)]$ by thin-layer electrochemical and spectroelectrochemical techniques, and have examined carefully the localization of the electron transfer with respect to this data. Thin-layer electrochemical and spectroelectrochemical measurements of [Re(dpp)$(CO)_3Cl$] and [Re(bipy)$(CO)_3Cl$] as well as excited-state absorption measurements of [Re(dpp)$(CO)_3Cl$] and [$\{Re(CO)_3Cl\}_2$(dpp)] have also been conducted and are reported herein to aid in the discussion.

Experimental

Materials.—The compounds [$Re(CO)_5Cl$], dpp and bipy were obtained from Aldrich and used without further purification. Dimethylformamide (dmf, Burdick and Jackson), methanol (Burdick and Jackson) and acetonitrile (Fisher) were used for all the electrochemical and spectroscopic measurements. Tetra-*n*-butylammonium hexafluorophosphate (NBu_4PF_6, Aldrich) was used as supporting electrolyte in all electrochemical measurements. Prior to use, the NBu_4PF_6 was recrystallized from ethanol and dried at 70 °C *in vacuo*. All other reagents were certified ACS grade and were used without further purification. No significant electroactive impurities were detected in either the solvent for electrochemistry or the supporting electrolyte.

The rhenium(I) carbonyl complexes were prepared by slight modification of literature procedures.[8c,14f] The complex [Re(dpp)$(CO)_3Cl$] was prepared by mixing dpp and [$Re(CO)_5Cl$] in a 3:1 mole ratio in methanol (100 cm^3). The mixture was refluxed under Ar for 40 h and cooled to ambient temperature. After the solution was concentrated, diethyl ether was added and the mixture was cooled in an ice-bath to obtain an orange precipitate. The precipitate was filtered, dissolved in the minimum amount of methylene chloride, and flash precipitated with diethyl ether. The product was collected, washed with diethyl ether and boiling methanol, and finally dried *in vacuo* at 40 °C. [$\{Re(CO)_3Cl\}_2$(dpp)] was obtained by refluxing a 3:1 mole ratio of [$Re(CO)_5Cl$] to dpp in methanol under Ar for 40 h. A red precipitate formed during the reaction and was collected by filtration of the hot solution. The product was washed with diethyl ether and boiling methanol, and vacuum dried at 40 °C. The complex [Re(bipy)$(CO)_3Cl$] was prepared by refluxing a 3:1 mole ratio of bipy to [$Re(CO)_5Cl$] in toluene (100 cm^3) under Ar for 12 h. The precipitate was collected and purified in a similar fashion as [Re(dpp)$(CO)_3Cl$], except methanol was not used to wash the product. All compounds gave satisfactory elemental analyses and UV/VIS spectra consistent with previous literature reports.[8c,14f]

Instrumentation.—A Varian Model Cary 5E UV/VIS/NIR spectrophotometer was used for all absorption measurements. Electrochemical experiments were performed with a Bioanalytical Systems, Inc. (BAS) CV-27 potentiostat coupled to an Allen Datagraph Model 725M XYT recorder. The potentials were monitored in the electrochemical experiments by a Keithley Model 179A digital multimeter. Optically-transparent thin-layer electrodes (OTTLEs) were constructed from quartz microscope slides (ESCO) and 100 wires per inch gold minigrid (Buckbee Mears) according to the design of DeAngelis and Heineman.[19] For conventional cyclic voltammetry the working electrode was a platinum disc electrode (BAS, PDE). An aqueous Ag–AgCl (BAS, Model RE1) and a platinum wire were used as reference and auxiliary electrodes, respectively.

Nanosecond[20] and picosecond[21] flash-photolysis experiments were carried out at the Notre Dame Radiation Laboratory and Argonne National Laboratory, respectively, with laser systems that have been previously described.

Methods.—Solutions of the complexes (1.0 mmol dm^{-3}) containing 0.1 mol dm^{-3} NBu_4PF_6 were prepared in dmf for the electrochemical and spectroelectrochemical measurements. All solutions were purged with argon in a glove-bag prior to the electrochemical experiments. For spectroelectrochemistry experiments, the sample solutions were transferred *via* pipette into the solution cup which housed the OTTLE working electrode, Ag–AgCl reference electrode and platinum auxiliary electrode. Solutions entered the OTTLE cell *via* capillary action. The entire assembly was placed in a plexiglas box with quartz optical windows and transferred to the spectrophotometer compartment, which was previously purged for 20 min with Ar. An Ar purge was maintained throughout the experiment. For potential-step spectroelectrochemistry experiments with the OTTLE cell, a potential 90 mV more negative than the E_{pc} value for each reduction wave from conventional cyclic voltammetry at the PDE was applied. Absorption spectra were recorded when the solution concentrations reached equilibrium at the applied potential; typically 2–8 min were determined to be sufficient to obtain equilibrium values of [oxidant]/[reductant] by observation of a steady-state spectrum.

Nanosecond flash photolysis experiments were conducted on an Ar-purged solution of [Re(dpp)$(CO)_3Cl$] in a 3 × 7 mm quartz cell. Solutions were prepared such that the absorbance at the excitation wavelength (354.7 nm) was ≈ 0.4. Typical pulse energies were 50 mJ. In the picosecond experiments, an acetonitrile solution of [$\{Re(CO)_3Cl\}_2$(dpp)] was also prepared with an absorbance of ≈ 0.4 at the excitation wavelength (412 nm). The solution was contained in a 1 cm cell and was stirred during the experiment. Pulses of 3 μJ (150 fs, 1.27 kHz) were employed.

Results and Discussion

Electrochemical Measurements.—Thin-layer electrochemical and conventional bulk solution electrochemical measurements were performed in dmf and are summarized in Table 1. The electrochemical data are in agreement with previous voltammetric measurements in acetonitrile, methylene chloride and dmf.[3,14e,f,h,j] Thin-layer cyclic voltammograms for the first ligand reduction of [Re(bipy)$(CO)_3Cl$], [Re(dpp)$(CO)_3Cl$] and [$\{Re(CO)_3Cl\}_2$(dpp)] indicate that all three complexes exhibit reversible behaviour on the first cycle; however, after multiple cycles only [$\{Re(CO)_3Cl\}_2$(dpp)] exhibits reversible behaviour. The monometallic complexes show a slight decrease in the anodic peak current and also a small shift ($\approx$20–30 mV) in peak potentials on subsequent scans. Previous electrochemical measurements at conventional electrodes in acetonitrile indicate that labilization of chloride from [Re(bipy)$(CO)_3Cl$] occurs following reduction and leads to Re–Re dimer formation.[22] Similar chemistry may occur on the thin-layer time scale for [Re(bipy)$(CO)_3Cl$] and [Re(dpp)$(CO)_3Cl$], although not as extensively in dmf or for the dpp mono- or bi-metallic complexes, see below. Extension of the negative potential limit to −2.0 V reveals irreversible reduction features similar to conventional cyclic voltammetry measurements although the peak potentials from the thin-layer cyclic voltammetry experiments are approximately 0.2 V more negative due to the uncompensated resistance inherent to the OTTLE cell configuration.[23]

Spectroelectrochemical Measurements.—(*i*) [Re(bipy)$(CO)_3Cl$]. Fig. 1 depicts the absorption spectra recorded for the bipy complex after sequential potential steps from 0.0 (*a*) to −1.34 (*b*) and then to −1.92 (*c*) V. One minute after a potential step to −1.34 V, absorption bands at 362 nm and at 509 nm are observed. These bands grow in intensity with the limiting spectrum reached after 3 min equilibration time. After 5 min, the intensity at 362 nm decreases and a shoulder grows in at $\approx$576 nm. Similar features for [Re(L–L)$(CO)_3Cl$] complexes have been observed in flash-photolysis experiments. Kalyanasundaram[3] has recorded the m.l.c.t. excited-state transient absorption spectrum of [Re(bipy)$(CO)_3Cl$] in degassed acetonitrile solution and found two maxima at 370 and 475 nm. Additional nanosecond laser photolysis experiments showed that reductive quenching by various amines resulted in formation of [Re(bipy)$(CO)_3Cl]^-$ with absorption maxima at 365

Table 1 Electrochemical data for 1.0 mmol dm^{-3} solutions of [Re(L–L)(CO)$_3$Cl] (L–L = bipy or dpp) and [{Re(CO)$_3$Cl}$_2$(dpp)] in 0.1 mol dm^{-3} NBu$_4$PF$_6$–dmf

	Conventional cyclic voltammetry[a]				Thin-layer voltammetry[d]		
	$E^{\circ\prime}$[b]	E_p[c]	E_p[c]	E_p[c]	$E^{\circ\prime}$[b]	E_p[c]	E_p[c]
[Re(bipy)(CO)$_3$Cl]	−1.21	—	−1.83	+1.55	−1.23	—	−1.93
[Re(dpp)(CO)$_3$Cl]	−0.88	—	−1.58	+1.48	−1.02	—	−1.68
[{Re(CO)$_3$Cl}$_2$(dpp)]	−0.40	−1.06	−1.55	+1.63	−0.48	−1.21	−1.72

[a] V *vs.* Ag–AgCl; scan rate = 100 mV s^{-1}; platinum disc electrode. [b] $E^{\circ\prime} = (E_{pc} + E_{pa})/2$. [c] Peak potential from cyclic voltammetry. [d] Scan rate is 2 mV s^{-1}, gold OTTLE.

and 510 nm and the oxidized amines. In a spectroelectrochemical investigation of the related complex [Re(dmbipy)(CO)$_3$Cl] (dmbipy = 4,4′-dimethyl-2,2′-bipyridine), Breikss and Abruña[24] detected an absorption maximum at 512 nm following reduction with slow growth of two peaks at 598 and 792 nm, and a decrease in the 512 nm absorption for [Re(dmbipy)(CO)$_3$Cl]$^-$. The new peaks were attributed to the formation of a metal–metal bonded dimer species following slow loss of Cl$^-$ similar to the behaviour reported for [Re(bipy)(CO)$_3$Cl].[22] The absorption bands at 362 and 509 nm, which are observed in this investigation, are therefore consistent with a reduced bipy ligand in [Re(bipy)(CO)$_3$Cl]$^-$ and the shoulder at ≈576 nm is consistent with slow loss of Cl$^-$. Prominent absorption features that might indicate dimer formation are not readily apparent and indicate minimal ligand loss in dmf under these experimental conditions.

Fig. 1(*c*) illustrates the absorption spectrum after the second reduction at −1.92 V. A broad structured band, with a maximum at ≈570 nm is observed. In the UV region, a plateau at 343 nm with a low-energy shoulder and a peak at 277 nm are observed. The highest energy UV peak shows an increased absorbance and is slightly blue shifted compared to the spectrum after the first reduction. At this potential, the solution is intensely purple; the colour has been attributed to [Re^0(bipy)(CO)$_3$]$^-$, which results from the reduction of [Re(bipy)(CO)$_3$Cl]$^-$ followed by rapid loss of Cl$^-$ and dimer formation.[22] Any dimer which may exist in solution is presumably reduced to the anionic species. In this work, the chemistry and electrochemistry appear reversible in the OTTLE cell because upon reoxidation at 0.0 V for ≈1 h, the spectrum attributed to the parent complex is quantitatively regenerated. Therefore, it is reasonable to believe the purple colour is unique to the doubly reduced species in dmf.

(*ii*) [Re(dpp)(CO)$_3$Cl]. Fig. 2 shows the absorption spectra recorded for [Re(dpp)(CO)$_3$Cl] after sequential potential steps from 0.0 (*a*) to −1.00 (*b*) and −1.67 (*c*) V. The absorption spectrum observed at −1.00 V [Fig. 2(*b*)] shows similar features as the singly reduced bipy complex. An absorption band appears at ≈370 nm; however, a distinct peak at 509 nm is absent. A tailing shoulder extends out to ≈550 nm and a slight increase in absorbance is observed at wavelengths > 700 nm. Repetitive scans during the 7 min equilibration period after the potential step reveal two isosbestic points at 344 and 280 nm, which indicates minimal decomposition. Compared to the bipy complex, the dpp monometallic complex appears to be more stable in dmf solution with respect to Cl$^-$ loss after the first reduction. After stepping the potential further to −1.67 V [Fig. 2(*c*)], a relatively broad peak at 530 nm and a smaller band at 422 nm are obtained after 1 min of electrolysis. The UV absorption typical of the intraligand π–π* transition near 300 nm increases slightly. After continued electrolysis at −1.67 V, the peak at 530 nm increases slightly in intensity while the intensity at 422 nm decreases slightly. A new isosbestic point is observed at 458 nm during repetitive scans during the 5 min equilibration period. Considering the rather similar features of these spectra compared to those of [Re(bipy)(CO)$_3$Cl], it is probable that this behaviour is explained by the formation of a small amount of [Re(dpp)(CO)$_3$]$^-$. A potential step back to 0.0 V regenerates 90% of the original absorbance after 35 min.

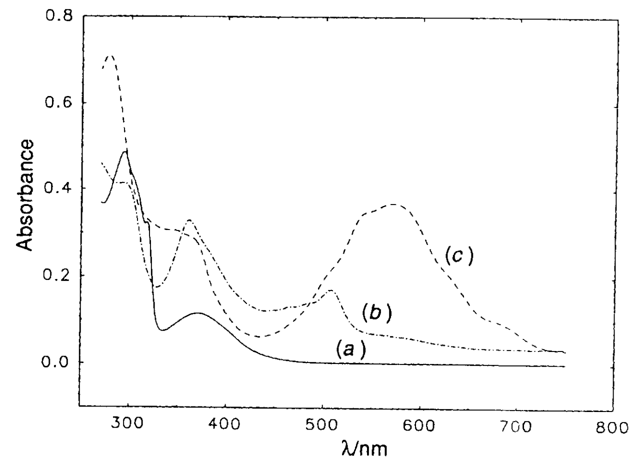

Fig. 1 Sequential absorption spectra obtained during a potential-step spectroelectrochemical experiment on 1.0 mmol dm^{-3} [Re(bipy)(CO)$_3$Cl] in 0.1 mol dm^{-3} NBu$_4$PF$_6$–dmf. Applied potentials in V *vs.* Ag–AgCl are (*a*) 0.0, (*b*) −1.34 (3 min) and (*c*) −1.92 (5 min). Equilibration time for each potential step is in parentheses

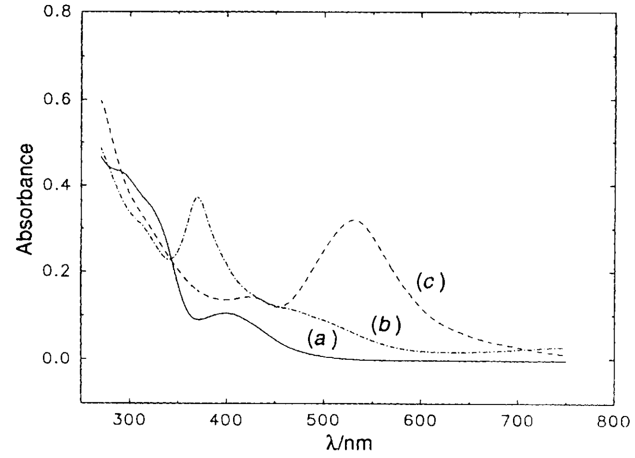

Fig. 2 Sequential absorption spectra obtained during a potential-step spectroelectrochemical experiment on 1.0 mmol dm^{-3} [Re(dpp)(CO)$_3$Cl] in 0.1 mol dm^{-3} NBu$_4$PF$_6$–dmf. Applied potentials in V *vs.* Ag–AgCl are (*a*) 0.0, (*b*) −1.00 (7 min) and (*c*) −1.67 (5 min). Equilibration time for each potential is in parentheses

(*iii*) [{Re(CO)$_3$Cl}$_2$(dpp)]. Fig. 3 illustrates the spectra recorded during the spectropotentiostatic reduction of

[{Re(CO)$_3$Cl}$_2$(dpp)] to [{Re(CO)$_3$Cl}$_2$(dpp)]$^-$. As the electrode is made more reducing, the lowest energy m.l.c.t. band at 450 nm disappears, and the peak at 339 nm is slightly red shifted to a maximum at 357 nm with a shoulder at 390 nm at a potential of −0.541 V. Four isosbestic points are maintained at 305, 357, 439 and 563 nm throughout the experiment, which suggests no decomposition occurs on this time-scale. A Nernstian analysis[19] from the absorbance data at 390 nm gives $E^{\circ\prime}$ = −0.434 V *vs.* Ag–AgCl and n = 1.14. The formal reduction potential compares favourably to the values obtained by conventional and thin-layer cyclic voltammetry. Spectra recorded after sequential potential steps from 0.0 (*a*) to −0.51 (*b*), −1.15 (*c*), and −1.64 V (*d*) *vs.* Ag–AgCl are shown in Fig. 4. Similar spectral features are observed in the potential-step experiment for the first reduction [Fig. 4(*b*)] as were observed for the one-electron reduction product in the spectropotentiostatic experiment. Reduction at −1.15 V results in spectral changes similar to the second reduction for [Re(dpp)(CO)$_3$Cl], with the loss of the near-UV band at 357 nm and appearance of a band at 550 nm. Further reduction at −1.64 V intensifies the spectral features of the doubly reduced complex and red shifts the 550 nm band. It is noteworthy that the spectrum of the triply and doubly reduced complexes exhibit the same general spectral features.

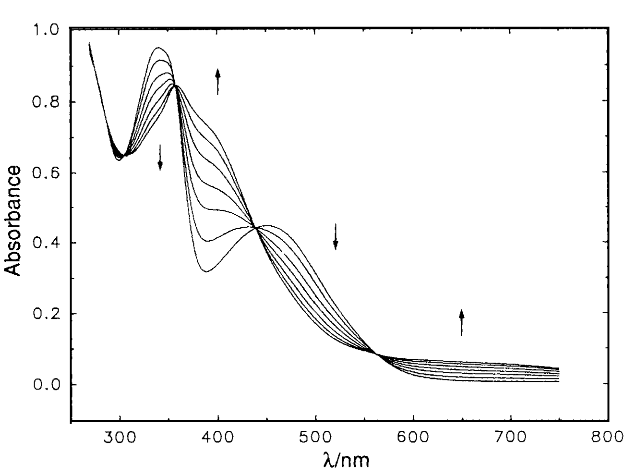

Fig. 3 Spectra recorded during an absorption spectropotentiostatic experiment on 1.0 mmol dm^{-3} [{Re(CO)$_3$Cl}$_2$(dpp)] in 0.1 mol dm^{-3} NBu$_4$PF$_6$–dmf. Applied potentials in V *vs.* Ag–AgCl are (*a*) +0.002, (*b*) −0.405, (*c*) −0.428, (*d*) −0.441, (*e*) −0.461, (*f*) −0.485 and (*g*) −0.541. Equilibration time for each potential is 2 min; arrows in direction (*a*)–(*g*)

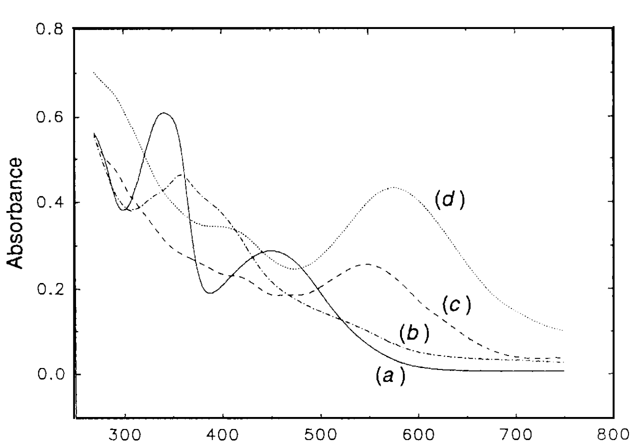

Fig. 4 Sequential absorption spectra obtained during a potential-step spectroelectrochemical experiment on 1.0 mmol dm^{-3} [{Re(CO)$_3$Cl}$_2$(dpp)] in 0.1 mol dm^{-3} NBu$_4$PF$_6$–dmf. Applied potentials in V *vs.* Ag–AgCl are (*a*) 0.0, (*b*) −0.51 (5 min), (*c*) −1.15 (5 min) and (*d*) −1.64 (8 min). Equilibration time for each potential is in parentheses

The UV/VIS spectroscopic data for [Re(bipy)(CO)$_3$Cl], [Re(dpp)(CO)$_3$Cl] and [{Re(CO)$_3$Cl}$_2$(dpp)] are summarized in Table 2.

Flash Photolysis.—The room-temperature excited-state absorption (difference) spectrum of [Re(dpp)(CO)$_3$Cl] in degassed acetonitrile solution recorded immediately after 354.7 nm laser excitation is presented in Fig. 5. The difference spectrum is dominated by maxima at 370 and *ca.* 470 nm. Except for weak bleaches at 320 and 400–420 nm, the Δ*A* values are positive. This indicates that, other than at the wavelengths noted, the excited state absorbs more strongly than the ground state. Negative Δ*A* values at ⩾600 nm are due to the onset of m.l.c.t. luminescence of the complex which is a maximum at 670 nm.[14f] The excited-state transient absorptions decay to preflash baseline, which indicates that no appreciable photodecomposition occurs during each laser pulse. In addition, the spectra in methanol and dmf solutions exhibit similar features as in acetonitrile. The lifetime of [Re(dpp)(CO)$_3$Cl] is barely resolvable from the 7 ns laser pulse. An estimated upper limit on the lifetime is approximately 10 ns in acetonitrile. This value is in reasonable agreement with previously reported estimated lifetimes of < 20[14e,g,j] and 15 ns,[25] as well as the estimate obtained in this work by picosecond spectroscopy.

For [{Re(CO)$_3$Cl}$_2$(dpp)] no transient could be observed when a degassed acetonitrile solution was excited at 354.7 nm. Picosecond flash photolysis studies of [{Re(CO)$_3$Cl}$_2$(dpp)] with 412 nm excitation indicate the m.l.c.t. excited-state lifetime is approximately 1.8 ns. The decrease in the m.l.c.t. excited state lifetime is consistent with the lower energy of the m.l.c.t. state and a more efficient non-radiative decay pathway in [{Re(CO)$_3$Cl}$_2$L^b] complexes relative to their monometallic analogues.[14g,h,j,25]

Electron Localization and Spectral Considerations.—The cyclic voltammetric behaviour of [{Re(CO)$_3$Cl}$_2$(dpp)] has been previously described by three reduction processes and one oxidation process.[14h] The first and second reductive waves have been assigned as two sequential one-electron reductions of the bridging ligand, while the third wave has been assigned as a metal-based Re$^{\mathrm{I}}$ to Re^0 reduction. The irreversible oxidation at about +1.5 V has been assigned as the metal-based Re$^{\mathrm{II}}$ to Re$^{\mathrm{I}}$ oxidation. These assignments have been made by comparison with the electrochemical behaviour of monometallic rhenium(I)

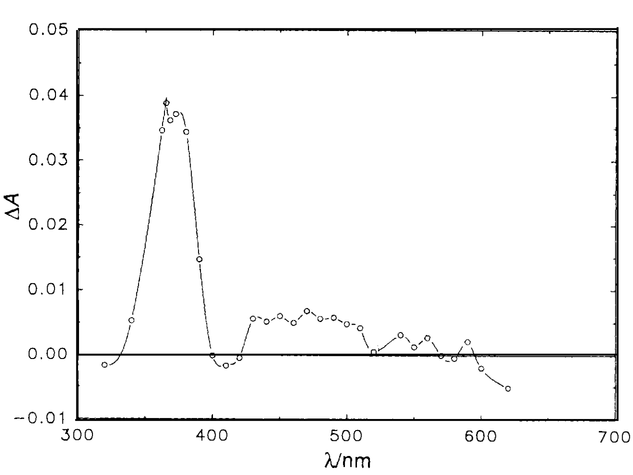

Fig. 5 Excited-state absorption difference spectrum of [Re(dpp)(CO)$_3$Cl] in acetonitrile taken immediately following 354.7 nm excitation

Table 2 UV/VIS spectroscopic data [a,b]

	$n = 0$	−1	−2	−3
$[Re(bipy)(CO)_3Cl]^n$	372 (3600)	509 (5700)	690 (sh)	
	318 (sh)	362 (11 100)	633 (sh)	
	294 (16 100)	294 (sh)	570 (12 100)	
			538 (sh)	
			500 (sh)	
			343 (17 900)	
			277 (23 700)	
$[Re(dpp)(CO)_3Cl]^n$	400 (3500)	468 (sh)	530 (10 900)	
	320 (sh)	370 (12 600)	422 (4800)	
	285 (sh)	312 (sh)	312 (sh)	
$[\{Re(CO)_3Cl\}_2(dpp)]^n$	450 (9400)	390 (sh)	550 (8800)	576 (14 250)
	339 (20 200)	357 (15 750)	421 (sh)	400 (11 350)
		328 (sh)	295 (sh)	295 (sh)

[a] Obtained from 1.0 mmol dm^{-3} complex in 0.1 mol dm^{-3} NBu_4PF_6–dmf at a gold OTTLE. The optical path length was determined by spectrophotometry to be 0.030 cm. [b] sh = shoulder.

analogues and by analogy with other metal complexes and ligand systems. Addition of a bridging ligand system and a second metal centre can significantly change the electronic properties of the molecule [14h,j] such that a second complementary technique is necessary for electron localization assignments. In this study, thin-layer electrochemical and spectroelectrochemical measurements of $[Re(bipy)(CO)_3Cl]$, $[Re(dpp)(CO)_3Cl]$ and $[\{Re(CO)_3Cl\}_2(dpp)]$ in dmf allow for direct observation of spectral trends that occur with sequential reduction of these related complexes. Therefore, electron localization assignments are facilitated for $[\{Re(CO)_3Cl\}_2(dpp)]$.

As a basis for understanding the spectroelectrochemistry and the electron localization, we chose $[Re(bipy)(CO)_3Cl]$ as our model compound for defining the spectral features associated with reduction of an α,α′-diimine ligand in a $Re(CO)_3Cl$-based complex. In accord with detailed studies in acetonitrile by Meyer and co-workers [22] of the relative sensitivity of the redox potential to the variation in X for a number of $[Re(bipy)(CO)_3X]$ complexes, the first and second reduction waves, and the oxidation wave, are firmly established as the reversible reduction of the bipy ligand, the irreversible metal-based reduction of Re^I to Re^0 and the irreversible metal-based oxidation of Re^I to Re^{II}, respectively. The spectrum of $[Re(bipy)(CO)_3Cl]^-$ from spectroelectrochemical measurements resembles features in the UV/VIS spectrum of singly reduced $[Ru(bipy)_3]^{2+}$,[15a,17a] $[bipy]^-$,[15a] and the m.l.c.t. excited-state spectrum of $[Re(bipy)(CO)_3Cl]$.[3] Thus it is reasonable to predict that the spectrum of a $[Re(L–L^-)(CO)_3Cl]$ complex will exhibit a sharpening or appearance of spectral features in the region of 350–400 nm with a corresponding increase in absorbance tailing out to 500–600 nm if the reduction is based on the L–L ligand. The second reduction of $[Re(bipy)(CO)_3Cl]$ provides a broad band characteristic for metal-based reduction at approximately 550 nm with conservation of the $L–L^-$ absorption features at *ca.* 350–400 nm [*cf.* Figs. 1(*b*) and (*c*)].

In a study similar to that performed on $[Re(bipy)(CO)_3X]$ complexes Baiano and Murphy [25] observed analogous redox behaviour with a series of $[Re(dpp)(CO)_3X]$ complexes, and concluded that the electrochemical assignments in the dpp complexes were identical to the bipy complexes. One-electron reduction of $[Re(dpp)(CO)_3Cl]$ is consistent with a dpp-based reduction due to the similarity of the spectral features for $[Re(bipy)(CO)_3Cl]^-$ [Fig. 1(*b*)] and $[Re(dpp)(CO)_3Cl]^-$ [Fig. 2(*b*)] except for the absence in Fig. 2(*b*) of the distinct peak at 509 nm, which is observed in the spectrum of the bipy complex. Both the bipy and dpp complexes exhibit the characteristic 350–400 nm band with the dpp band red-shifted relative to the bipy complex owing to the additional pyridyl substitution on dpp. The UV/VIS spectrum of the dpp complex also compares favourably to the excited-state spectrum in Fig. 5. Apart from the lack of a strong bleach in the 400–500 nm region, the observed difference spectrum of $[Re(dpp)(CO)_3Cl]$ is similar to the m.l.c.t. excited state absorption spectrum of $[Ru(bipy)_2(dpp)]^{2+}$,[17b,26,27] which is also described by electron localization on dpp. Therefore, the absorption spectra of singly reduced rhenium(I) α,α′-diimine complexes are also dominated by intraligand $\pi \longrightarrow \pi^*$ transitions of the L–L radical anion. The second reduction of the monometallic dpp complex is characterized by a broad absorption in the range 530–580 nm analogous to $[Re(bipy)(CO)_3Cl]^{2-}$, which is attributable to reduction of the Re^I centre. In contrast, the peak in the 350–400 nm region is not present, whereas a relatively weak absorption at *ca.* 420 nm is observed.

Reduction of $[\{Re(CO)_3Cl\}_2(dpp)]$ to $[\{Re(CO)_3Cl\}_2(dpp)]^-$ [Fig. 4(*b*)] is quite similar to both monometallic complexes except for a much broader near-UV band with a contribution from a low-energy shoulder at 390 nm. Recent X-ray crystallographic determination of $[\{Re(CO)_3Cl\}_2(dpp)]$ indicates that co-ordination of the second $Re(CO)_3Cl$ unit results in the distortion of the pyrazine ring in dpp [28] relative to the unco-ordinated dpp ligand.[29] This structural consequence on dpp in the bimetallic co-ordination may be in part related to the broadening of the absorption spectrum for the singly reduced bimetallic complex. The electrochemical and spectroelectrochemical results for the initial reduction are consistent with results for other $[\{Re(CO)_3Cl\}_2L^b]$ systems [14e,h,j] and support the reduction of L^b in these complexes. However, spectroelectrochemical measurements for further reduction of $[\{Re(CO)_3Cl\}_2(dpp)]^-$ lead to a different conclusion for electron localization than was previously proposed. Addition of the second and third electrons have been previously associated with the second reduction of dpp and the reduction of Re^I, respectively.[14h,j] From this work, the second reduction [Fig. 4(*c*)] exhibits a spectrum analogous to the second reduction of $[Re(dpp)(CO)_3Cl]$ with an absorption maximum at 550 nm, a small peak at 421 nm, and loss of the peak at 357 nm. Subsequent addition of a third electron [Fig. 4(*d*)] results in the same general absorption features as the doubly reduced complex; the difference is primarily an increase in absorbance by almost a factor of two over the entire spectral region and a red shift in the lowest energy absorption maximum to 576 nm. In contrast, addition of the second electron to dpp in the spectroelectrochemical experiment of $[(bipy)_2Ru(dpp)Ru(bipy)_2]^{4+}$ results in little change in absorbance in the 350–400 nm region, a decrease in the band at approximately 470, and slight sharpening of the low-energy absorption(s) near 630 nm.[17b] The similarity of the spectra in Figs. 4(*c*), 4(*d*), 2(*c*) and 1(*c*), the irreversible nature of the second and third reduction waves in the cyclic voltammogram of $[\{Re(CO)_3Cl\}_2(dpp)]$ and the differences observed during spectroelectrochemical reduction of dpp between the rhenium(I) and ruthenium(II) bimetallic complexes suggests the second and third reductions of $[\{Re(CO)_3Cl\}_2(dpp)]$ are reductions of both Re^I metal centres.

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