EPR study of paramagnetic rhenium(I) complexes $(bpy^{\bullet -})Re(CO)_3X$ relevant to the mechanism of electrocatalytic CO_2 reduction †

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In situ **reduction of $(bpy)Re(CO)_3Cl$, bpy = 2,2′-bipyridine, at a platinum cathode under CO_2 atmosphere in acetonitrile or acetone has produced a series of distinct EPR spectra which are attributed to $(bpy^{\bullet -})$ containing species and which invariably reveal the interaction of the unpaired electron with the metal nuclei ($^{185,187}Re$, $I = 5/2$). The EPR investigation of various model complexes $(bpy^{\bullet -})Re(CO)_3X$, generated by electrochemical reduction under argon of diamagnetic precursors $(bpy)Re(CO)_3X$, X = Cl^-, $CF_3SO_3^-$, CH_3O^-, H^-, tetrahydrofuran, CH_3CN, CO, HCO_2^-, HCO_3^- and $CH_3C(O)^-$ has been used to interpret the results from the reactions under CO_2 atmosphere.**

Tricarbonylrhenium(I) complexes *fac*-(α-diimine)$Re(CO)_3X$ of α-diimine chelate ligands such as 1,4-disubstituted 1,4-diazabuta-1,3-dienes[1,2] or 2,2′-bipyridine (bpy) and related chelating N-heterocycles N^N[1,3–5] have received interest because of their stability and remarkable photo-[2–4] and electro-chemistry.[5] More specifically, the incentive for much recent work on these systems[1,4–6] originates from their possible photo- and electrocatalytic role in the activation and reduction of CO_2.[7] The latter was shown to proceed *via* a primary (α-diimine)-centred reduction to EPR detectable anion radical complexes $[(N^\wedge N^{-1})Re(CO)_3(Hal)]^{\bullet -}$[6,8] which can then undergo dissociation of the halide Hal^- (not the carbonyl, CO)[7d] at quite variable rates. The mechanistic steps following that initial activation were studied by techniques such as IR spectroelectrochemistry;[6a] however, there has not yet been a corresponding EPR study of the actual reduction in the presence of CO_2.

In this paper we describe a first such study, reporting: (*i*) the EPR spectroscopic response of $(bpy)Re(CO)_3Cl$ on *intra muros* electrochemical reduction under CO_2 in acetonitrile– or acetone–0.1 mol dm^{-3} Bu_4NPF_6, and (*ii*) the EPR spectroscopy of species which could be relevant to reaction (*i*) and which were electrogenerated from complexes $(bpy)Re(CO)_3X$, X = Cl^-, $CF_3SO_3^-$, CH_3O^-, H^-, tetrahydrofuran (THF), CH_3CN, CO, HCO_2^-, HCO_3^- and $CH_3C(O)^-$.[9–12]

Experimental

Materials and syntheses

The complexes $(bpy)Re(CO)_3X$ with X = CO,[9] $NCCH_3$,[1,3] $CF_3SO_3^-$,[10] Cl^-,[3,8] THF,[11] HCO_2^-,[10] HCO_3^- [10] and H^- [10] were obtained according to literature procedures. All other reagents were used as commercially available. Preparations and physical measurements were carried out in dried solvents under an argon atmosphere, using Schlenk techniques. Solvents for cyclic voltammetry experiments were additionally degassed by three subsequent freeze–pump–thaw cycles.

New $(bpy)Re(CO)_3X$ complexes[12]

2,2′-Bipyridine(tricarbonyl)methoxyrhenium(I), $(bpy)Re(CO)_3(OCH_3)$. Sodium methoxide (28 mg, 0.52 mmol) was added to a solution of 150 mg (0.26 mmol) of acetonitrile(2,2′-bipyridine)tricarbonylrhenium(I) hexafluorophosphate in 20 cm^3 of methanol. Stirring at room temp. for 16 h produced a dark orange solution and a yellow precipitate. After filtration the solution was extracted several times with 10 cm^3 of dichloromethane. The combined liquids were dried. The resulting orange solid was recrystallised from methanol to yield 50 mg (0.11 mmol) of a dark-orange solid (yield 42%) [Found: C, 35.77; H, 2.11; N, 7.51%. $C_{14}H_{11}N_2O_4Re$ (457.46 g mol^{-1}) requires: C, 36.76; H, 2.42; N, 6.13%]. ν/cm^{-1} (CH_2Cl_2): ν(CO) 2014 (s), 1909 (s), 1890 (s). δ_H([$^2H_6$]-acetone) 1.45 (s, 3H, $ReOCH_3$), 7.69 (t, 2H), 8.26 (t, 2H), 8.62 (d, 2H) and 9.16 (d, 2H).

Acetyl(2,2′-bipyridine)tricarbonylrhenium(I), $(bpy)Re(CO)_3(COCH_3)$. A solution of 60 mg (0.1 mmol) of (2,2′-bipyridine)tricarbonylrhenium(I) trifluoromethanesulfonate[10] in 15 ml of THF was cooled to −78 °C and treated with 0.1 ml of a 5% solution of methyllithium in THF. The reaction mixture changed immediately to a dark-red colour. After stirring for 30 min the solution was allowed to warm to room temp. and 10 ml of methanol were added. After evaporation of the solvents a dark red solid was obtained which was recrystallised from ethanol to yield 30 mg (0.06 mmol) of the product (yield 63%) [Found: C, 37.37; H, 2.56; N, 5.64%. $C_{15}H_{11}N_2O_4Re$ (469.46 g mol^{-1}) requires: C, 38.38; H, 2.36; N, 5.97%]. ν/cm^{-1} (CH_2Cl_2): ν(CO) 1999 (s), 1899 (s), 1889 (s); 1591 (w, acetyl). δ_H([$^2H_6$]-acetone) 2.18 (s, 3H, $ReCOCH_3$), 7.55 (t, 2H), 8.20 (t, 2H), 8.66 (d, 2H) and 8.95 (d, 2H).

Instrumentation

EPR spectra were recorded in the X band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. EPR spectral simulation was performed using a modified program derived from the shareware program of Oehler and Janzen[13] (Gaussian line forms, no corrections for second-order or variable line-width effects). Input data were taken from experimental spectra. A two-electrode capillary was used for *intra muros* EPR studies. ^1H NMR spectra were taken on a Bruker AC 250 spectrometer; infrared spectra were obtained using Perkin-Elmer 684 and 283 instruments. Cyclic voltammetry was carried out in acetonitrile–0.1 mol dm^{-3} Bu_4NPF_6 using a three-electrode configuration (glassy carbon electrode, Pt counter electrode Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal reference.

Results and discussion

Reduction of $(bpy)Re(CO)_3Cl$ under CO_2

Under an inert atmosphere such as argon the reduction of the

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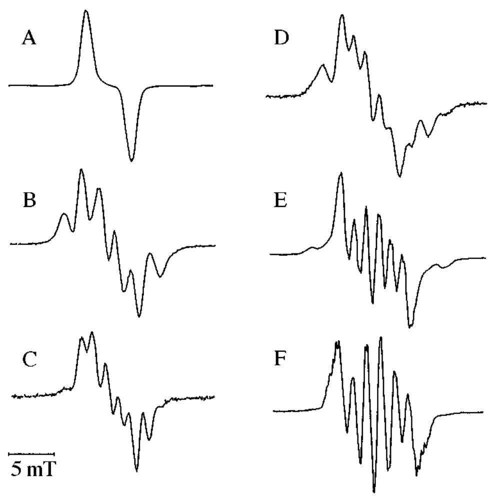


Fig. 1 EPR spectra observed on *in situ* electroreduction of (bpy)Re(CO)$_3$Cl under CO$_2$ (1 bar) in acetonitrile–0.1 mol dm^{-3} Bu$_4$NPF$_6$ after 1 min (A), 10 min (B), 30 min (C), 40 min (D), 60 min (E) and 120 min electrolysis (F, final spectrum)

electrocatalyst precursor complex (bpy)Re(CO)$_3$Cl in acetonitrile proceeds in an initially reversible one-electron step to yield the radical anion [(bpy)Re(CO)$_3$Cl]$^{\bullet -}$,[8a] *i.e.* with chloride still bound to the metal. Depending on external conditions[7] and on the chelate ligand[1] such complexes undergo dissociation with loss of halide, a process which combines reductive activation and the creation of an open coordination site for substrate binding. Analysis of the EPR signal [*cf.* Fig. 1(A)] reveals the interaction of the unpaired electron with the metal nuclei ^{185}Re ($I = 5/2$, 37.4% natural abundance) and ^{187}Re ($I = 5/2$, 62.6%); the difference between the magnetic moments of the two nuclei is about 1% and thus not resolved under these conditions. The metal coupling constant of 1.2 mT for [(bpy)Re(CO)$_3$Cl]$^{\bullet -}$ and the rather large linewidth are not only responsible for the unusually shaped EPR signal which results from cancellation of signal intensity in the central region[1] and leaves just the two outermost lines of the sextet visible [Fig. 1(A)],[8a] they also combine to obscure further hyperfine splitting from ligand nuclei (^{1}H, ^{14}N, ^{35,37}Cl) which, however, can be detected for some other complexes (α-diimine^{-1})Re(CO)$_3$X.[1] In spite of this dominance of the spectrum by the metal isotope hyperfine lines, the comparatively[14] small metal coupling with a(Re)/A_{iso}(Re)[15] < 0.007 and the g factors close to $g_{\mathrm{electron}} = 2.0023$ clearly confirm a predominantly chelate ligand-centred spin and a largely diamagnetic rhenium(I) centre with 5d^6 configuration.[1,8,14]

If continuous cathodic reduction of (bpy)Re(CO)$_3$Cl is performed at 298 K and at −2.0 V under CO$_2$ (1 bar, saturated) the primary reduction product [(bpy)Re(CO)$_3$Cl]$^{\bullet -}$ with its 'two-line' EPR signal[8a] [Fig. 1(A)] is no longer stable but converts to other species within minutes and hours [Fig. 1(B–F)]. The improved resolution of the sextet features (due to ^{185,187}Re) and some partially visible ligand hyperfine structure [see Fig. 1(F)] is a consequence of chloride dissociation which removes line-broadening contributions from ^{35,37}Cl ($I = 3/2$) and causes an increase in the metal hyperfine coupling constant.[1] The ligand hyperfine splitting visible in Fig. 1(F) amounts to 0.4 mT and can be attributed to coupling with two ^{14}N and two ^{1}H (H^5) nuclei—typical values for complexes of the 2,2′-bipyridine anion radical.[16] There are generally only slight variations in the g factors, centred around 2.0033. However, the metal hyperfine coupling increases from 1.2 mT [Fig. 1(A)] to 2.2 mT for the new emerging species of Fig. 1(B) and 1.9 mT for the species in Fig. 1(F). Although there is clearly overlap of two or more EPR spectra in some of the stages depicted in Fig. 1, there are apparently several distinct radical products with the (bpy$^-$)Re(CO)$_3$X structure being formed as a function of time. Clearly discernible are species **I** = [(bpy)Re(CO)$_3$Cl]$^{\bullet -}$ [8a] in Fig. 1(A), species **II** [main feature in Fig. 1(B)] with a(Re) = 2.2 mT, species **III** [main feature in Fig. 1(C)] with a(Re) = 1.6 mT, and species **IV** [Fig. 1(F)] with a(Re) = 1.9 and a(N) = a(H^5) = 0.4 mT.

Table 1 Electrochemical and EPR data of paramagnetic complexes [(bpy$^-$)Re(CO)$_3$X][a]

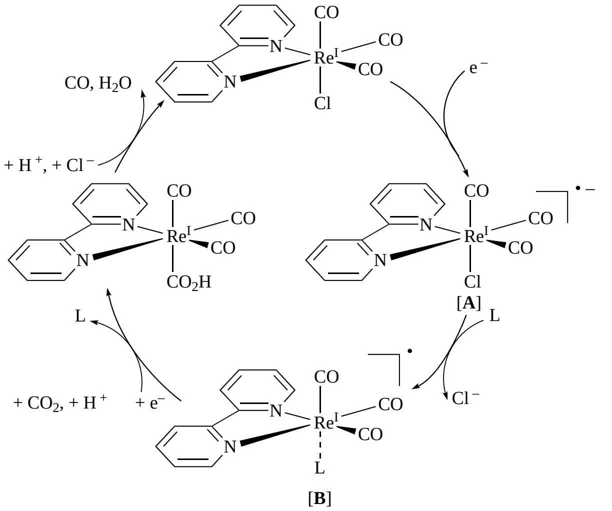
X	$E_{1/2}$ [b]	g [c]	a(^{185,187}Re) [d]	pK_a (XH$^+$) [e]
CO	−1.56[f]	[g]		<−25
CH$_3$CN$_3$	−1.61	[g]		<−10
CF$_3$SO$_3^-$	−1.61	2.0031	10.8	<−6
Cl$^-$	−1.72	2.0032	12.0	−6
THF	−1.68	2.0026	11.5	<−3.5
HCO$_2^-$	−1.71	2.0035	11.4	−3.7
HCO$_3^-$	(−1.85)	[g]		−6.5
CH$_3$O$^-$	−1.76	2.0031	19.2	−15.5
CH$_3$C(O)$^-$	−1.85	2.0024	19.6	−16.5
H$^-$	−1.83	2.0029	17.9	>20

[a] Generated from neutral precursors by *in situ* cathodic reduction in acetonitrile–0.1 mol dm^{-3} Bu$_4$NPF$_6$. [b] Reduction potentials in V *vs.* ferrocenium/ferrocene from cyclic voltammetry. [c] Isotropic g values, measured at 298 K in solution. [d] Isotropic coupling constants in mT, from computer simulation. [e] Acidity constants, from refs. 17 and 18. [f] Cathodic peak potential for irreversible reduction. [g] Not available.

Similar results were obtained in acetone–0.1 mol dm^{-3} Bu$_4$NPF$_6$ where the spectra appeared to be more complicated due to the simultaneous presence of several species.

Reduction of complexes (bpy)Re(CO)$_3$X

To tentatively assign the paramagnetic species observed in the CO$_2$ experiment (Fig. 1) and thus gather more information on the electroreductive process (Scheme 1) for the paramagnetic compounds, we prepared various complexes (bpy)Re(CO)$_3$X and studied their electrochemical and EPR behaviour in acetonitrile solution. The axial ligands X were chosen as to resemble possible solvents or their derivatives (CH$_3$CN, THF, CH$_3$O$^-$), counter ions (Cl$^-$, CF$_3$SO$_3^-$) and conceivable reaction products [HCO$_2^-$, HCO$_3^-$, CO, CH$_3$C(O)$^-$, H$^-$]. The acetyl and methoxy derivatives are new compounds; their complete characterisation will be described elsewhere.[12]



Scheme 1

Table 1 summarises the reduction behaviour as measured by cyclic voltammetry and the EPR data, if unambiguously available. Fig. 2 shows three representative EPR spectra.

As was described previously,[9] the tetracarbonylrhenium(I) complex of bpy could not be reduced reversibly. The acetonitrile solvate and the hydrogencarbonate complex showed reversible waves in their respective cyclic voltammograms; however, the reduced species were not sufficiently stable for EPR.

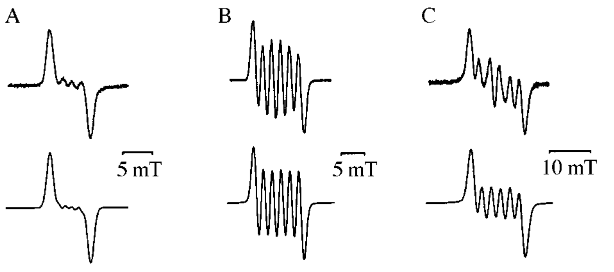


Fig. 2 EPR spectra of anion radical complexes obtained *via in situ* cathodic reduction in acetonitrile–0.1 mol dm^{-3} Bu_4NPF_6 of (bpy)-$Re(CO)_3X$, X = HCO_2^- (A), CH_3O^- (B), $CH_3C(O)^-$ (C), with respective computer simulations

Both neutral ligands X = CO and CH_3CN are distinguished by very low basicity as quantified by pK_a(XH^+) (Table 1).[17,18]

The reduction potentials $E_{1/2}$ for the neutral complexes (bpy)$Re(CO)_3X$ vary only slightly but seem to correlate approximately with the donor capacity of X, as measured by pK_a(XH^+). Less basic groups X facilitate the reduction of the complex, the effect being small because of the bpy-centred addition of the electron.[1,8] The *g* factors exhibit hardly any significant variation and lie close to the free ligand radical value of 2.0030, in accordance with a balanced frontier orbital situation;[8] however, there seems to be a dichotomy concerning the rhenium hyperfine splitting.

The complexes $[(bpy)Re(CO)_3X]^{\bullet -}$ with less basic X ligands have $a(^{185,187}Re)$ of about 1.1 mT (Table 1). This includes, *e.g.* the chloride and the formate complex, the latter with better EPR resolution [Fig. 2(A) *vs.* Fig. 1(A)] because of the absence of line broadening $^{35,37}Cl$ hyperfine contributions. On the other hand, the radical species with very basic groups X have metal coupling constants around 1.9 mT (Table 1).

On the basis of this correlation the species **I**–**IV** clearly observed in the CO_2 experiment [Fig. 1(A–F)] can be discussed as follows.

The one-electron-reduced precursor complex $[(bpy)Re(CO)_3Cl]^{\bullet -}$ contains an activated metal–halide bond as apparent from the indirect effects of $^{35,37}Cl$ hyperfine interactions. After halide dissociation the neutral radical species $[(bpy)Re(CO)_3]$ may dimerize[2d,6] or accept a solvent molecule to reestablish six-coordination; however, five-coordinate systems are also conceivable[1] because of the strong σ and π donating influence from reduced chelate ligands.[19] With 2.2 mT, the paramagnetic species **II** following **I** exhibits an unusually (Table 1) large rhenium coupling constant. We therefore no longer[1] associate species **II** with the coordination of weakly basic acetonitrile but with the addition of CO_2 to the free axial site. Carbon dioxide is a weak base but is distinguished by low lying π^* orbitals, making it a π acceptor ligand.[20] The EPR effects are thus similar to those of triorganophosphine coordination,[1] *i.e.* a considerable increase of the metal hyperfine coupling.

The main species **III** from Fig. 1(C) exhibits an intermediate rhenium coupling of 1.6 mT which we could not model in our series (Table 1). Since the tetracarbonyl is unstable as a radical species the formate may be considered as an early $2e^-$-reduction product of coordinated CO_2 (H^+ being provided from the solvent).[20] However, the actual paramagnetic formate complex has a smaller metal coupling constant of 1.14 mT [Table 1, Fig. 1(A)]. We thus cannot identify the radical species **III** which is, however, present only in small amounts [Fig. 1(C)]. The next clear (and final) major radical species is **IV** [Fig. 1(F)] with a rhenium coupling of 1.9 mT. This value is close to that of the new acetyl complex (Table 1) which suggests formation of a formyl compound as the $4e^-$-product of long-term CO_2 reduction. Syntheses and more detailed studies of neutral and anionic acyl complexes are thus necessary to investigate this alternative and complement the present study of exclusively paramagnetic intermediates.

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