Electrocatalytic Reduction of CO_2 Using the Complexes $[Re(bpy)(CO)_3L]^n$ ($n = +1$, L = $P(OEt)_3$, CH_3CN; $n = 0$, L = Cl^-, Otf^-; bpy = 2,2′-Bipyridine; $Otf^- = CF_3SO_3$) as Catalyst Precursors: Infrared Spectroelectrochemical Investigation

Frank P. A. Johnson,*,† Michael W. George,† Frantisek Hartl,*,‡ and
James J. Turner†

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K., and
Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, J. H. van't Hoff Instituut,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

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This article describes the results of an IR spectroelectrochemical study of the electrocatalytic reduction of carbon dioxide using the complexes $[Re(CO)_3(bpy)L]^n$ (bpy = 2,2′-bipyridine; $n = 0$, L = Cl^-, $CF_3SO_3^-$; $n = +1$, L = CH_3CN, $P(OEt)_3$) as catalyst precursors. The study was performed for the first time with an optically transparent thin-layer electrochemical (OTTLE) cell. The results confirm unambiguously the catalytic activity of the reduced five-coordinate complexes, the radical $[Re(CO)_3(bpy)]^\bullet$ and the anion $[Re(CO)_3(bpy)]^-$. The catalytic behavior of these species could be investigated separately for the first time due to the application of complexes other than those with L = halide, whose catalytic routes may involve simultaneously both radical and anionic catalysis depending on the solvent used. The complex $[Re(CO)_3(bpy)Cl]$, so far the most studied catalyst precursor, upon one-electron reduction gives the corresponding radical-anion $[Re(CO)_3(bpy)Cl]^{\bullet -}$, which was previously believed to react directly with CO_2. By contrast, this study demonstrates its stability toward attack by CO_2, which may only take place after dissociation of the chloride ligand. This conclusion also applies to other six-coordinate radicals $[Re(CO)_3(bpy)L]^\bullet$ (L = CH_3CN (in CH_3CN) and $P(OEt)_3$) whose catalytic route requires subsequent one-electron reduction to produce the anionic catalyst $[Re(CO)_3(bpy)]^-$ (the 2e pathway). The catalytic route of $[Re(CO)_3(bpy)Cl]$ in CH_3CN therefore deviates from that of the related $[Re(CO)_3(dmbpy)Cl]$, the other complex studied by IR (reflectance) spectroelectrochemistry, with the more basic ligand, 4,4′-dimethyl-2,2′-bipyridine (dmbpy). The latter complex tends to form the five-coordinate radicals $[Re(CO)_3(dmbpy)]^\bullet$, capable of CO_2 reduction (the 1e pathway), even in CH_3CN, hence eliminating the possibility of the 2e pathway via the anion $[Re(CO)_3(dmbpy)]^-$, which operates in the case of the 2,2′-bipyridine complex. For $[Re(CO)_3(bpy)L]^n$ ($n = 0$, L = Cl^-, $CF_3SO_3^-$; $n = +1$, L = CH_3CN), the 1e catalytic route becomes possible in weakly coordinating THF, due to the instability of the radical $[Re(CO)_3(bpy)(THF)]^\bullet$. The inherent stability of the radical $[Re(CO)_3(bpy)\{P(OEt)_3\}]^\bullet$ was found convenient for the investigation of the 2e pathway via $[Re(CO)_3(bpy)]^-$. The main, spectroscopically observed products of the CO_2 reduction are, independent of the 1e and 2e catalytic routes, CO, CO_3^{2-}, and free CO_2H^-. The latter product is formed *via* one-electron reduction of the radical anion $[Re(CO)_3(bpy)(CO_2H)]^{\bullet -}$, which is the main byproduct in the catalytic cycle.

Introduction

Since the initial discovery by Lehn and co-workers[1] that $[Re(bpy)(CO)_3Cl]$ (bpy = 2,2′-bipyridine) acts as an efficient electrocatalyst for the reduction of CO_2, there have been numerous investigations of the electrochemical behavior of this and related catalytic systems.[1−14] In general the mechanistic studies have been restricted to bulk electrolysis and cyclic voltammetry and, until the recent comprehensive work by Stor *et al.*,[14] there have been relatively few IR spectroelectrochemical studies.[7,11,13] Of these spectroelectrochemical investigations only one is predominantly concerned with elec-

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† University of Nottingham.

‡ Universiteit van Amsterdam.

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trocatalytic CO_2 reduction[11] and involves the catalytic behavior of [Re(dmbpy)$(CO)_3$Cl] (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) which, however, displays significant differences from that of the most widely studied electrocatalyst [Re(bpy)$(CO)_3$Cl]. This lack of spectroscopic data has made it difficult to determine conclusively the nature of the majority of the species involved in the electrocatalytic cycle, especially in the case of [Re(bpy)$(CO)_3$Cl].

It is well established from voltammetric[1−6,8−10,12] and IR spectroelectrochemical[7,11,13,14] investigations that the first step in the reduction is the bipyridine-based one-electron reduction of the rhenium complex to produce the corresponding radical anion, $[Re(bpy)(CO)_3Cl]^{\bullet-}$, eq 1. The secondary chemical reaction of this radical,

$$[Re(bpy)(CO)_3Cl] + e^- \Rightarrow [Re(bpy)(CO)_3Cl]^{\bullet-} \quad (1)$$

$$[Re(bpy)(CO)_3Cl]^{\bullet-} \rightarrow [Re(bpy)(CO)_3]^{\bullet} + Cl^- \quad (2)$$

$$[Re(bpy)(CO)_3]^{\bullet} \rightarrow 1/2[Re(bpy)(CO)_3]_2 \quad (3)$$

$${}^1/_2[Re(bpy)(CO)_3]_2 + e^- \Rightarrow [Re(bpy)(CO)_3]^- \quad (4)$$

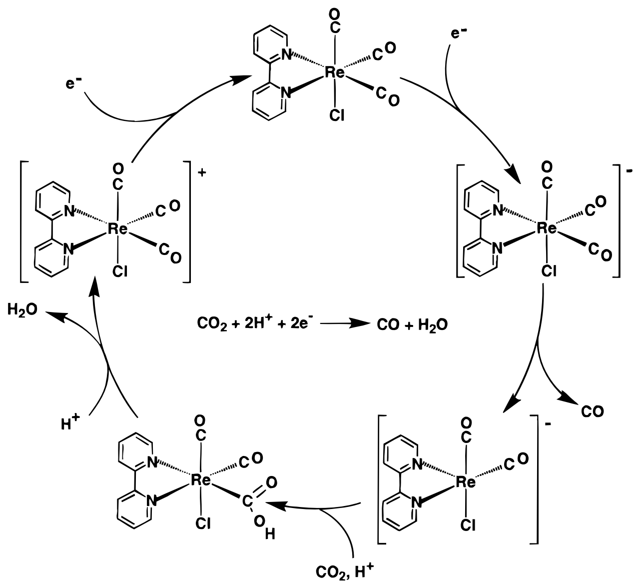
described in eq 2, has been proposed by a number of authors on the basis of voltammetric studies and confirmed by the IR spectrelectrochemical results of Christensen *et al.* for [Re(dmbpy)$(CO)_3$Cl][11] and Stor *et al.* for [Re(bpy)$(CO)_3$Cl].[14] The radical $[Re(bpy)(CO)_3Cl]^{\bullet-}$ can be stabilized at lower temperature,[15] but at room temperature it decomposes via chloride loss to the coordinatively unsaturated radical $[Re(bpy)(CO)_3]^{\bullet}$, which in the *absence* of strongly coordinating solvents or CO_2 dimerizes rapidly to $[Re(bpy)(CO)_3]_2$, eqs 2 and 3. Further, rhenium-based reduction of the dimer leads to the formation of the five-coordinate anionic species $[Re(bpy)(CO)_3]^-$, eq 4 (bpy refers to both 2,2′-bipyridine and dmbpy in eqs 1−4).

It has also been shown[15] that in coordinating solvents such as *n*-butyronitrile (*n*-PrCN), $[Re(bpy)(CO)_3]^-$ is in equilibrium with its solvated six-coordinate form $[Re(bpy)(CO)_3(n\text{-}PrCN)]^-$, eq 5.

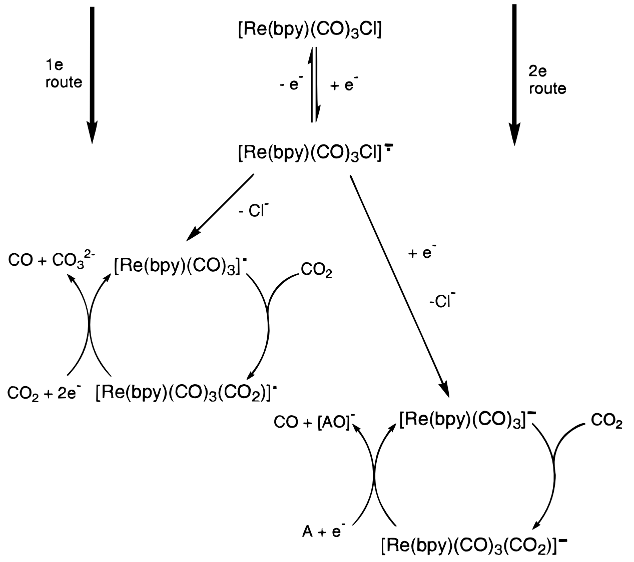
$$[Re(bpy)(CO)_3]^- + n\text{-}PrCN \rightleftarrows [Re(bpy)(CO)_3(n\text{-}PrCN)]^- \quad (5)$$

Equations 1−5 describe the reduction of [Re(bpy)$(CO)_3$Cl] in the absence of CO_2; however, the mechanism of the electrocatalytic reduction of CO_2 remains unclear. Three principal mechanistic schemes have been proposed involving [Re(bpy)$(CO)_3$Cl] and [Re(dmbpy)$(CO)_3$Cl]:

Scheme 1



Scheme 2



(i) Mechanism of Lehn and Co-workers[5] (Scheme 1). In this study the catalytic precursor [Re(bpy)$(CO)_3$Cl] was investigated using bulk electrolysis and cyclic voltammetry in *dimethylformamide* solution containing excess Cl^-. This mechanism differs from those by other authors, as the formation of $[Re(bpy)(CO)_2Cl]^{\bullet-}$ is proposed via loss of CO from $[Re(bpy)(CO)_3Cl]^{\bullet-}$. This possibility was suggested as the loss of Cl^-, and subsequent formation of the dimer $[Re(bpy)(CO)_3]_2$ (eqs 2 and 3) was believed to be inhibited by the presence of excess Cl^- in solution. This CO loss step has not been observed in any of the spectroelectrochemical experiments to date although up to now none has used excess Cl^-. This mechanism has also been discounted by Christensen *et al.*,[11] as it cannot account for the large amount of CO_3^{2-} produced as described below. Moreover, it has been noted previously by Sullivan *et al.*[8] that the mechanism "appears to invoke a contra-thermodynamic step, *i.e.* the production of the strong oxidant $[Re^{II}(bpy)(CO)_3Cl]^{+}$", and as with the CO loss process there is no IR evidence for this species.

(ii) Mechanism of Sullivan and Meyer and Co-workers[3,8,9] (Scheme 2). Sullivan and Meyer and co-workers studied [Re(bpy)$(CO)_3$Cl] in *acetonitrile* solution using predominantly cyclic voltammetry and bulk electrolysis. This mechanism was the first to consider the

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Table 1. Reduction Potentials[a] of the Various Complexes under Study (Potentials in V vs Fc/Fc$^+$)

complex (no.)	solvent	$E_{1/2}$ (I)	$E_{p,c}$ (II)	ref
[Re(bpy)(CO)$_3$Cl] (**1**)	THF	−1.86	−2.38	14
	THF/CH$_3$CN[c]	−1.76	−2.21	*b*
[Re(bpy)(CO)$_3$]$_2$ (**6**)	THF	−2.03		14
[Re(bpy)(CO)$_3$(CH$_3$CN)]$^+$ (**7**)	THF/CH$_3$CN[c]	−1.58	−1.80	*b*
[Re(bpy)(CO)$_3$(THF)]$^+$ (**8**)	THF	−1.69	−2.23	14
[Re(bpy)(CO)$_3$(O$_2$CH)] (**9**)	CH$_3$CN	−1.81	−2.33	*b*
[Re(bpy)(CO)$_3$(Otf)] (**11**)	THF	−1.49		14
[Re(bpy)(CO)$_3${P(OEt)$_3$}]$^+$ (**12**)	CH$_3$CN	−1.63	−2.40	*b*
[Re(bpy)(CO)$_2${P(OEt)$_3$}$_2$]$^+$	CH$_3$CN	−1.79	−2.82	*b*
[Re(bpy)(CO)$_3$(n-PrCN)]$^+$	*n*-PrCN	−1.58	−1.97	15
[Re(bpy)(CO)$_3$(PPh$_3$)]$^+$	THF	−1.58	−2.10	14
	THF/CH$_3$CN[c]	−1.58	−2.10	*b*

[a] Conditions: $T = 293$ K, $v = 100$ mV/s, Pt disk electrode. [b] This work. [c] THF:CH$_3$CN = 3:2 (v/v).

possibility of simultaneous one− and two-electron pathways involving [Re(bpy)(CO)$_3$]$^•$ and [Re(bpy)(CO)$_3$]$^−$, respectively. The initial investigations led to the mechanism shown in Scheme 2,[3,8] where A is an “oxide ion acceptor”.

There are a number of problems with this scheme; the production of [Re(bpy)(CO)$_3$]$^−$ was assumed to come mainly from reduction of [Re(bpy)(CO)$_3$Cl]$^{•−}$ (or [Re(bpy)(CO)$_3$]$_2$[8]). This cannot be correct since reduction of [Re(bpy)(CO)$_3$Cl]$^{•−}$ requires a potential significantly negative of that used (see Table 1). As for the dimer [Re(bpy)(CO)$_3$]$_2$, this is not produced in the presence of CO$_2$ since the reaction of [Re(bpy)(CO)$_3$]$^•$ with CO$_2$ is apparently faster than electron transfer from the cathode.[5,11] A later publication,[9] however, hinted at another route[6] to the five-coordinate anion [Re(bpy)(CO)$_3$]$^−$, *via* [Re(bpy)(CO)$_3$(CH$_3$CN)]$^•$, eqs 6 and 7. The reduction in

$$[\mathrm{Re(bpy)(CO)_3}]^\bullet + \mathrm{CH_3CN} \rightarrow [\mathrm{Re(bpy)(CO)_3(CH_3CN)}]^\bullet \quad (6)$$

$$[\mathrm{Re(bpy)(CO)_3(CH_3CN)}]^\bullet + e^- \Longrightarrow [\mathrm{Re(bpy)(CO)_3}]^- + \mathrm{CH_3CN} \quad (7)$$

eq 7 occurs at a potential (see Table 1) very close to that of the reduction of [Re(bpy)(CO)$_3$Cl] to [Re(bpy)(CO)$_3$Cl]$^{•−}$ (eq 1), and hence, [Re(bpy)(CO)$_3$]$^•$ and [Re(bpy)(CO)$_3$]$^−$ can be produced simultaneously in *acetonitrile* solution. The initial scheme was altered slightly[9] from that proposed in the earlier publications, but the main points remain the same; *i.e.*, [Re(bpy)(CO)$_3$]$^•$ and [Re(bpy)(CO)$_3$]$^−$ are present in solution at the same time and can catalyze both the reduction of CO$_2$ to CO and CO$_3{}^{2−}$ *via* the one- and two-electron pathways, respectively.

(iii) Mechanism of Christensen et al.[11] This mechanism was formulated on the basis of an IR spectroelectrochemical investigation of [Re(dmbpy)(CO)$_3$Cl] in *acetonitrile*. In contrast to Sullivan and Meyer and co-workers, Christensen *et al.* had doubts about the simultaneous formation of [Re(dmbpy)(CO)$_3$]$^•$ and [Re(dmbpy)(CO)$_3$]$^−$ since they saw “no evidence for the production of [Re(dmbpy)(CO)$_3$]$^−$ at the relatively positive potentials at which CO$_2$ is first reduced.”[16] A possible explanation for this is the higher basicity of the dmbpy$^{•−}$ ligand relative to bpy$^{•−}$, which could prevent the coordination of CH$_3$CN to the five-coordinate radical and hence suppress the production of [Re(dmbpy)(CO)$_3$(CH$_3$CN)]$^•$. As stated above, Sullivan and Meyer and co-workers intimated[9] that the production of [Re(dmbpy)(CO)$_3$(CH$_3$CN)]$^•$ is required if [Re(dmbpy)(CO)$_3$]$^•$ and [Re(dmbpy)(CO)$_3$]$^−$ are to be generated simultaneously (eqs 6 and 7). Therefore, the scheme of Christensen *et al.* generally follows the one-electron mechanism of Sullivan and Meyer and co-workers with the exception that it contains, for the first time, the influence of adventitious water in CH$_3$CN which causes the formation of the formate complex [Re(dmbpy)(CO)$_3$(O$_2$CH)] and its singly reduced form, which are known byproducts of the CO$_2$ reduction using these rhenium catalysts,[3,5,11] eqs 8 and 9.

$$[\mathrm{Re(dmbpy)(CO)_3(CO_2)}]^\bullet + e^- + \mathrm{H_2O} \Longrightarrow [\mathrm{Re(dmbpy)(CO)_3(O_2CH)}] + \mathrm{OH}^- \quad (8)$$

$$[\mathrm{Re(dmbpy)(CO)_3(O_2CH)}] + e^- \Longrightarrow [\mathrm{Re(dmbpy)(CO)_3(O_2CH)}]^{\bullet -} \quad (9)$$

The mechanism of Sullivan and Meyer and co-workers[9] is an elegant scheme although, until the IR spectroelectrochemical data were produced,[11] there was little spectroscopic evidence for the suggested reactive species. Unfortunately, as stated above, these IR results are for [Re(dmbpy)(CO)$_3$Cl] and have shown that its behavior is different from that of [Re(bpy)(CO)$_3$Cl] in that the 2e path seems to be absent and therefore the catalytic activity of [Re(bpy)(CO)$_3$]$^−$ could not be studied. We have therefore undertaken an IR spectroelectrochemical study of the title complexes with four major goals in mind:

Goal 1. To Provide IR Spectroscopic Evidence for the Mechanism of CO$_2$ Reduction Using [Re(bpy)(CO)$_3$Cl]. This paper describes the first published[17] IR spectroelectrochemical work on the most studied catalytic precursor [Re(bpy)(CO)$_3$Cl] and as such provides the first IR spectroscopic evidence for the one- and two-electron pathways proposed by Sullivan and Meyer and co-workers; this proved impossible using [Re(dmbpy)(CO)$_3$Cl] as the catalytic precursor.

Goal 2. To Study Separately the One- and Two-Electron Pathways for CO$_2$ Reduction and To Confirm the Catalytic Activity of both [Re(bpy)(CO)$_3$]$^•$ and [Re(bpy)(CO)$_3$]$^−$. As was stated above, the catalytic cycle of [Re(bpy)(CO)$_3$Cl] involves both these species and therefore their individual catalytic activities cannot be investigated. In order to separate the one- and two-electron pathways it is necessary to study Re(bpy) species with different reduction behavior. It is known[14] that, upon reduction, [Re(bpy)(CO)$_3$(Otf)] forms [Re(bpy)(CO)$_3$(THF)]$^+$ (in an electrode-catalyzed step), which is then reduced to give the dimer [Re(bpy)(CO)$_3$]$_2$. In this case no six-coordinate [Re(bpy)(CO)$_3$(THF)]$^•$ radicals are detected, and this combined with the relatively positive reduction potential of [Re(bpy)(CO)$_3$(Otf)] (Table 1) ensures that no [Re(bpy)(CO)$_3$]$^−$ is produced *via* the equivalent of eqs 6 and 7, with only

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[16] It should be noted that, as previously indicated by Stor *et al.*,[14] Christensen *et al.*[11] wrongly assigned three of the four frequencies of [Re(dmbpy)(CO)$_3$]$_2$ to the coordinatively unsaturated radical [Re(dmbpy)(CO)$_3$]$^•$. Radicals of this type are known to be stable only in nonpolar solvents such as cyclohexane and toluene. See for example: Andréa, R. R.; de Lange, W. G. J.; van der Graaf, T.; Rijkhoff, M.; Stufkens, D. J.; Oskam, A. *Organometallics* **1988**, *7*, 1100.

[17] Shu and Wrighton have made preliminary studies on this system, but their results remain unpublished.[7]

$[Re(bpy)(CO)_3]^{\bullet}$ radicals present as catalytically active species; *i.e.*, the only potential route for CO_2 reduction is the one-electron pathway. In contrast to this behavior $[Re(bpy)(CO)_3\{P(OEt)_3\}]^{\bullet}$ radicals are extremely stable in the absence of excess $P(OEt)_3$[18] (see below) and do not decay to the dimer but are subsequently reduced to the five-coordinate anion $[Re(bpy)(CO)_3]^-$ allowing the independent study of the two-electron pathway. This is the first IR spectroelectrochemical study of the electrocatalytic behavior of $[Re(bpy)(CO)_3(X)]^n$ complexes other than the halide derivatives ($X = Cl^-, Br^-$; $n = 0$).

Goal 3. To Study the Reduction of the Formate Complex [Re(dmbpy)(CO)$_3$(O$_2$CH)] by IR Spectroelectrochemistry. This complex and its radical anion appear to be important side products in the catalytic mechanism of CO_2 reduction,[3,5,11] and their existence indirectly provides evidence for the existence of the radical $[Re(bpy)(CO)_3(CO_2)]^{\bullet}$ and its reaction with adventitious water (eq 8). The independent study of this formate complex should confirm the validity of eqs 8 and 9 and also whether $[Re(bpy)(CO)_3(O_2CH)]$ may be reduced to the corresponding radical anion $[Re(bpy)(CO)_3(O_2CH)]^{\bullet-}$ (eq 9) at the reduction potentials of the various complexes under study. It has been suggested that $[Re(bpy)(CO)_3(O_2CH)]$ is a source of free formate in solution[8] (eqs 10 and 11) and the IR OTTLE (optically transparent thin-layer electrochemical) experiments should be able to validate this proposal.

$$[Re(bpy)(CO)_3(O_2CH)]^{\bullet-} \rightarrow [Re(bpy)(CO)_3]^{\bullet} + HCO_2^- \tag{10}$$

$$[Re(bpy)(CO)_3(O_2CH)]^{\bullet-} + e^- \rightarrow [Re(bpy)(CO)_3]^- + HCO_2^- \tag{11}$$

Goal 4. To Study the Potential Catalytic Activity of the Six-Coordinate Anions [Re(bpy)(CO)$_3$(L)]$^-$. The reduction of $[Re(bpy)(CO)_3Cl]$ in CH_3CN at 293−213 K always leads finally to a mixture of the *five*- and *six*-coordinate anions[15] (eq 5). The potential catalytic activity of the six-coordinate anion $[Re(bpy)(CO)_3(CH_3CN)]^-$, which has not been previously considered in the existing catalytic cycles, cannot be studied independently of the five-coordinate derivatives. We have therefore studied the reduction of $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ in the presence of excess $P(OEt)_3$ in an attempt to obtain the six-coordinate anion $[Re(bpy)(CO)_3\{P(OEt)_3\}]^-$ without the involvement of a five-coordinate derivative.

Experimental Section

Materials and Preparations. Tetrahydrofuran (THF, Janssen or Aldrich) was distilled from a Na/benzophenone mixture under nitrogen atmosphere or from CaH_2 under argon. Acetonitrile (CH_3CN, Janssen or Aldrich) was refluxed with CaH_2 under nitrogen and distilled prior to use. Bu_4NPF_6 (Fluka or Aldrich) was dried under vacuum overnight at 80 °C. Et_4NCl (Fluka) was dried at 50 °C. $P(OMe)_3$ was distilled under vacuum from CaH_2. $AgCF_3SO_3$ (Aldrich), NH_4O_2CH (Aldrich), and acetone (Aldrich HPLC grade) were used as supplied. The complexes $[Re(bpy)(CO)_3Cl]$,[14] $[Re(bpy)(CO)_3(Otf)]$,[14] $[Re(bpy)(CO)_3\{P(OEt)_3\}]PF_6$,[18,19] and $[Re(bpy)(CO)_3(CH_3CN)]SbF_6$[20] were prepared as previously described. $[Re(bpy)(CO)_3(O_2CH)]$ was prepared by the thermal substitution of Otf in $[Re(bpy)(CO)_3(Otf)]$.[21] In a typical preparation, $[Re(bpy)(CO)_3Cl]$ (300 mg, 0.65 mmol) was dissolved in acetone (50 mL). $AgCF_3SO_3$ (184 mg, 0.72 mmol) was added, and the solution was refluxed under argon in the dark for 1 h, producing $[Re(bpy)(CO)_3(Otf)]$ and AgCl that was filtered off. NH_4O_2CH (ca. 1 g, 16 mmol) was added to the filtrate, and the solution was refluxed under argon for 8 h. The solution was then cooled, and the product was precipitated by the addition of water, filtered out, and then washed with copius amounts of water. The yellow powdery product $[Re(bpy)(CO)_3(O_2CH)]$ was obtained in approximately 70% yield.

All spectroelectrochemical samples were handled carefully under a nitrogen or argon atmosphere. CO_2 was introduced into the solutions by bubbling through a S3 frit.

Spectroscopic and (Spectro)electrochemical Instrumentation. FTIR spectra were measured on Perkin-Elmer 2000 (2 cm^{-1} resolution) or Bio-Rad FTS-7 (2 cm^{-1} resolution) spectrometers. An IR OTTLE cell[22] equipped with a masked Pt-minigrid working electrode (32 wires/cm) and CaF_2 windows was employed for the IR spectroelectrochemical experiments. Cyclic voltammetry and controlled-potential electrolyses within the OTTLE cell were carried out by using a PA4 (EKOM, Czech Republic) potentiostat or a PAR 362 scanning potentiostat connected to an EG&G Condecon 310 system. For all spectroelectrochemical experiments the concentrations of the complexes and Bu_4NPF_6 (and/or Et_4NCl) were 3×10^{-3}–10^{-2} and 0.3 M, respectively. The cyclic voltammetric experiments, performed in neat THF or in THF:CH_3CN = 3:2 (v/v), used concentrations of 10^{-3} and 10^{-1} M in the complexes and Bu_4NPF_6, respectively. CV measurements were performed in either a single-compartment gastight cyclic voltammetric cell equipped with a Pt-disk working electrode of 0.4 mm radius, a Pt-gauze auxiliary electrode, and an Ag-wire pseudoreference electrode or in argon-purged solutions using Pt-bead working and auxiliary electrodes and an Ag-wire pseudoreference electrode. The potentials in Table 1 are reported against the standard ferrocene/ferrocenium (Fc/Fc$^+$) redox couple.[23]

IR Spectroelectrochemical Experiment. The following procedure has been employed for all spectroelectrochemical experiments described in this paper. Initially, the Pt minigrid working electrode was set at a rest potential. The measurement started by sweeping the potential negatively and recording the thin-layer cyclic voltammogram. The potential sweep was halted when an electrolytic current begun to flow due to the first cathodic step. The potential was then varied carefully within the potential range of the cathodic peak in approximately 50 mV steps. At each potential step an IR spectrum was taken after the electrolytic current had dropped to 5−10% of its initial value. The electrolysis time per step did not exceed 30 s. After having passed the reduction of the parent complex, the IR spectroelectrochemical experiment continued in the same manner with the reduction of the products. The application of the small potential steps, in order to avoid high electrolytic currents i_c and subsequent uncontrolled potential shifts due to a large ohmic potential drop i_cR ($\Delta E = E_{appl} - i_cR$), was particularly necessary in the case of a complicated reduction path like those depicted in Schemes 3 and 4. (Note the small differences between the reduction potentials of the starting complexes and some of the reduction products as revealed by conventional cyclic voltammetry, Table 1.) The electrocatalytic CO_2 reduction was monitored by IR spectroscopy for a period of 2−15 min, dependent on the development of free CO at the minigrid cathode that finally precluded

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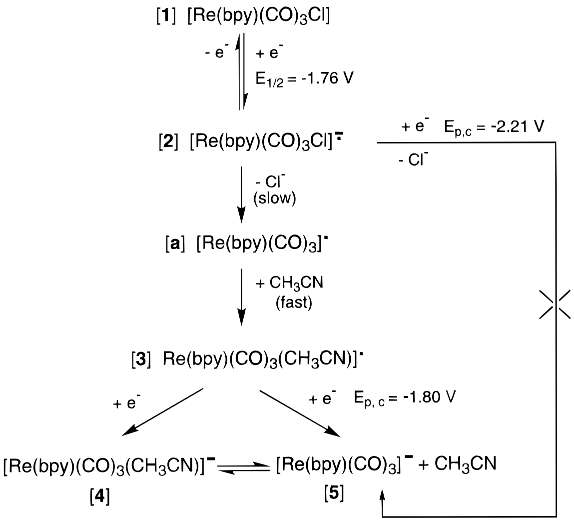
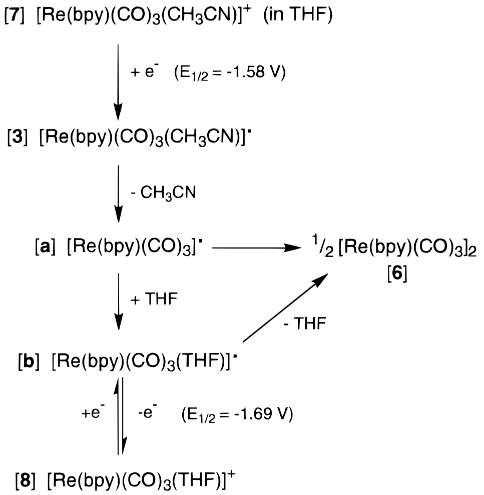
Scheme 3



Scheme 4



further monitoring. During this time the potential of the working electrode was kept close to the peak potential of the cathodic process that created the catalyst. It is important to note that diffusion and mixing of the redox products, generated at the working and auxiliary electrodes in the IR OTTLE cell used,[22] was reasonably suppressed within the total experimental time (typically 20−25 min for one complete measurement), which might otherwise lead to ambiguous results.

Results

The ν(CO) frequencies of all the starting materials and the reduction products are collected in Table 2. The assignment of the reduced species largely follows the reported literature data on these or closely related compounds[5,7,11,13−15,38] (see Table 2), and it is not discussed hereinafter in detail.

1. Reduction of [Re(bpy)(CO)$_3$Cl] (1) in Acetonitrile Solution with Excess Cl$^-$ under Argon (Figure 1). Initially, upon one-electron reduction, the three ν(CO) bands of [Re(bpy)(CO)$_3$Cl] (**1**) are seen to decrease with the concomitant production of three new bands readily assigned to the radical anion [Re(bpy)(CO)$_3$Cl]$^{\bullet-}$ (**2**)[7,24] (Figure 1a). After approximately 50% of the parent complex is reduced, features assignable to the solvated radical [Re(bpy)(CO)$_3$(CH$_3$CN)]$^{\bullet}$ (**3**) begin to appear[15] (Figure 1b), formed by the substitution of Cl$^-$by CH$_3$CN, demonstrating the lability of the Re−Cl bond in **2** at room temperature even in the presence of excess Cl$^-$. The lower frequency absorptions are masked somewhat by those of the other species, but the high frequency band at 2003 cm^{-1} is clearly visible. The formation of **3** is accompanied by the concomitant growth of bands due to both the six- and five-coordinate anions [Re(bpy)(CO)$_3$(CH$_3$CN)]$^-$ (**4**) and [Re(bpy)(CO)$_3$]$^-$ (**5**), respectively. It is not surprising that the concentration of the six-coordinate anion **4** is much higher in CH$_3$CN with respect to the five-coordinate anion **5** since CH$_3$CN is a relatively soft base and coordinates well to the rhenium center. There is no detectable amount of the dimer, [Re(bpy)(CO)$_3$]$_2$, as the radicals appear to react too rapidly with CH$_3$CN for dimerization to occur. Figure 1b clearly shows that the 2e-reduced anions **4** and **5** can be produced at the same potential as the singly reduced species [Re(bpy)(CO)$_3$Cl]$^{\bullet-}$ (**2**) and [Re(bpy)(CO)$_3$(CH$_3$CN)]$^{\bullet}$ (**3**) and can exist in solution not only with these but also with the neutral starting complex [Re(bpy)(CO)$_3$Cl] (**1**)! This behavior can be readily explained by eqs 1, 2, 6, 7, and 5 and by Scheme 3. In Scheme 3, and the later schemes, the **bold** numbers (*i.e.* [**1**], [**2**], *etc.*) refer to species identified by infrared spectroscopy and the **bold** letters refer (*i.e.* [**a**], [**b**], *etc.*) to postulated intermediates not so identified. Also in Scheme 3, the quoted $E_{\mathrm{p,c}}$ values refer to solution in THF/CH$_3$CN.

Table 2. ν(CO) Frequencies of the Various Complexes under Study, Their Reduction Products, and Closely Related Compounds

complex (no.)	ν(CO)/cm^{-1}	solvent	ref
[Re(bpy)(CO)$_3$Cl] (**1**)	2020.5, 1914, 1897	CH$_3$CN	*a*
	2019, 1917, 1895	THF	14
	2019, 1914, 1893	DMF	7
	2020, 1920, 1900	CH$_2$Cl2	5
[Re(bpy)(CO)$_3$Cl]$^{\bullet-}$ (**2**)	1998, 1885, 1867.5	CH$_3$CN	*a*
	1996, 1883, 1868	THF	14
	1994, 1880, 1862	DMF	7
[Re(bpy)(CO)$_3$(CH$_3$CN)]$^{\bullet}$ (**3**)	2011,[b] 1895 (br)	CH$_3$CN	*a*
[Re(bpy)(CO)$_3$(CH$_3$CN)]$^-$ (**4**)	1986, 1868, 1852	CH$_3$CN	*a*
[Re(bpy)(CO)$_3$]$^-$ (**5**)	1947, 1843 (br)	THF	14
	1948, ~1846	CH$_3$CN	*a*
[Re(bpy)(CO)$_3$]$_2$ (**6**)	1986, 1950, 1888, 1857	THF	14
[Re(bpy)(CO)$_3$(CH$_3$CN)]$^+$ (**7**)	2041, 1937 (br)	CH$_3$CN	*a*, 38
	2038, 1933 (br)	THF	*a*
[Re(bpy)(CO)$_3$(THF)]$^+$ (**8**)	2018, 1915, 1891	THF	14
[Re(bpy)(CO)$_3$(O$_2$CH)] (**9**)	2019, 1915.5, 1893.5	THF	*a*
[Re(bpy)(CO)$_3$(O$_2$CH)]$^{\bullet-}$ (**10**)	1996.5, 1878.5 (br)	THF	*a*
[Re(bpy)(CO)$_3$(Otf)] (**11**)	2032, 1923, 1918	THF	14
[Re(bpy)(CO)$_3${P(OEt)$_3$}]$^+$ (**12**)	2043, 1961.5, 1926.5	THF	*a*
[Re(bpy)(CO)$_3${P(OEt)$_3$}]$^{\bullet}$ (**13**)	2020, 1927, 1896	THF	*a*
[Re(bpy)(CO)$_2${P(OEt)$_3$}$_2$]$^{\bullet}$ (**14**)	1930, 1851	THF	*a*
	1928.5, 1848.5	CH$_3$CN	13
[Re(bpy)(CO)$_3${P(OEt)$_3$}]$^-$ (**15**)	1998, 1889.5, 1879	THF	*a*
[Re(bpy)(CO)$_3$(*n*-PrCN)]$^-$	1980, 1861, 1851	*n*-PrCN[c]	15
[Re(bpy)(CO)$_3$(*n*-PrCN)]$^{\bullet}$	2010, 1905, 1885	*n*-PrCN[c]	15
[Re(dapa)(CO)$_3${P(OMe)$_3$}]$^+$ [d]	2044, 1963, 1929	THF	14
[Re(dapa)(CO)$_3${P(OMe)$_3$}]$^{\bullet}$ [d]	2020, 1929, 1898	THF	14
[Re(dapa)(CO)$_2${P(OMe)$_3$}$_2$]$^{\bullet}$ [d]	1940, 1862	THF	14
[Re(dapa)(CO)$_3${P(OMe)$_3$}]$^-$ [d]	1997, 1892, 1872	THF	14

[a] This work. [b] Between 2008 and 2003 cm^{-1} in CH$_3$CN/excess Cl$^-$. [c] Butyronitrile. [d] dapa = 2,6-diacetylpyridinebis(anil).

The data in Table 1 show that [Re(bpy)(CO)$_3$(CH$_3$CN)]$^{\bullet}$ (**3**) can be reduced simultaneously with the starting complex, [Re(bpy)(CO)$_3$Cl] (**1**), to give the anions **4** and **5** since the reduction potentials of **1** and **3**

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[24] George, M. W.; Johnson, F. P. A.; Westwell, J. R.; Hodges, P. M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1994**, 2977.

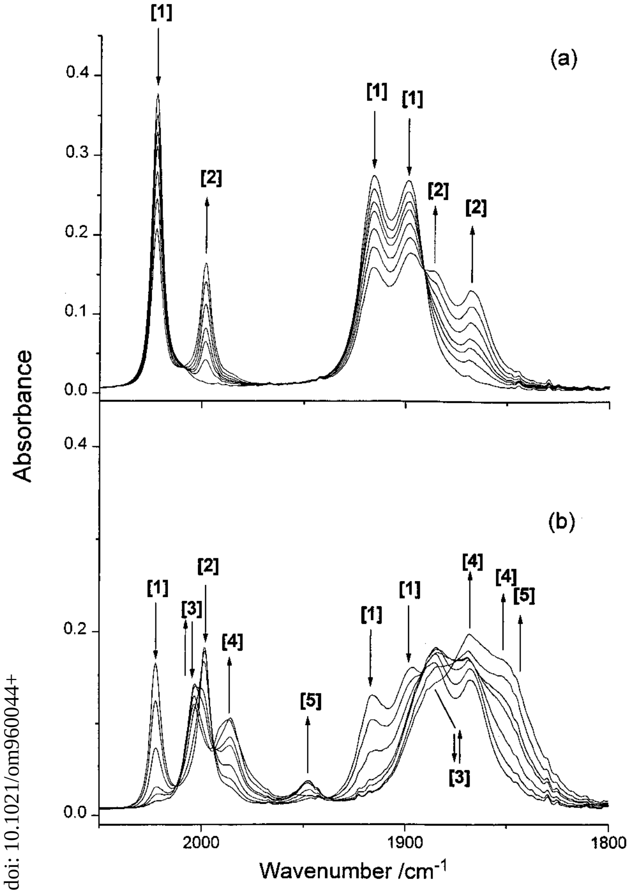

Figure 1. ν(CO) IR spectral changes following OTTLE cell reduction of $[Re(bpy)(CO)_3Cl]$ (**1**) in *acetonitrile* solution containing excess Et_4NCl as electrolyte (arrows indicate whether the bands decrease ↓ or increase ↑): (a) Initial reduction of $[Re(bpy)(CO)_3Cl]$ (**1**) leading to the growth of the one-electron reduced radical anion $[Re(bpy)(CO)_3Cl]^{\bullet -}$ (**2**); (b) the three ν(CO) bands assigned to $[Re(bpy)(CO)_3Cl]$ (**1**) continuing to decrease. The radical anion $[Re(bpy)(CO)_3Cl]^{\bullet -}$ (**2**) is unstable and decays to produce the solvento radical $[Re(bpy)(CO)_3(CH_3CN)]^{\bullet}$ (**3**), which is reduced at a similar potential to $[Re(bpy)(CO)_3Cl]$ (**1**) to give the two-electron reduced anions, $[Re(bpy)(CO)_3(CH_3CN)]^-$ (**4**) and $[Re(bpy)(CO)_3]^-$ (**5**).

are almost identical. Observation of the formation of $[Re(bpy)(CO)_3(CH_3CN)]^{\bullet}$ (**3**) *without* any anions would require a potential difference between the two of at least 250 mV. This explains, as was intimated previously,[9] how the one- and two-electron pathways can co-exist at lower potentials in CH_3CN. This is in complete contrast to the behavior of $[Re(dmbpy)(CO)_3Cl]$,[11] which gives the dimer, $[Re(dmbpy)(CO)_3]_2$, upon one-electron reduction even in CH_3CN and requires a negative potential shift to form $[Re(dmbpy)(CO)_3]^-$, hence eliminating the two-electron anionic reduction pathways at the less negative potentials used by Christensen *et al.*[11]

2. Reduction of $[Re(bpy)(CO)_3Cl]$ (1) in THF Solution with Excess Cl^- under Argon (Figure 2). Stor *et al.*[14] reported that IR OTTLE one-electron reduction of $[Re(bpy)(CO)_3Cl]$ (**1**) in THF/PF_6^- (*in the absence of excess Cl^-*) led to a very small amount of $[Re(bpy)(CO)_3Cl]^{\bullet -}$ (**2**) which was in equilibrium with the major product, the dimer $[Re(bpy)(CO)_3]_2$ (**6**). In contrast to the results in CH_3CN described above, no $[Re(bpy)(CO)_3(THF)]^{\bullet}$ is observed, presumably since THF has much weaker coordination properties being a hard base compared with CH_3CN. The IR OTTLE experiment under the title conditions was performed in order to observe how much the radical anion $[Re(bpy)(CO)_3)Cl]^{\bullet -}$ (**2**) could be stabilized with respect to Cl^- loss and to observe subsequent dimerization in the presence of large excess (~×50) of Cl^-.

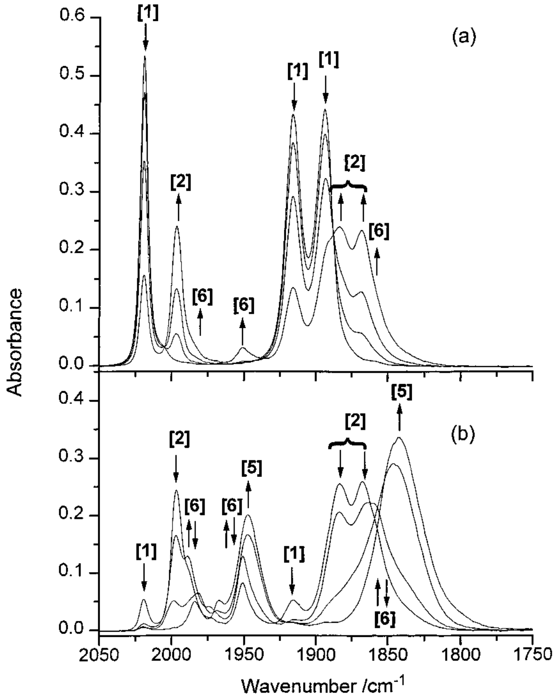

Figure 2. ν(CO) IR spectral changes following OTTLE cell reduction of $[Re(bpy)(CO)_3Cl]$ (**1**) in *THF* solution containing excess Et_4NCl as electrolyte (arrows indicate whether the bands decrease ↓ or increase ↑): (a) Initial reduction of $[Re(bpy)(CO)_3Cl]$ (**1**) leading to the growth of the one-electron reduced radical anion $[Re(bpy)(CO)_3Cl]^{\bullet -}$ (**2**). Small features due to the dimer $[Re(bpy)(CO)_3]_2$ (**6**) can been seen to appear as the unstable radical anion **2** begins to decay. (b) The starting complex $[Re(bpy)(CO)_3Cl]$ (**1**) is further reduced. The three ν(CO) bands of **2** decrease with a concomitant increase in the intensity of the ν(CO) bands assigned to the dimer **6**. As the potential is shifted more negatively, the dimer is reduced leading to the appearance of two new bands assigned to the two-electron reduced, five-coordinate anion $[Re(bpy)(CO)_3]^-$ (**5**).

Figure 2 shows that under these conditions the dissociation of Cl^- could be slowed down since reduction of approximately the first 30% of $[Re(bpy)(CO)_3Cl]$ (**1**) led only to the corresponding radical anion **2**; however, at this point the dimer $[Re(bpy)(CO)_3]_2$ (**6**) began to appear (Figure 2a). This contradicts the assumption[5] that in the presence of excess Cl^- ions the radical anion would be stable; this is clearly not the case. In order to complete the reduction of $[Re(bpy)(CO)_3Cl]$ (**1**) the potential was shifted more negative which led to the partial reduction of the dimer giving the five-coordinate anion, $[Re(bpy)(CO)_3]^-$ (**5**), as the only two-electron reduced species (Figure 2b). Due to the weak coordinating ability of THF, no six-coordinate anion, $[Re(bpy)(CO)_3(THF)]^-$, was observed . This result clearly indicates, in accordance with previous results,[14,15] that the reduction pathway of $[Re(bpy)(CO)_3Cl]$ (**1**) is strongly dependent on the solvent and concentration of free Cl^- ions. It would appear that the reduction pathway of $[Re(\textit{bpy})(CO)_3Cl]$ (**1**) in *THF* is identical to that of $[Re(\textit{dmbpy})(CO)_3Cl]$ in *CH_3CN*; *i.e.* the one-electron radical pathway is predominant at lower potentials due to the

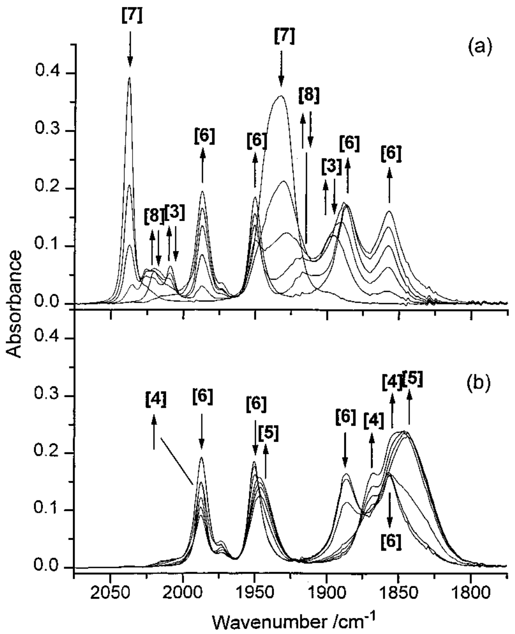

Figure 3. ν(CO) IR spectral changes following OTTLE cell reduction of $[Re(bpy)(CO)_3(CH_3CN)]^+$ (**7**) in *THF* solution (arrows indicate whether the bands decrease ↓ or increase ↑): (a) Initial reduction of $[Re(bpy)(CO)_3(CH_3CN)]^+$ (**7**) leading to the formation of $[Re(bpy)(CO)_3(CH_3CN)]^•$ (**3**) and $[Re(bpy)(CO)_3(THF)]^+$ (**8**). Subsequent one-electron reduction of the cation $[Re(bpy)(CO)_3(THF)]^+$ (**8**), accompanied also by rapid decay of $[Re(bpy)(CO)_3(CH_3CN)]^•$ (**3**), results in the formation of the dimer $[Re(bpy)(CO)_3]_2$ (**6**), which has four clearly resolved ν(CO) bands.[14] (b) Reduction of the dimer **6** leads initially to the five-coordinate anion $[Re(bpy)(CO)_3]^-$ (**5**). which reacts partially with the CH_3CN liberated previously from $[Re(bpy)(CO)_3(CH_3CN)]^•$ (**3**) to form the six-coordinate anion $[Re(bpy)(CO)_3(CH_3CN)]^-$ (**4**).

lack of a readily available route to the two-electron reduced anionic species.

3. Reduction of $[Re(bpy)(CO)_3(CH_3CN)]^+$ (7) in THF Solution under Argon (Figure 3). $[Re(bpy)(CO)_3(CH_3CN)]^•$ (**3**), produced by reduction of $[Re(bpy)(CO)_3(CH_3CN)]^+$ (**7**), is inherently stable in *CH_3CN*;[15] however, Figure 3 demonstrates that the reduction of $[Re(bpy)(CO)_3(CH_3CN)]^+$ (**7**) in *THF* leads to three identifiable products:[14,15] $[Re(bpy)(CO)_3(THF)]^+$ (**8**), $[Re(bpy)(CO)_3(CH_3CN)]^•$ (**3**), both in low concentration, and the dimer $[Re(bpy)(CO)_3]_2$ (**6**) as the major product (see Figure 3a). This result clearly shows that the CH_3CN ligand dissociates from $[Re(bpy)(CO)_3(CH_3CN)]^•$ (**3**) in THF as illustrated in Scheme 4.

The substitution followed by instantaneous oxidation of the THF-radical complex is possible since $[Re(bpy)(CO)_3(CH_3CN)]^+$ (**7**) is reduced 110 mV more positively than $[Re(bpy)(CO)_3(THF)]^+$ (**8**) (see Table 1), and therefore some amount of $[Re(bpy)(CO)_3(THF)]^•$ (**b**) will be oxidized immediately to the stable cation and the remainder will dimerize as observed. As the amount of liberated CH_3CN increased the more stable the $[Re(bpy)(CO)_3(CH_3CN)]^•$ (**3**) radical became, and hence, toward the end of the one-electron reduction its concentration began to increase more rapidly.

Figure 3b shows the effects of further reduction, and it is clear that the final reduction products are again the two electron reduced anions $[Re(bpy)(CO)_3(CH_3CN)]^-$ (**4**) and $[Re(bpy)(CO)_3]^-$ (**5**). In contrast to the experiment in CH_3CN, the concentration of $[Re(bpy)(CO)_3(CH_3CN)]^-$ (**4**) is much lower relative to that of $[Re(bpy)(CO)_3]^-$ (**5**) since there is only an equimolar amount of CH_3CN available for coordination.

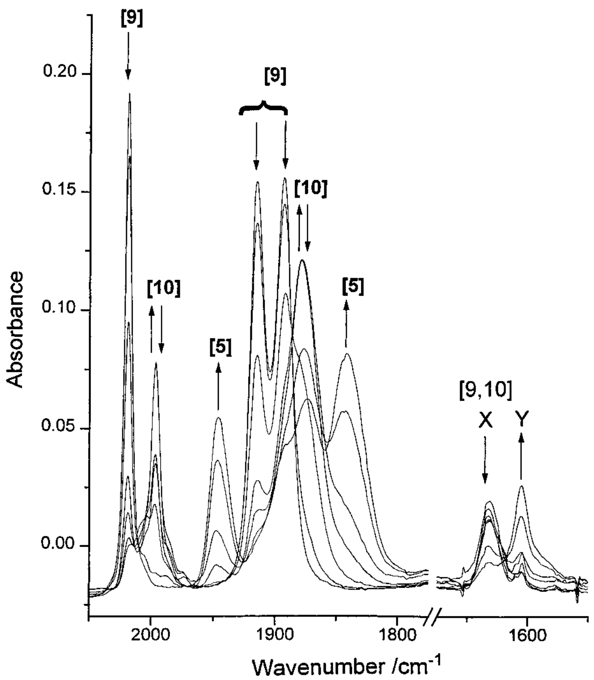

Figure 4. ν(CO) IR spectral changes following OTTLE cell reduction of $[Re(bpy)(CO)_3(O_2CH)]$ (**9**) in *THF* solution (arrows indicate whether the bands decrease ↓ or increase ↑). One-electron reduction of $[Re(bpy)(CO)_3(O_2CH)]$ (**9**) leads to the formation of the radical anionic species $[Re(bpy)(CO)_3(O_2CH)]^{•-}$ (**10**). The ν_{as}(COO) bands of the coordinated formate in both **9** and **10** are coincident and marked X. Further reduction causes the production of the five-coordinate two-electron-reduced species $[Re(bpy)(CO)_3]^-$ (**5**), confirmed by the appearance of a new feature assignable to the ν_{as}(COO) vibration of free formate in solution, marked Y in the figure.

4. Reduction of $[Re(bpy)(CO)_3(O_2CH)]$ (9) in THF Solution under Argon (Figure 4). As stated in the Introduction, $[Re(bpy)(CO)_3(O_2CH)]$ is a known side product of the catalytic reduction of CO_2 using $[Re(bpy)(CO)_3Cl]$,[3,5,11] and therefore an IR OTTLE study of an independently synthesized sample was performed. The CV of $[Re(bpy)(CO)_3(O_2CH)]$ takes essentially the same form as that of $[Re(bpy)(CO)_3Cl]$ showing one chemically and electrochemically reversible, bipyridine-based reduction and one chemically irreversible, probably rhenium-based reduction (see Table 1). Figure 4 shows that $[Re(bpy)(CO)_3(O_2CH)]$ (**9**) exhibits three ν(CO) bands in very similar positions to those of $[Re(bpy)(CO)_3Cl]$ (**1**) (see Table 2) along with the formate vibrations, ν_{as}(COO) at 1630 cm^{-1} and ν_s(COO) at 1280 cm^{-1} (not shown) as expected.[5] Upon one-electron reduction two new ν(CO) bands were observed assigned to the radical anion $[Re(bpy)(CO)_3(O_2CH)]^{•-}$ (**10**) (Table 2). This species appeared to be stable with respect to formate loss as no dimer formation, and no change in the ν_{as}(COO) region (which would indicate the production of free formate ($\nu_{as}(COO) = 1604$ cm^{-1}) via eq 10), was observed. After approximately 80% of $[Re(bpy)(CO)_3(O_2CH)]$ (**9**) had been reduced to $[Re(bpy)(CO)_3(O_2CH)]^{•-}$ (**10**), the two-electron reduced five-coordinate

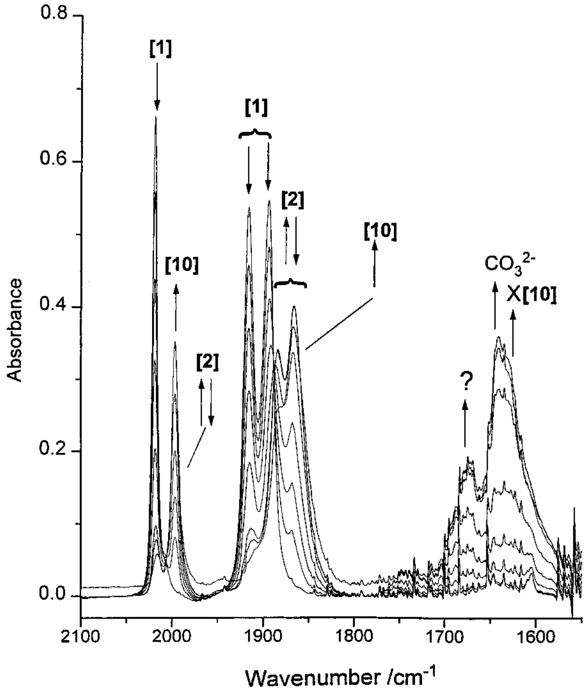

Figure 5. ν(CO) IR spectral changes following OTTLE cell reduction of [Re(bpy)(CO)$_3$Cl] (**1**) in CO_2-saturated *THF* solution in the presence of excess Cl^- (arrows indicate whether the bands decrease ↓ or increase ↑). One-electron reduction of [Re(bpy)(CO)$_3$Cl] (**1**) initially produces [Re(bpy)(CO)$_3$Cl]$^{\bullet-}$ (**2**), which leads slowly to the reduction of CO_2 producing CO and CO_3^{2-}. As the CO_2 reduction progresses, the concentration of [Re(bpy)(CO)$_3$Cl] (**1**) decreases and [Re(bpy)(CO)$_3$Cl]$^{\bullet-}$ (**2**) is converted into [Re(bpy)(CO)$_3$(O$_2$CH)]$^{\bullet-}$ (**10**). This is evidenced by the shoulder marked X on the low-frequency side of the feature due to CO_3^{2-}, assigned to the ν_{as}(COO) band of the coordinated formate in **10**. The band marked **?** is that of the unknown carboxylato product (see text).

anion [Re(bpy)(CO)$_3$]$^-$ (**5**) began to form,[25] accompanied by the production of free formate, as evidenced by the ν_{as}(COO) band at 1604 cm^{-1} (eq 11).

It is clear from these results that the reduction of [Re(bpy)(CO)$_3$(O$_2$CH)] (**9**) leads to an essentially stable radical anion, in contrast to [Re(bpy)(CO)$_3$Cl] (**1**), since none of the dimer [Re(bpy)(CO)$_3$]$_2$ (**6**) and hence no five-coordinate radicals are produced. The production of [Re(bpy)(CO)$_3$(O$_2$CH)]$^{\bullet-}$ (**10**) in any of the experiments described below is therefore *not* a route to the one-electron catalytic pathway, although upon two-electron reduction it can produce free formate.

The four experiments described above demonstrate a number of points relevant to CO_2 reduction: In CH_3CN, the one-electron (radical) and two-electron (anionic) CO_2 reduction pathways can run simultaneously at the potential required to initiate the one-electron reduction of [Re(bpy)(CO)$_3$Cl] (Scheme 3), whereas, in THF, the one-electron pathway will dominate at less negative potentials since little or no anionic species can be formed. The six-coordinate anion can be obtained even in a THF solution containing a relatively low concentrations of CH_3CN (equimolar), and therefore, the two-electron pathway is complicated since it is not known whether one or both of the five- and six-coordinate anions are catalytically active. The IR OTTLE experiments performed in the presence of CO_2 are described below.

5. Reduction of [Re(bpy)(CO)$_3$Cl] (1) in THF Solution with Excess Cl^- in the Presence of CO_2 (Figure 5). The one-electron reduction of [Re(bpy)(CO)$_3$Cl] (**1**) under the title conditions initially leads, as expected,[7,11,24] to the radical anion [Re(bpy)(CO)$_3$Cl]$^{\bullet-}$ (**2**). Initially CO_2 reduction is slow as can be seen by the very small changes in the 1700−1500 cm^{-1} region of the spectrum[26] confirming that production of [Re(bpy)(CO)$_3$Cl]$^{\bullet-}$ (**2**) alone is not sufficient to catalyze CO_2 reduction. This observation disproves the assumption[8,9] that CO_2 reacts directly with **2**. CO_2 reduction was considerably accelerated at the point when, according to the blank experiment in the absence of CO_2 (see part 2 above), the dimer [Re(bpy)(CO)$_3$]$_2$ (**6**) would be formed. There is no evidence for the dimer in this experiment. Instead, a new species is produced along with the continued growth of bands due to [Re(bpy)(CO)$_3$Cl]$^{\bullet-}$ (**2**). This new species has very similar ν(CO) stretching frequencies to the radical anion and can be most easily identified by the changes in the low-frequency ν(CO) region toward the end of the reduction of **1** where it is clear that the two ν(CO) bands due to [Re(bpy)(CO)$_3$Cl]$^{\bullet-}$ (**2**) are changing to one broad band. This band, along with one that is coincident with the high-frequency band of [Re(bpy)(CO)$_3$Cl]$^{\bullet-}$ (**2**) at 1996 cm^{-1}, can be assigned to the stable radical anion [Re(bpy)(CO)$_3$(O$_2$CH)]$^{\bullet-}$ (**10**) (Table 2), along with the shoulder appearing at 1628 cm^{-1} due to coordinated formate (see part 4 above). The reduction of [Re(bpy)(CO)$_3$(O$_2$CH)] (**9**) to the radical anion **10** at the reduction potential of [Re(bpy)(CO)$_3$Cl] (**1**) is certainly possible (see Table 1), and the inherent stability of [Re(bpy)(CO)$_3$(O$_2$CH)]$^{\bullet-}$ (**10**) at the reduction potential of the parent complex, [Re(bpy)(CO)$_3$Cl] (**1**), was demonstrated by the independent IR OTTLE experiment described above. This formate complex can reasonably be considered as a side product in the catalytic mechanism (see eqs 8 and 9)[3,5,11] and can remain in the solution even after all the [Re(bpy)(CO)$_3$Cl] (**1**) had been reduced. CO gas was produced, as evidenced by the small band due to free CO in solution (not shown), and by the appearance of bubbles in the thin solution layer at the surface of the Pt minigrid working electrode in the latter stages of reduction. The other products of CO_2 reduction could be seen in the 1700−1500 cm^{-1} region of the IR spectrum. The most intense band at 1640 cm^{-1} is ascribed to free CO_3^{2-} in the form of an ion pair.[11,27] As shown in part 4 above, the shoulder at 1628 cm^{-1} belongs to the coordinated O_2CH^- ligand in [Re(bpy)(CO)$_3$(O$_2$CH)]$^{\bullet-}$ (**10**). The band at 1680 cm^{-1}, which grows independently of the band at 1640 cm^{-1} and which possesses a comparable intensity with the latter peak (particularly at the beginning of the CO_2 reduction), might be assigned to some other organic carboxylato product or its salt (*i.e.* not to a ligand coordinated to the Re(bpy)(CO)$_3$ unit since no ν(CO) bands of some

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[25] The reduction of [Re(bpy)(CO)$_3$(O$_2$CH)] is well separated from that of [Re(bpy)(CO)$_3$(O$_2$CH)]$^{\bullet-}$ (see Table 1), and therefore, the production of [Re(bpy)(CO)$_3$]$^-$ before the completion of the first reduction step is probably due to an i_cR drop across the minigrid working electrode.

[26] The various products of CO_2 reduction also have absorptions in the 1100−1500 cm^{-1} region of the spectrum,[11] which has been omitted for clarity since most of the products can be assigned from the 1500−1700 cm^{-1} region only.

[27] Christensen, P.; Hamnett, A.; Muir, A. V. G.; Freeman, N. A. *J. Electroanal. Chem.* **1990**, *288*, 197.

other carbonyl complex were found). Note that the bands at 1640 and 1680 cm^{-1} are always present in the IR spectra obtained in the course of the CO_2 reduction (see below).

The mechanism is thus a combination of the one-electron mechanisms of Sullivan and Meyer and co-workers (Scheme 2) and Christensen *et al.* (eqs 8 and 9); however, the two-electron mechanism *via* the formation of $[Re(CO)_3(bpy)]^-$ (**5**) cannot be completely excluded. Although the reduction of $[Re(bpy)(CO)_3Cl]$ (**1**) is well separated from those of $[Re(bpy)(CO)_3(O_2CH)]^{\bullet -}$ (**10**) and $[Re(bpy)(CO)_3Cl]^{\bullet -}$ (**2**), the reduction of $[Re(CO)_3(bpy)]_2$ (**6**) lies only 170 mV more negative (see Table 1). Generation of a small amount of $[Re(CO)_3(bpy)]^-$ (**5**) *via* reduction of the dimer **6** (eq 4) is therefore possible and may also contribute to the overall catalytic mechanism. The absence of the dimer proves that CO_2 reacts directly with the radicals $[Re(CO)_3(bpy)]^\bullet$ (**a**), as was spectroscopically observed for $[Re(CO)_3(dmbpy)]^\bullet$.[11] On the other hand, it seems that CO_2 does not react directly with $[Re(bpy)(CO)_3Cl]^{\bullet -}$ (**2**) as this product was formed at the same transient concentration with respect to the parent complex as observed in the absence of CO_2 (see part 2 above).

6. Reduction of $[Re(bpy)(CO)_3(Otf)]$ (11) in THF Solution in the Absence and Presence of CO_2 (Figure 6). Stor *et al.*[14] studied the reduction of $[Re(bpy)(CO)_3(Otf)]$ (**11**) in THF, and from their results it can be concluded that the one-electron reduction of the parent complex leads to the dimer, $[Re(bpy)(CO)_3]_2$ (**6**), *via* the electrode-catalyzed[14] formation of $[Re(bpy)(CO)_3(THF)]^+$ (**8**) and its subsequent reduction. Since the reduction of $[Re(bpy)(CO)_3(THF)]^+$ (**8**) lies 170 mV more positive than $[Re(bpy)(CO)_3Cl]$ (**1**) (see Table 1), it is more separated from the reduction of the dimer **6**; this prevents the reduction of **6** to $[Re(bpy)(CO)_3]^-$ (**5**) prior to the complete reduction of $[Re(bpy)(CO)_3(THF)]^+$ (**8**). Moreover, the radical $[Re(bpy)(CO)_3(THF)]^\bullet$ (**b**) is much less stable than $[Re(bpy)(CO)_3Cl]^{\bullet -}$ (**2**)[14] and the dimer can thus be formed as a single reduction product. These changes are illustrated in Figure 6a.

It is therefore apparent that the reduction of CO_2 using $[Re(bpy)(CO)_3(Otf)]$ (**11**) as a catalyst precursor should provide a better chance to distinguish between the one- and two-electron catalytic reduction pathways, *i.e.*, to prove unambiguously the inherent catalytic activity of the five-coordinate radical $[Re(bpy)(CO)_3]^\bullet$ (**a**). This was not completely possible for $[Re(bpy)(CO)_3Cl]$ (**1**) in CO_2-saturated THF (see part 5 above).

The data from the IR OTTLE experiment under the title conditions in CO_2-saturated THF are shown in Figure 6b. The reduction of $[Re(bpy)(CO)_3(Otf)]$ (**11**) led, as was expected,[14] first to the cation $[Re(bpy)(CO)_3(THF)]^+$ (**8**). The reduction of this cation then initiated the electrocatalytic reduction of CO_2. The dimer $[Re(bpy)(CO)_3]_2$ (**6**) was only formed as a minor transient. The major carbonyl complex formed was again the reduced radical $[Re(bpy)(CO)_3(O_2CH)]^{\bullet -}$ (**10**). The IR spectra reveal that, under these specific conditions given by the rather positive reduction potential of $[Re(bpy)(CO)_3(THF)]^+$ (**8**), the neutral formato complex $[Re(bpy)(CO)_3(O_2CH)]$ (**9**) was also present as a minor product in the solution, in agreement with the data in Table 1. The 1700−1500 cm^{-1} region again exhibited the bands of free CO_3^{2-} (1640 cm^{-1}), coordinated O_2CH^- (1628 cm^{-1}, sh) and the unassigned carboxylato compound (at 1679 cm^{-1}). Free CO was also formed as evidenced by the large production of bubbles at the working electrode. We can thus conclude that in this case, *i.e.* in the absence of $[Re(bpy)(CO)_3Cl]^{\bullet -}$ (**2**) as a potential catalyst, the CO_2 reduction was initiated only by the formation of the reactive radicals $[Re(bpy)(CO)_3]^\bullet$ (**a**), *i.e.*, *via* the one-electron reduction pathway (see Scheme 2), since the reduction potential was kept sufficiently positive with respect to the reduction of the dimer $[Re(bpy)(CO)_3]_2$ (**6**), the only source[14] of $[Re(bpy)(CO)_3]^-$ (**5**) in the absence of CO_2.

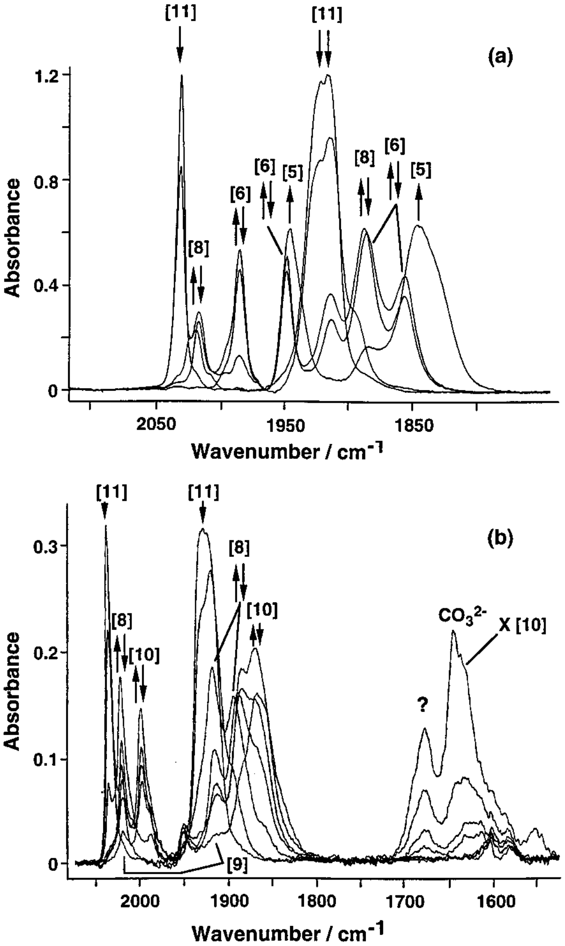


Figure 6. ν(CO) IR spectral changes following OTTLE cell reduction of $[Re(bpy)(CO)_3(Otf)]$ (**11**) in (a) *THF* solution and in (b) CO_2-saturated *THF* solution (arrows indicate whether the bands decrease ↓ or increase ↑). One-electron reduction of $[Re(bpy)(CO)_3(Otf)]$ (**11**) leads to the production of $[Re(bpy)(CO)_3(THF)]^+$ (**8**), the reduction of which initiates CO_2 reduction producing CO and CO_3^{2-}. The dimeric product, $[Re(bpy)(CO)_3]_2$ (**6**), is seen as a minor intermediate. The final carbonyl product is the radical anion, $[Re(bpy)(CO)_3(O_2CH)]^{\bullet -}$ (**10**), which, because of the rather positive reduction potential, is accompanied by a small amount of its neutral form $[Re(bpy)(CO)_3(O_2CH)]$ (**9**). X marks the shoulder due to the ν_{as}(COO) band of the coordinated formate in **10**, and **?** marks the bands due to yet unknown carboxylato products.

7. Reduction of $[Re(bpy)(CO)_3Cl]$ (1) in CH_3CN Solution with Excess Cl^- in the Presence of CO_2 (Figure 7). Having established that the one-electron pathway involving the five-coordinate radicals could lead to efficient CO_2 reduction (see parts 5 and 6 above), an IR OTTLE experiment, using the title conditions,

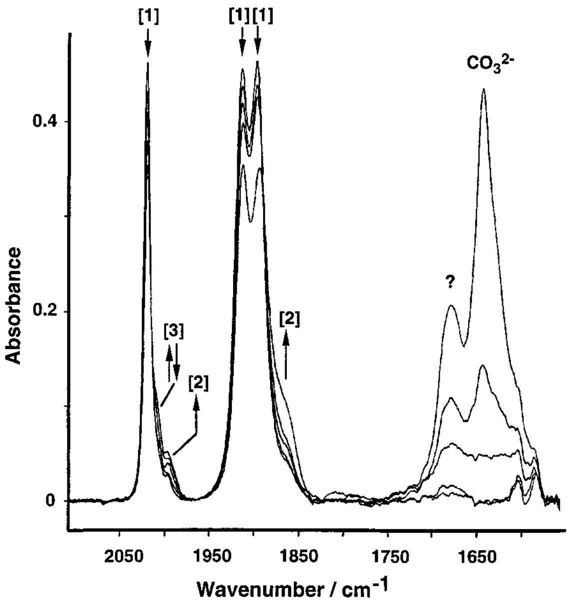


Figure 7. ν(CO) IR spectral changes following OTTLE cell reduction of [Re(bpy)(CO)$_3$Cl] (**1**) in CO$_2$-saturated *acetonitrile* solution containing excess Cl$^-$ (arrows indicate whether the bands decrease ↓ or increase ↑). Reduction of [Re(bpy)(CO)$_3$Cl] (**1**) causes a rapid production of CO and CO$_3{}^{2-}$ and the carboxylato product (marked **?**). Only small changes are visible in the ν(CO) region, but on computer subtraction (not shown) these can be seen to be due to the production of [Re(bpy)(CO)$_3$Cl]$^{\bullet-}$ (**2**) and [Re(bpy)(CO)$_3$(CH$_3$CN)]$^{\bullet}$ (**3**).

was performed to see the effect of introducing the two-electron anionic pathway. Figure 7 shows that reduction of approximately 20% [Re(bpy)(CO)$_3$Cl] (**1**) in CH$_3$CN/excess Cl$^-$ was accompanied by very fast formation of free CO$_3{}^{2-}$ (sharp band at 1643 cm^{-1}) and CO, together with the unassigned product (band at 1679 cm^{-1}) which appeared earlier than the CO$_3{}^{2-}$. The IR spectra in the ν(CO) region revealed the presence of comparably small amounts of [Re(bpy)(CO)$_3$Cl]$^{\bullet-}$ (**2**) and [Re(bpy)(CO)$_3$(CH$_3$CN)]$^{\bullet}$ (**3**). It is interesting to note that no bands due to the [Re(bpy)(CO)$_3$(O$_2$CH)]$^{\bullet-}$ (**10**) side product are present in either the ν(CO) or the 1500−1700 cm^{-1} region of the IR spectrum. Unfortunately, the development of large amounts of free CO gas at the working minigrid electrode made further monitoring of the experiment impossible.

The IR OTTLE experiments in the absence of CO$_2$ illustrate that the reduction pathway of [Re(bpy)(CO)$_3$Cl] (**1**) in CH$_3$CN differs considerably from that in THF as described in sections 1 and 2 above. The labilization of the Cl$^-$ ligand in the one-electron reduced radical anion led to the formation of [Re(bpy)(CO)$_3$(CH$_3$CN)]$^{\bullet}$ (**3**) which could be directly reduced to the anions [Re(bpy)(CO)$_3$]$^-$ (**5**) and the predominant [Re(bpy)(CO)$_3$(CH$_3$CN)]$^-$ (**4**) without the production of any dimer, [Re(bpy)(CO)$_3$]$_2$ (**6**). The availability of the two-electron pathway appears to make the catalytic CO$_2$ reduction in CH$_3$CN much more efficient in comparison with that in THF as demonstrated by the rapid formation of free CO$_3{}^{2-}$ and CO (Figure 7).

8. Reduction of [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^+$ (12) in THF Solution in the Absence and Presence of CO$_2$ (Figures 8 and 9). As was stated in the Introduction, the stability of [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^{\bullet}$ affords an excellent opportunity to study the two-electron catalytic pathway in the absence of the one-electron radical route to CO$_2$ reduction. The reduction of [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^+$ (**12**) in THF led smoothly to the one-electron reduced radical [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^{\bullet}$ (**13**) (Figure 8) which was completely stable as expected.[18] Further reduction of this complex produced solely the five-coordinate anion, [Re(bpy)(CO)$_3$]$^-$ (**5**). There is no evidence in Figure 8 for the production of the six-coordinate anion [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^-$ (**15**).

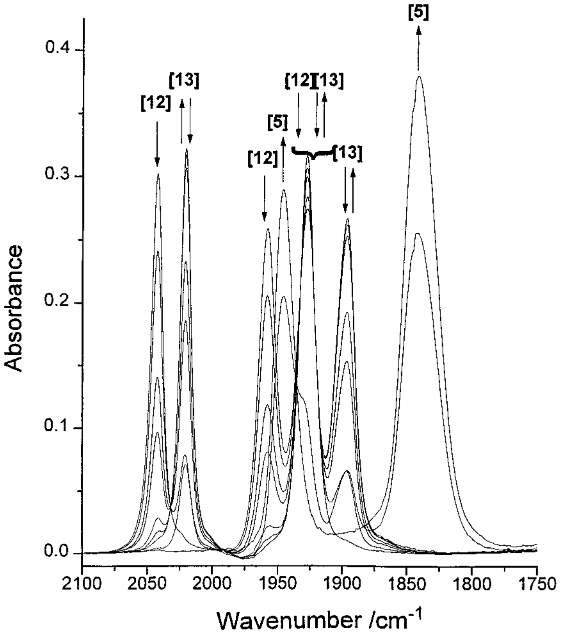


Figure 8. ν(CO) IR spectral changes following OTTLE cell reduction of [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^+$ (**12**) in THF solution (arrows indicate whether the bands decrease ↓ or increase ↑). One-electron reduction of [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^+$ (**12**) leads to the production of the radical [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^{\bullet}$ (**13**). (N.B.: the lowest frequency band of **12** overlaps exactly the center band of **13**; see Table 2.) Further reduction produces the five-coordinate anion [Re(bpy)(CO)$_3$]$^-$ (**5**).

In the presence of CO$_2$, the reduction of [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^+$ (**12**) again led initially to the corresponding stable radical (omitted from Figure 9 for clarity). During this step, neither a decrease in the concentration of dissolved CO$_2$ nor appearance of its reduction products could be observed, indicating again that CO$_2$ cannot react with the one-electron-reduced six-coordinate radicals (see part 5 above) but only with the five-coordinate radical [Re(bpy)(CO)$_3$]$^{\bullet}$ (**a**), which is not produced here due to the inherent stability of [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^{\bullet}$ (**13**). The subsequent reduction of the radical, forming the coordinatively unsaturated anion [Re(bpy)(CO)$_3$]$^-$ (**5**), initiated the CO$_2$ reduction. The reduction of the six-coordinate radical was accompanied by the rapid production of CO$_3{}^{2-}$ and the unassigned band at 1680 cm^{-1} along with bands due to coordinated (1628 (sh) cm^{-1}) and uncoordinated (1604 (sh) cm^{-1}) formate. Surprisingly, the five-coordinate anion **5** was still spectroscopically detectable during the catalytic process and was accompanied by [Re(bpy)(CO)$_3$(O$_2$CH)]$^{\bullet-}$ (**10**), which exhibits a very similar reduction potential to that of [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^{\bullet}$ (**13**). On shifting of the reduction potential more negative, both [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^{\bullet}$ (**13**) and [Re(bpy)(CO)$_3$(O$_2$CH)]$^-$ (**10**) were completely reduced. A number of new unknown complexes were formed in place of [Re(bpy)(CO)$_3$]$^-$ (**5**), of

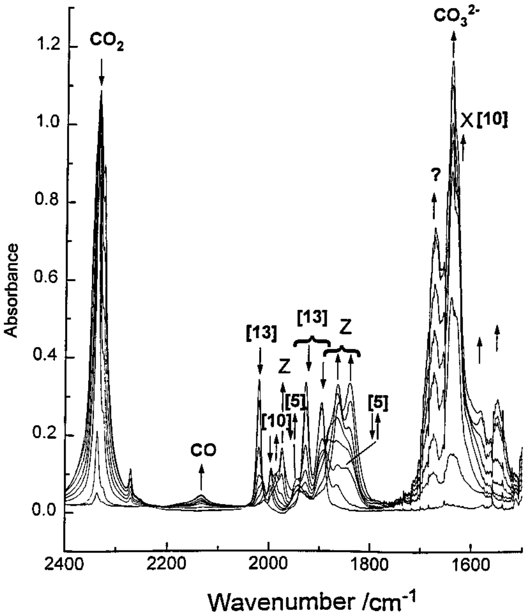


Figure 9. IR spectral changes following OTTLE cell reduction of $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (**12**) in CO_2 saturated *THF* solution (arrows indicate whether the bands decrease ↓ or increase ↑). The reduction of $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (**12**) to $[Re(bpy)(CO)_3\{P(OEt)_3\}]^•$ (**13**) has been omitted as it is identical to that shown in Figure 8. Reduction of $[Re(bpy)(CO)_3\{P(OEt)_3\}]^•$ (**13**) initiates the rapid reduction of CO_2 leading to the production of CO, CO_3^{2-}, and the carboxylato product (marked **?**). The changes in the ν(CO) region and the shoulder X at 1628 cm^{-1} indicate the formation of $[Re(bpy)(CO)_3(O_2CH)]^{•-}$ (**10**). As the CO_2 concentration decreases, the ν(CO) bands due to $[Re(bpy)(CO)_3(O_2CH)]^{•-}$ (**10**) are replaced by three new ν(CO) bands and new features in the 1500−1700 region are observed (all marked **Z**). These are due to unknown products (see text).

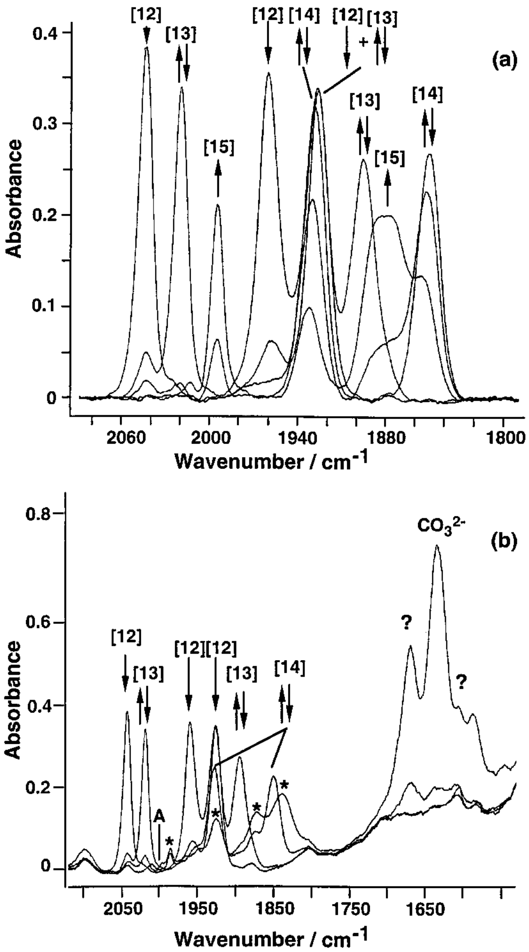


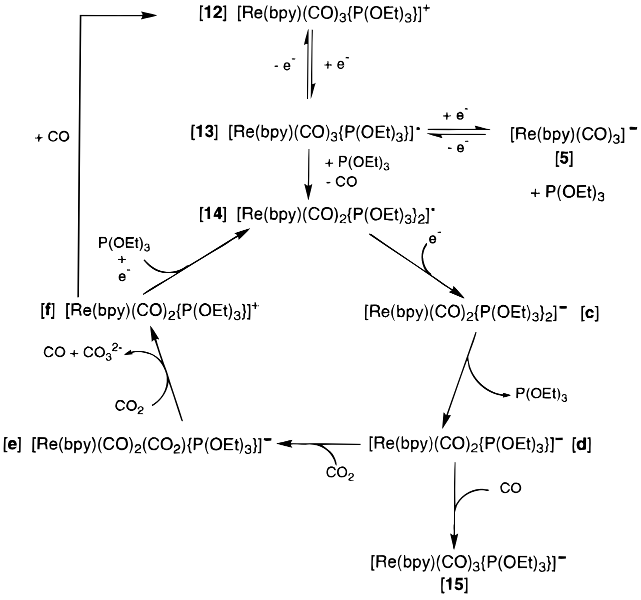
Figure 10. ν(CO) IR spectral changes following OTTLE cell reduction of $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (**12**) in *THF* solution containg a 100-fold excess of $P(OEt)_3$ (arrows indicate whether the bands decrease ↓ or increase ↑). (a) In the absence of CO_2, $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (**12**) is reduced in a one-electron step to the corresponding radical $[Re(bpy)(CO)_3\{P(OEt)_3\}]^•$ (**13**). This radical undergoes CO substitution with $P(OEt)_3$ to produce $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^•$ (**14**). Upon further reduction this dicarbonyl radical is reduced and reacts back with the CO lost in the early reaction to produce the two-electron-reduced six-coordinate anion $[Re(bpy)(CO)_3\{P(OEt)_3\}]^-$ (**15**). (b) In the presence of CO_2 the reaction proceeds as above until $[Re(bpy)(CO)_3\{P(OEt)_3\}]^-$ (**15**) was expected to be produced. At this point rapid CO_2 reduction occurs producing CO, CO_3^{2-}, the unknown carboxylato product, and a number of other minor products in the 1500−1700 cm^{-1} region. There are a number of unassigned ν(CO) bands remaining after the CO_2 reduction is completed (marked *****). The small band marked A is possibly due to a very small amount of $[Re(bpy)(CO)_3\{P(OEt)_3\}]^-$ (**15**).

which the major product (Z in Figure 9) exhibited ν(CO) bands at 1974, 1861, and 1839 cm^{-1} with the highest ν(CO) frequency band approximately between those of $[Re(bpy)(CO)_3]^-$ (**5**) and $[Re(bpy)(CO)_3\{P(OEt)_3\}]^-$ (**15**) (see Table 2). There was also the production of new bands in the 1500−1700 cm^{-1} region at 1550 and 1580 cm^{-1}. All the latter unknown species were mainly formed when the amount of CO_2 in solution had substantially decreased, and therefore, they may not play a major role in the catalytic CO_2 reduction pathways and their characterization was not pursued further.

The use of $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (**12**) as a catalytic precursor is a less convenient system than those described above owing to the rather negative reduction potential required to produce the two-electron reduced anions needed to trigger the reduction; however, it provided an exceptional chance to prove the catalytic activity of $[Re(bpy)(CO)_3]^-$ (**5**) (*i.e.* the two-electron pathway) independently from the influence of $[Re(bpy)(CO)_3]^•$ (**a**) and six-coordinate doubly reduced complexes. This is in contrast to the systems described above in which mixtures of various catalytically active species were always present in solution, *i.e.*, $[Re(bpy)(CO)_3Cl]^{•-}$/$[Re(bpy)(CO)_3]_2$/$[Re(bpy)(CO)_3]^-$ or $[Re(bpy)(CO)_3(CH_3CN)]^•$/$[Re(bpy)(CO)_3(CH_3CN)]^-$/$[Re(bpy)(CO)_3]^-$ (see above).

9. Reduction of $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (12) in THF Solution with Excess $P(OEt)_3$ in the Absence and Presence of CO_2 (Figure 10). Having established the catalytic activity of both $[Re(bpy)(CO)_3]^•$ (**a**) and $[Re(bpy)(CO)_3]^-$ (**5**), we made an attempt to study the reactivity of the six-coordinate anions $[Re(bpy)(CO)_3L]^-$. In order to do this, an IR OTTLE experiment was performed on $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (**12**) in the presence of a 100-fold excess of $P(OEt)_3$ with the aim of stabilizing the six-coordinate anion $[Re(bpy)(CO)_3\{P(OEt)_3\}]^-$ (**15**) by halting the dissociation of $P(OEt)_3$ upon reduction of the corresponding radical, as was observed in the absence of excess $P(OEt)_3$ (see part 8 above). In the absence of CO_2, one-electron reduction of $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (**12**) gave, as

Scheme 5



expected, the radical $[Re(bpy)(CO)_3\{P(OEt)_3\}]^\bullet$ (**13**) (Figure 10a). This radical, however, was readily transformed to the substituted radical $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^\bullet$ (**14**)[13] by reaction with free $P(OEt)_3$. It was hoped that despite this reaction it would still be possible to stabilize a six-coordinate anion, namely $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^-$. The subsequent reduction of the dicarbonyl radical, however, proved to be more complex and led to a species that appeared to be a tricarbonyl complex. The most obvious assignment for this species is the six-coordinate anion $[Re(bpy)(CO)_3\{P(OEt)_3\}]^-$ (**15**) formed by the reduction of $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^\bullet$ (**14**) and concomitant substitution reaction of primarily produced $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^-$ with the CO liberated in the initial formation of $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^\bullet$ (see Scheme 5) and still present in the thin solution layer. Supporting evidence for this assignment came from an identical reduction mechanism described by Stor *et al.*[14] for the related complex $[Re(dapa)(CO)_3\{P(OMe)_3\}]^+$, where dapa = 2,6-diacetylpyridinebis(anil) (see Table 2). The complete shift of the equilibrium between $[Re(bpy)(CO)_3]^-$ (**5**) and $[Re(CO)_3(bpy)L]^-$ toward the six-coordinate anion for L = $P(OEt)_3$ in the presence of excess $P(OEt)_3$ is thus in contrast with the situation for L = CH_3CN, where **5** is still formed at room temperature even in neat CH_3CN (see Figure 1). This difference in the stability of $[Re(bpy)(CO)_3L]^-$ is ascribed to the strong π-acceptor character of the $P(OEt)_3$ ligand.

The reduction pathway of $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (**12**) thus affords us the opportunity to study the catalytic activity of the six-coordinate anion $[Re(bpy)(CO)_3\{P(OEt)_3\}]^-$ (**15**), albeit produced *via* a more complex mechanism than we initially predicted.

The reduction of $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (**12**) in the presence of CO_2 is depicted in Figure 10b. The sequence of reactions is identical to that described above up to and including the formation of the radical, $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^\bullet$ (**13**). This observation illustrates that CO_2 is not able to react with stable six-coordinate radicals, probably not even with $[Re(bpy)(CO)_3(CH_3CN)]^\bullet$ (**3**) and $[Re(bpy)(CO)_3Cl]^{\bullet-}$ (**2**) (see above) provided the Re−L bond (L = CH_3CN, Cl^-) is stabilized by the presence of a large excess of L. In contrast to the results in the absence of CO_2 (see above) further reduction of $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^\bullet$ (**13**) led to very little or no $[Re(bpy)(CO)_3\{P(OEt)_3\}]^-$ (**15**). Instead, almost all the CO_2 was reduced rapidly within 2 min to give again free CO, CO_3^{2-}, and the unidentified carboxylate compound absorbing at 1680 cm^{-1} as the major products and a small amount of free formate absorbing at 1610 cm^{-1}. Other, less intense bands were observed in the 1700−1500 cm^{-1} region at 1585 and 1545 cm^{-1}. In the ν(CO) region, bands of unidentified species were found at 1987, 1926.5, 1873, and 1840 cm^{-1} (marked by * in Figure 10), after the reduction of CO_2 had been completed. The reduction potential of $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^\bullet$ (**14**) is in fact very close to that of the reduction of free CO_2 at a Pt cathode;[27] however, the observed transformation of CO_2 during the last reduction step was so fast that it cannot be ascribed to the latter process alone. We propose the two-electron mechanism shown in Scheme 5 as the most likely CO_2 reduction pathway using this catalytic system. The unsaturated anion $[Re(bpy)(CO)_2\{P(OEt)_3\}]^-$ (**d**)[28] is more electronically rich than its $[Re(bpy)(CO)_3]^-$ (**5**) derivative and will probably be trapped by CO_2 rather than by the CO liberated from $[Re(bpy)(CO)_3\{P(OEt)_3\}]^\bullet$ (**13**) (see above), since CO_2 is present in the solution at much higher concentration than the CO. It therefore seems likely that in this case CO_2 reacts readily with the unsaturated transient five-coordinate anion $[Re(bpy)(CO)_2\{P(OEt)_3\}]^-$ (**d**) rather than with the six-coordinate anion $[Re(bpy)(CO)_3\{P(OEt)_3\}]^-$ (**15**), which would otherwise be formed in the absence of CO_2 (see above).

Discussion

The results of this IR spectroelectrochemical (OTTLE) study, as summarized in Scheme 6, clearly show that it is the stability of the radical $[Re(bpy)(CO)_3(CH_3CN)]^\bullet$ (**3**) in CH_3CN which introduces the two-electron pathway for the electrocatalytic reduction of CO_2. Having studied CO_2 reduction mediated by $[Re(bpy)(CO)_3(Cl)]$ (**1**) in CH_3CN, we provide for the first time *spectroscopic* evidence that CO_2 does not interact directly with the radical anion $[Re(bpy)(CO)_3(Cl)]^{\bullet-}$ (**2**). The latter complex can thus only be viewed as the catalyst precursor, which excludes the associative one-electron pathway.[8] Such evidence could not be obtained[11] in this solvent for closely related $[Re(dmbpy)(CO)_3(Cl)]^{\bullet-}$ since it readily decomposes to give the CO_2-catalyst $[Re(dmbpy)(CO)_3]^\bullet$ instead of the stable solvento radical $[Re(dmbpy)(CO)_3(CH_3CN)]^\bullet$. The reduction of parent $[Re(dmbpy)(CO)_3(Cl)]$ in the presence of CO_2 hence leads instantaneously to the formation of CO, CO_3^{2-}, and formato complexes, thus making it impossible to confirm or disprove the catalytic activity of $[Re(dmbpy)(CO)_3(Cl)]^{\bullet-}$ itself. In contrast to this pathway, the secondary chemical reaction of **2** in CH_3CN leads to the 18e radical $[Re(bpy)(CO)_3(CH_3CN)]^\bullet$ (**3**) and *does not* produce a detectable amount of the dimer $[Re(bpy)(CO)_3]_2$ (**6**). This spectroelectrochemical result seems to be in disagreement with the cyclic voltammetric studies[8] of $[Re(bpy)(CO)_3Br]$ in CH_3CN, which is reduced in the absence of CO_2 to give both the radical **3** and the dimer **6**. However, Stor *et al.* have shown[14] that the primary

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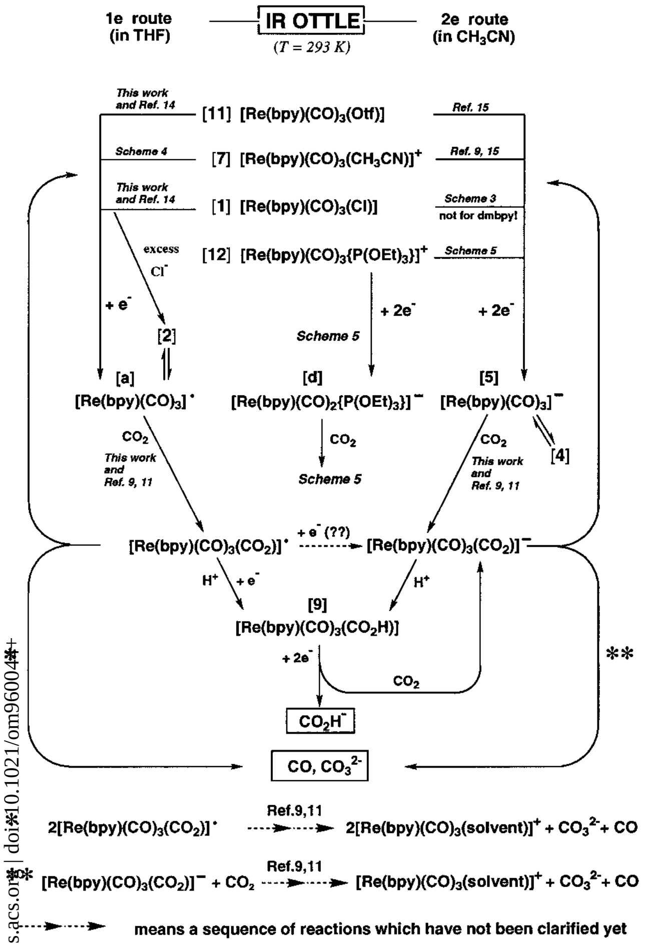
[28] The anion $[Re(bpy)(CO)_2\{P(OEt)_3\}]^-$ (**d**) can be produced[18] smoothly by stepwise two-electron reduction of $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^+$ in the absence of excess $P(OEt)_3$.

Scheme 6



reduction product, the radical anion $[Re(bpy)(CO)_3Br]^{\bullet -}$, is much less stable than **2** and decomposes *rapidly* to give a large amount of $[Re(bpy)(CO)_3]^{\bullet}$ (**a**), which then dimerizes. The latter reaction may take place even in CH_3CN. The *slow* replacement of Cl^- by CH_3CN in the case of **2**, especially in the presence of excess Cl^-, may therefore be viewed as an associative process where CH_3CN reacts directly with **2** to give **3**; this prevents the dimerization reaction and, in the presence of CO_2, hinders coordination of CO_2 to the coordinatively unsaturated $[Re(bpy)(CO)_3]^{\bullet}$ (**a**), *i.e.* the dissociative X^--loss pathway considered by Sullivan, Meyer, *et al.*[8] Instead, CO_2 attacks the coordinatively unsaturated catalyst $[Re(bpy)(CO)_3]^-$ (**5**) produced *via* concomitant reduction of **3** and becomes thus reduced *via* the two-electron pathway. It should be remarked here that, in the absence of CO_2, **5** has been found to exist in an equilibrium with the six-coordinate anion $[Re(bpy)(CO)_3(CH_3CN)]^-$ (**4**) which is probably not capable of CO_2 coordination.

The two-electron catalytic pathway also applies to the complex $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (**12**) in the *absence* of excess $P(OEt)_3$, with the exception that the equilibrium between the catalyst $[Re(bpy)(CO)_3]^-$ (**5**) and its inactive form $[Re(bpy)(CO)_3\{P(OEt)_3\}]^-$ (**15**) is completely shifted toward **5**. This difference, together with the more negative reduction potential of the radical $[Re(bpy)(CO)_3\{P(OEt)_3\}]^{\bullet}$ (**13**) with respect to **3**, makes the electrocatalytic CO_2 reduction more efficient in comparison with the catalyst precursor **1** in CH_3CN. The same conclusion can probably be drawn also for other chemically reversible redox couples $[Re(bpy)(CO)_3(PR_3)]^{+/\bullet}$, *e.g.* with R = Ph.[14]

The dissociative one-electron catalytic pathway is always indicated in the *absence* of CO_2 by the production of the dimer $[Re(bpy)(CO)_3]_2$ (**6**), which indirectly proves the existence of the reactive five-coordinate radical $[Re(bpy)(CO)_3]^{\bullet}$ (**a**). This pathway becomes dominant in solvents like THF or DMF that cannot stabilize the 18e radicals $[Re(bpy)(CO)_3(solvent)]^{\bullet}$ due to their weaker coordination as compared with CH_3CN. The same situation probably applies also to related radical complexes with a strongly basic α-diimine ligand like 1,10-phenathroline and 2,2′-bipyridine with electron-releasing substituents[11] or with pyridine ligands.[29]

The one-electron pathway in Scheme 6 might be linked to the two-electron one *via* fast one-electron reduction of the radical intermediate $[Re(bpy)(CO)_3(CO_2)]^{\bullet}$, as was suggested previously.[9] Thus far, however, there has been no supporting evidence for this reduction step, although in principle it cannot be excluded supposing the reduction potential of the above radical lies sufficiently more positive with respect to that of the parent catalyst precursor.

The production of the major side product $[Re(bpy)(CO)_3(CO_2H)]^{\bullet -}$ (**10**) becomes largely suppressed in the case of a very efficient two-electron catalytic pathway, for example using $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (**12**) or $[Re(bpy)(CO)_3Cl]$ (**1**) in CH_3CN as catalyst precursors.

We can now compare these conclusions with the behavior of the related complex $[Mn(bpy)(CO)_3Cl]$. This complex, which is reduced[30] both in THF and CH_3CN to give at room temperature exclusively $[Mn(bpy)(CO)_3]_2$ and subsequently $[Mn(bpy)(CO)_3]^-$, shows no catalytic activity toward CO_2 reduction.[31] The absence of the 1e catalytic pathway in the case of $[Mn(bpy)(CO)_3Cl]$ may reasonably be explained by a very short lifetime of the five-coordinate radical $[Mn(bpy)(CO)_3]^{\bullet}$ due to its instantaneous reduction to the anion $[Mn(bpy)(CO)_3]^-$, still at the applied reduction potential of the parent complex. $[Mn(bpy)(CO)_3]^-$ then reacts with parent $[Mn(bpy)(CO)_3Cl]$ to give the dimer $[Mn(bpy)(CO)_3]_2$. This intriguing reduction pathway appears to be a characteristic property of the complexes [Mn(α-diimine)$(CO)_3$(halide)] with basic α-diimine ligands, as it was also observed for the related compound [Mn(iPr-DAB)$(CO)_3$Br] (iPr-DAB = *N*,*N*′-diisopropyl-1,4-diaza-1,3-butadiene).[32]

On the other hand, the reason for the absence of the 2e catalytic route in the case of $[Mn(bpy)(CO)_3Cl]$ seems to be different. Recent studies of bonding properties of the anions $[M(iPr\text{-}DAB)(CO)_3]^-$ (M = Mn, Re),[32,33] which can also be extended for $[M(bpy)(CO)_3]^-$ (M = Mn, Re), have revealed that the electron density on the five-coordinate metal center significantly increases in the order Re < Mn, *i.e.* upon proceeding from 5d to 3d transition metals, respectively. This remarkable difference between the Re and Mn centers can be explained

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by considering a decreasing diffusion character of their frontier d_π orbitals in the same order, which are involved in the π-bonding with the formally doubly-reduced α-diimine ligand.[32,33] The better matching of the d_π orbitals with the lowest π^* orbital of the reduced α-diimine in the same order then results in a stronger π-back-bonding from the reduced α-diimine toward the metal center. The stronger the delocalized π-bonding over the M(α-diimine) chelate ring, the higher is the electron density on the metal center and the more stable is its five-coordinate geometry.[14,32] Consequently, the stabilizing delocalization of the π-bonding in the five-coordinate anions prevents coordination of a sixth ligand, which may explain why the complexes $[Mn(\alpha\text{-diimine})(CO)_3]^-$ remain inert with respect to the CO_2 reduction. The validity of the above relation between the strongly delocalized π-bonding and the stable five-coordinate geometry has been documented recently for other series of five-coordinate complexes of formally d^6-metals: $[M^{III}(\text{triphos})(\text{DBCat})]^+$ (M = Co, Rh, Ir),[34] $[M^I(L)_n(CO)_3(\text{DBCat})]^-$ (M = Mn, n = 0,1; M = Re, n = 1),[35,36] and $[M^0(CO)_3(\text{DBCat})]^{2-}$ (M = Cr, Mo, W)[37] (DBCat = 3,5-di-*tert*-butylcatecholate dianion). In general, the complexes with the 3d-metal center are the most stable members of the series with respect to coordination of a sixth ligand.

Replacing the bpy ligand in $[Re(bpy)(CO)_3]^-$ by less basic α-diimines like 2,2′-bipyrimidine (bpym) or azo-2,2′-pyridine (apy) leads to facile coordination of a sixth ligand, producing stable $[Re(\alpha\text{-diimine})(CO)_3L]^-$ (L = *e.g.* THF or PPh_3).[14,15] Electrocatalytic reduction of CO_2 was also not observed in this case.[31] The relatively low electron density on the Re center in the six-coordinate anions $[Re(\alpha\text{-diimine})(CO)_3L]^-$, as documented[14] by their significantly higher ν(CO) frequencies in comparison with those of five-coordinate $[Re(\alpha\text{-diimine})(CO)_3]^-$ (this situation also applies for the anions **4** and **5**; see Table 2), and the absence of a vacant coordination site make the CO_2 reduction with these complexes forbidden.

In conclusion, availability of a free coordination site is a necessary prerequisite of the Re(bpy) catalysts for the CO_2 reduction; however this is also coupled with the requirement for a proper distribution of the π-electron density within the Re(bpy) chelate bond. In other words, the Re center in $[Re(CO)_3(bpy)]^\bullet$ is sufficiently electronically poor to allow coordination of Lewis bases like phosphines or CH_3CN instead of rapid dimerization, but it is still electronically rich enough to coordinate and reduce CO_2 *via* the one-electron pathway. On the other hand, $[Re(CO)_3(bpy)]^-$ possesses the electron density on the Re center sufficiently high to exist as five-coordinate in the absence of a large excess of a strongly coordinating basic ligand (CH_3CN, $P(OEt)_3$). However, coordination and efficient reduction of CO_2 is allowed. In this respect $[Re(bpy)(CO)_3]^-$ differs significantly from $[Mn(CO)_3(bpy)]^-$ and related Mn complexes, which remain always five-coordinate due to an extremely strongly delocalized π-bonding in the $\{Mn(bpy)\}^-$ metallacycle.[32,33]

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