Electrocatalytic Reduction of CO2 Using the Complexes $[\text{Re(bpy})(\text{CO})_3L]_n$ ($n=+1$, $L=\text{P(\text{OEt})}_3$, CH$_3$CN; $n =0$, $L=\text{Cl}^-$, $\text{Otf}^-$; bpy=$2,2'$-Bipyridine; $\text{Otf}^-=\text{CF}_3\text{SO}_3$) as Catalyst Precursors: Infrared Spectroelectrochemical Investigation.

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Electrocatalytic Reduction of CO₂ Using the Complexes

[Re(bpy)(CO)₃L]ⁿ (n = +1, L = POEt₃, CH₃CN; n = 0,
L = Cl⁻, Otf⁻; bpy = 2,2'-Bipyridine; Otf⁻ = CF₃SO₃⁻)
as Catalyst Precursors: Infrared Spectroelectrochemical Investigation

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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⁻, CF₃SO₃⁻; n = +1, L = CH₃CN, POEt₃) 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)]⁺ 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 both 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]⁻, which was previously believed to react directly with CO₂. By contrast, this study demonstrates its stability toward attack by CO₂, 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]⁺ (L = CH₃CN (in CH₃CN) and POEt₃) 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 CH₃CN 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)]⁻, capable of CO₂ reduction (the 1e pathway), even in CH₃CN, 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 = 0, L = Cl⁻, CF₃SO₃⁻; n = +1, L = CH₃CN), the 1e catalytic route becomes possible in weakly coordinating THF, due to the instability of the radical [Re(CO)₃(bpy)(THF)]⁻. The inherent stability of the radical [Re(CO)₃(bpy)(POEt₃)]⁻ was found convenient for the investigation of the 2e pathway via [Re(CO)₃(bpy)]⁻. The main, spectroscopically observed products of the CO₂ reduction are, independent of the 1e and 2e catalytic routes, CO, CO₃²⁻, and free CO₂⁻. The latter product is formed via one-electron reduction of the radical anion [Re(CO)₃(bpy)(CO₂H)]⁻, which is the main byproduct in the catalytic cycle.

Introduction

Since the initial discovery by Lehn and co-workers that [Re(bpy)(CO)₃Cl] (bpy = 2,2'-bipyridine) acts as an efficient electrocatalyst for the reduction of CO₂, 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...
trocatalytic CO₂ reduction\textsuperscript{11} and involves the catalytic behavior of \([\text{Re(dmbpy)(CO)}_3\text{Cl}]\) (dmbpy = 4,4'-dimethyl-2,2'-bipyridine) which, however, displays significant differences from that of the most widely studied electrocatalyst \([\text{Re(bpy)(CO)}_3\text{Cl}]\). 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 \([\text{Re(bpy)(CO)}_3\text{Cl}]\).

It is well established from voltammetric\textsuperscript{1,6,8,10,12} and IR spectroelectrochemical\textsuperscript{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, \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\), eq 1. The secondary chemical reaction of this radical, \([\text{Re(bpy)(CO)}_3\text{Cl}]^- + e^- \rightarrow [\text{Re(bpy)(CO)}_3\text{Cl}]^{2-}\) (1)

\([\text{Re(bpy)(CO)}_3\text{Cl}]^- \rightarrow [\text{Re(bpy)(CO)}_3]^+ + \text{Cl}^-\) (2)

\([\text{Re(bpy)(CO)}_3]^+ \rightarrow 1/2[\text{Re(bpy)(CO)}_3]_2\) (3)

\(1/2[\text{Re(bpy)(CO)}_3]_2 + e^- \rightarrow [\text{Re(bpy)(CO)}_3]^2-\) (4)

described in eq 2, has been proposed by a number of authors on the basis of voltammetric studies and confirmed by the IR spectroelectrochemical results of Christensen et al. for \([\text{Re(dmbpy)(CO)}_3\text{Cl}]\)\textsuperscript{11} and Stor et al. for \([\text{Re(bpy)(CO)}_3\text{Cl}]\).\textsuperscript{14} The radical \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) can be stabilized at lower temperature,\textsuperscript{15} but at room temperature it decomposes via chloride loss to the coordinatively unsaturated radical \([\text{Re(bpy)(CO)}_3]^2-\), which in the absence of strongly coordinating solvents or CO₂ dimerizes rapidly to \([\text{Re(bpy)(CO)}_3]_2\), eqs 2 and 3. Further, rhenium-based reduction of the dimer leads to the formation of the five-coordinate anionic species \([\text{Re(bpy)(CO)}_3]^-\), eq 4 (bpy refers to both 2,2'-bipyridine and dmbpy in eqs 1–4).

It has also been shown\textsuperscript{15} that in coordinating solvents such as n-butyrtrinitril (n-PrCN), \([\text{Re(bpy)(CO)}_3]^2-\) is in equilibrium with its solvated six-coordinate form \([\text{Re(bpy)(CO)}_3(n-\text{PrCN})]^2-\), eq 5.

\([\text{Re(bpy)(CO)}_3]^2- + n-\text{PrCN} \rightleftharpoons [\text{Re(bpy)(CO)}_3(n-\text{PrCN})]^2-\) (5)

Equations 1–5 describe the reduction of \([\text{Re(bpy)(CO)}_3\text{Cl}]\) in the absence of CO₂; however, the mechanism of the electrocatalytic reduction of CO₂ remains unclear.

Three principal mechanistic schemes have been proposed involving \([\text{Re(bpy)(CO)}_3\text{Cl}]\) and \([\text{Re(dmbpy)(CO)}_3\text{Cl}]\):

(i) Mechanism of Lehn and Co-workers\textsuperscript{5} (Scheme 1).

In this study the catalytic precursor \([\text{Re(bpy)(CO)}_3\text{Cl}]\) 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 \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) is proposed via loss of CO from \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\). This possibility was suggested as the loss of Cl⁻, and subsequent formation of the dimer \([\text{Re(bpy)(CO)}_3]_2\) (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.,\textsuperscript{11} as it cannot account for the large amount of CO₃²⁻ produced as described below. Moreover, it has been noted previously by Sullivan et al.,\textsuperscript{8} that the mechanism "appears to invoke a contra-thermodynamic step, i.e. the production of the strong oxidant \([\text{Re}^{II}(\text{bpy})(\text{CO})_3\text{Cl}]^+\), and as with the CO loss process there is no IR evidence for this species.

(ii) Mechanism of Sullivan and Meyer and Co-workers\textsuperscript{3,8,9} (Scheme 2).

Sullivan and Meyer and co-workers studied \([\text{Re(bpy)(CO)}_3\text{Cl}]\) in acetonitrile solution using predominantly cyclic voltammetry and bulk electrolysis. This mechanism was the first to consider the
Table 1. Reduction Potentials of the Various Complexes under Study (Potentials in V vs Fc/Fc⁺)

<table>
<thead>
<tr>
<th>complex (no.)</th>
<th>solvent</th>
<th>E'a (i)</th>
<th>E'a (ii)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Re(bpy)(CO)3Cl] (1)</td>
<td>THF</td>
<td>-1.86</td>
<td>-2.38</td>
<td>14</td>
</tr>
<tr>
<td>[Re(bpy)(CO)3]²⁺</td>
<td>THF</td>
<td>-2.03</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>[Re(bpy)(CH₃CN)]⁺</td>
<td>THF</td>
<td>-1.58</td>
<td>-1.80</td>
<td>b</td>
</tr>
<tr>
<td>[Re(bpy)(THF)³⁺]²⁻</td>
<td>THF</td>
<td>-1.69</td>
<td>-2.23</td>
<td>14</td>
</tr>
<tr>
<td>[Re(bpy)(CH₃CN)]⁻</td>
<td>CH₃CN</td>
<td>-1.81</td>
<td>-2.33</td>
<td>b</td>
</tr>
<tr>
<td>[Re(bpy)(Ott)]⁻</td>
<td>THF</td>
<td>-1.49</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>[Re(bpy)(P(OEt)₃)³⁺]⁻</td>
<td>CH₃CN</td>
<td>-1.63</td>
<td>-2.40</td>
<td>b</td>
</tr>
<tr>
<td>[Re(bpy)(P(OEt)₃)]⁺</td>
<td>n-PrCN</td>
<td>-1.79</td>
<td>-2.82</td>
<td>b</td>
</tr>
<tr>
<td>[Re(bpy)(nP-CrCN)]⁺</td>
<td>THF</td>
<td>-1.58</td>
<td>-2.10</td>
<td>14</td>
</tr>
<tr>
<td>[Re(bpy)(PPh₃)]⁺</td>
<td>THF/CH₃CN</td>
<td>-1.58</td>
<td>-2.10</td>
<td>b</td>
</tr>
</tbody>
</table>

Conditions: T = 293 K, v = 100 mV/s, Pt disk electrode. a This work. THF:CH₃CN = 3:2 (v/v).

There are a number of problems with this scheme; the production of [Re(bpy)(CO)3Cl]⁻ was assumed to come mainly from reduction of [Re(bpy)(CO)3Cl]⁺ (or [Re(bpy)(CO)3])². This cannot be correct since reduction of [Re(bpy)(CO)3Cl]⁻ 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 CO₂ since the reaction of [Re(bpy)(CO)3]⁺ with CO₂ is apparently faster than electron transfer from the cathode.⁵¹ A later publication, however, hinted at another route to the five-coordinate anion [Re(bpy)(CO)3]⁻ via [Re(bpy)(CO)3(CH₃CN)]⁺, eqs 6 and 7. The reduction in [Re(bpy)(CO)3]⁺ + CH₃CN

Goal 1. To Provide IR Spectroscopic Evidence for the Mechanism of CO₂ Reduction Using [Re(bpy)(CO)3]Cl. This paper describes the first published 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]²⁺ as the catalytic precursor.

Goal 2. To Study Separately the One- and Two-Electron Pathways for CO₂ Reduction and To Confirm the Catalytic Activity of both [Re(bpy)(CO)3]³⁻ and [Re(dmbpy)(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 known⁹ 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 fixed reduction potential of [Re(bpy)(CO)3(Otf)]⁻ (Table 1) ensures that no [Re(bpy)(CO)3]³⁻ is produced via the equivalent of eqs 6 and 7, with only possibilities of simultaneous one- and two-electron pathways involving [Re(bpy)(CO)3]⁺ and [Re(bpy)(CO)3]²⁺, 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)3Cl]⁻ (or [Re(bpy)(CO)3])². This cannot be correct since reduction of [Re(bpy)(CO)3Cl]⁻ 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 CO₂ since the reaction of [Re(bpy)(CO)3]⁺ with CO₂ is apparently faster than electron transfer from the cathode.⁵¹ A later publication, however, hinted at another route to the five-coordinate anion [Re(bpy)(CO)3]⁻ via [Re(bpy)(CO)3(CH₃CN)]⁺, eqs 6 and 7. The reduction in [Re(bpy)(CO)3]⁺ + CH₃CN

(iii) Mechanism of Christensen et al. The mechanism was formulated on the basis of the IR spectroelectrochemical investigation of [Re(dmbpy)(CO)3]Cl in acetonitrile. In contrast to Sullivan and Meyer and co-workers, Christensen et al.²¹ had doubts about the simultaneous formation of [Re(dmbpy)(CO)3]⁺ and [Re(dmbpy)(CO)3]⁺ since they saw “no evidence for production of [Re(dmbpy)(CO)3]⁺ at the relatively positive potentials at which CO₂ is first reduced.”¹⁶ A possible explanation for this is the higher basicity of the dmbox⁻ ligand relative to bpy⁻, which could prevent the coordination of CH₃CN to the five-coordinate radical and hence suppress the production of [Re(dmbpy)(CO)3(CH₃CN)]. As stated above, Sullivan and Meyer and co-workers intimaten⁹ that the production of [Re(dmbpy)(CO)3(CH₃CN)]⁻ 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 advantageous water in CH₃CN which causes the formation of the formate complex [Re(dmbpy)(CO)3(O₂CH)]⁻ and its singly reduced form, which are known byproducts of the CO₂ reduction using these rhenium catalysts,³,⁵,¹¹ eqs 8 and 9.

[Re(dmbpy)(CO)3(O₂CH)]⁻ + e⁻ + H₂O → [Re(dmbpy)(CO)3(OC₂H₃)]⁻ + OH⁻ (8)

[Re(dmbpy)(CO)3(O₂CH)]⁻ + e⁻ → [Re(dmbpy)(CO)3(O₂CH)]⁻ (9)

The mechanism of Sullivan and Meyer and co-workers 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 CO₂ Reduction Using [Re(bpy)(CO)3]Cl. This paper describes the first published 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]²⁺ as the catalytic precursor.

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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: Andráe, 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.
[Re(bpy)(CO)3]+ radicals present as catalytically active species; i.e., the only potential route for CO2 reduction is the one-electron pathway. In contrast to this behavior, [Re(bpy)(CO)3][P(OMe)3] radicals are extremely stable in the absence of excess P(OMe)3 which has not been previously described. [Re(bpy)(CO)3(O2CH)]+ was prepared by the thermal substitution of Ott in [Re(bpy)(CO)3(Otf)]21 in a typical preparation, [Re(bpy)(CO)3Cl](300 mg, 0.65 mmol) was dissolved in acetonitrile (50 mL). AgCF3SO3 (184 mg, 0.72 mmol) was added, and the solution was refluxed under argon in the dark for 1h, producing [Re(bpy)(CO)3Cl] that was filtered off. NH4O2CH (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 copious amounts of water. The yellow powdery product [Re(bpy)(CO)3(O2CH)]+ was obtained in approximately 70% yield.

All spectroelectrochemical samples were handled carefully under a nitrogen or argon atmosphere. CO2 was introduced into the solutions by bubbling through a S3 frit.

**Spectroscopic and (Spectro)electrochemical instrumentation.** FTIR spectra were measured on a Nicolet 2000 (2 cm−1 resolution) or Bio-Rad FTS-7 (2 cm−1 resolution) spectrometers. An OTTLE cell equipped with a Pt-mini grid working electrode (32 wires/cm) and CaF2 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 Bu4NPF6 (and/or Et4NCl) were 3 × 10−3−10−2 and 0.3 M, respectively. The cyclic voltammetric experiments, performed in neat THF or in THF:CH3CN = 3:2 (v/v), used concentrations of 10−3 and 10−2 M in the complexes and Bu4NPF6, 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 Agwire 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 mini grid 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 began 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, and subsequent uncontrolled potential shifts due to a large ohmic potential drop ∆E = E_expt − iR, 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 CO2 reduction was monitored by IR spectroscopy for a period of 2−15 min, dependent on the development of free CO at the miniature cathode that finally precluded

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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, might otherwise lead to ambiguous results. It is not surprising that the concentration of the ReI dimer, [Re(bpy)(CO)3]2, as the radicals appear to react with the presence of excess Cl⁻, but the high frequency band at 2003 cm⁻¹ is clearly visible. The formation of the six-coordinate anion, [Re(bpy)(CO)3(CH₃CN)]⁻, is much higher in CH₃CN than in THF/CH₃CN.

### 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. 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, was reasonably suppressed within the total experimental time (typically 10–20 min for one complete measurement), which might otherwise lead to ambiguous results.

<table>
<thead>
<tr>
<th>Complex (no.)</th>
<th>ν(CO)/cm⁻¹</th>
<th>Solvent</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Re(bpy)(CO)3Cl] (1)</td>
<td>2020, 1914, 1897</td>
<td>CH₃CN</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>1998, 1885, 1867.5</td>
<td>CH₃CN</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>1996, 1883, 1868</td>
<td>THF</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>1994, 1880, 1862</td>
<td>DMF</td>
<td>7</td>
</tr>
<tr>
<td>[Re(bpy)(CO)3Cl]⁻ (2)</td>
<td>2011, 1895 (br)</td>
<td>CH₃CN</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>1986, 1868, 1852</td>
<td>CH₃CN</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>1947, 1843 (br)</td>
<td>THF</td>
<td>14</td>
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<tr>
<td></td>
<td>1948, 1846</td>
<td>CH₃CN</td>
<td>a</td>
</tr>
<tr>
<td>[Re(bpy)(CO)3(CH₃CN)]⁻ (6)</td>
<td>2018, 1929, 1898</td>
<td>THF</td>
<td>14</td>
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<tr>
<td></td>
<td>2013, 1980, 1895</td>
<td>CH₃CN</td>
<td>13</td>
</tr>
<tr>
<td>[Re(bpy)(CO)3(CH₃CN)]⁺ (7)</td>
<td>1996, 1898, 1879</td>
<td>CH₃CN</td>
<td>a</td>
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<tr>
<td>[Re(bpy)(CO)3(CH₃CN)]²⁻ (8)</td>
<td>2018, 1915, 1891</td>
<td>THF</td>
<td>14</td>
</tr>
<tr>
<td>[Re(bpy)(CO)3(CH₃CN)]³⁻ (9)</td>
<td>1998, 1889.5, 1879</td>
<td>THF</td>
<td>a</td>
</tr>
<tr>
<td>[Re(bpy)(CO)3(CH₃CN)]⁴⁻ (10)</td>
<td>1930, 1851</td>
<td>THF</td>
<td>a</td>
</tr>
<tr>
<td>[Re(bpy)(CO)3(CH₃CN)]⁵⁻ (11)</td>
<td>1930, 1851</td>
<td>n-PrCN</td>
<td>15</td>
</tr>
<tr>
<td>[Re(bpy)(CO)3(CH₃CN)]⁶⁻ (12)</td>
<td>2004, 1611.5, 1926.5</td>
<td>THF</td>
<td>a</td>
</tr>
<tr>
<td>[Re(bpy)(CO)3(CH₃CN)]⁷⁻ (13)</td>
<td>2020, 1927, 1896</td>
<td>THF</td>
<td>a</td>
</tr>
<tr>
<td>[Re(bpy)(CO)3(CH₃CN)]⁸⁻ (14)</td>
<td>2032, 1923, 1918</td>
<td>THF</td>
<td>a</td>
</tr>
<tr>
<td>[Re(bpy)(CO)3(CH₃CN)]⁹⁻ (15)</td>
<td>1986, 1860, 1851</td>
<td>n-PrCN</td>
<td>15</td>
</tr>
</tbody>
</table>

This work. a Between 2008 and 2003 cm⁻¹ in CH₃CN/excess Cl⁻. b Butyronitrile. c dapa = 2,6-diacylpyridinebis(anil).

Assignables to the solvated radical [Re(bpy)(CO)3(CH₃CN)]⁺ (3) begin to appear (Figure 1b), formed by the substitution of Cl⁻ by CH₃CN, 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(CH₃CN)]⁻ (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 CH₃CN with respect to the five-coordinate anion 5 since CH₃CN 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 CH₃CN 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)3Cl]⁻ (2) and [Re(bpy)(CO)3(CH₃CN)]⁻ (3) and can exist in solution not only with these but also with the neutral starting complex [Re(bpy)(CO)3Cl] (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, 6, 7, and 5) and by Scheme 3. In Scheme 3, and the later schemes, the bold numbers (i.e. 1, 2, 6, 7, and 5) and by Scheme 3. In Scheme 3, the quoted Eₚc values refer to solution in THF/CH₃CN.

The data in Table 1 show that [Re(bpy)(CO)3(CH₃CN)]⁺ (3) can be reduced simultaneously with the starting complex, [Re(bpy)(CO)3Cl] (1), to give the anions 4 and 5 since the reduction potentials of 1 and 3
to form \([\text{Re(dmbpy)(CO)}_3]\) the one-electron reduced radical anion \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\)
containing excess \(\text{Et}_4\text{NCl}\) as electrolyte (arrows indicate whether the bands decrease or increase): (a) Initial reduction of \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]\) (1) leading to the growth of the one-electron reduced radical anion \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (2); (b) the three \(\nu(\text{CO})\) bands assigned to \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (1) continuing to decrease. The radical anion \([\text{Re(bpy)}(\text{CO})_3(\text{CH}_3\text{CN})]^-\) (3) which is reduced at a similar potential to \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (2) is unstable and decays to produce the solvent radical \([\text{Re(bpy)}(\text{CO})_3(\text{CH}_3\text{CN})]^-\) (3) which is reduced at a similar potential to \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (2) and \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (5).

The three \(\nu(\text{CO})\) bands of 2 decrease with a concomitant increase in the intensity of the \(\nu(\text{CO})\) 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 \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (5).

Figure 1. \(\nu(\text{CO})\) IR spectral changes following OTTLE cell reduction of \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]\) (1) in acetonitrile solution containing excess \(\text{Et}_4\text{NCl}\) as electrolyte (arrows indicate whether the bands decrease or increase): (a) Initial reduction of \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]\) (1) leading to the growth of the one-electron reduced radical anion \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (2); (b) the three \(\nu(\text{CO})\) bands assigned to \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (1) continuing to decrease. The radical anion \([\text{Re(bpy)}(\text{CO})_3(\text{CH}_3\text{CN})]^-\) (3) which is reduced at a similar potential to \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (2) is unstable and decays to produce the solvent radical \([\text{Re(bpy)}(\text{CO})_3(\text{CH}_3\text{CN})]^-\) (3) which is reduced at a similar potential to \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (2) and \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (5).

2. Reduction of \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]\) (1) in THF Solution with Excess \(\text{Cl}^-\) under Argon (Figure 2).

Stor et al.\(^{14}\) reported that IR OTTLE one-electron reduction of \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]\) (1) in THF/\(\text{PF}_6^-\) (in the absence of excess \(\text{Cl}^-\)) led to a very small amount of \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (2) which was in equilibrium with the major product, the dimer \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]_2\) (6). In contrast to the results in CH\(_3\)CN described above, no \([\text{Re(bpy)}(\text{CO})_3\text{THF}]^-\) is observed, presumably since THF has much weaker coordination properties being a hard base compared with CH\(_3\)CN. The IR OTTLE experiment under the title conditions was performed in order to observe how much the radical anion \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (2) could be stabilized with respect to \(\text{Cl}^-\) loss and to observe subsequent dimerization in the presence of large excess (~×50) of \(\text{Cl}^-\).

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

3. Reduction of [Re(bpy)(CO)3(CH3CN)]+ (7) in THF Solution under Argon (Figure 3). [Re(bpy)(CO)3(CH3CN)]+ (7), produced by reduction of [Re(bpy)(CO)3(O2CH)] (9) in THF solution under Argon (Figure 4).

Figure 3. ν(CO) IR spectral changes following OTTLE cell reduction of [Re(bpy)(CO)3(CH3CN)]+ (7) in THF solution (arrows indicate whether the bands decrease or increase): (a) Initial reduction of [Re(bpy)(CO)3(CH3CN)]+ (7) leading to the formation of [Re(bpy)(CO)3(CH3CN)]• (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(CH3CN)]• (3), results in the formation of the dimer [Re(bpy)(CO)3]2 (6), which has four clearly resolved ν(CO) bands.14 Reduction of the dimer 6 leads initially to the five-coordinate anion [Re(bpy)(CO)3(CH3CN)]• (5), which reacts partially with the CH3CN liberated previously from [Re(bpy)(CO)3(CH3CN)]• (3) to form the six-coordinate anion [Re(bpy)(CO)3(CH3CN)]• (4).

Figure 4. ν(CO) IR spectral changes following OTTLE cell reduction of [Re(bpy)(CO)3(O2CH)] (9) in THF solution (arrows indicate whether the bands decrease or increase). One-electron reduction of [Re(bpy)(CO)3(O2CH)] (9) leads to the formation of the radical anionic species [Re(bpy)(CO)3(O2CH)]• (10). The νas(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 νas(COO) vibration of free formate in solution, marked Y in the figure.

ment in CH3CN, the concentration of [Re(bpy)(CO)3(CH3CN)]• (4) is much lower relative to that of [Re(bpy)(CO)3]• (5) since there is only an equimolar amount of CH3CN available for coordination.

4. Reduction of [Re(bpy)(CO)3(O2CH)] (9) in THF Solution under Argon (Figure 4). As stated in the Introduction, [Re(bpy)(CO)3(O2CH)] is a known side product of the catalytic reduction of CO2 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(O2CH)] 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(O2CH)] (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, νas(COO) at 1630 cm−1 and νs(COO) at 1280 cm−1 (not shown) as expected. Upon one-electron reduction two new ν(CO) bands were observed assigned to the radical anion [Re(bpy)(CO)3(O2CH)]• (10) (Table 2). This species appeared to be stable with respect to formate loss as no dimer formation, and no change in the νas(COO) region (which would indicate the production of free formate) was observed. After approximately 80% of [Re(bpy)(CO)3(O2CH)] (9) had been reduced to [Re(bpy)(CO)3(O2CH)]• (10), the two-electron reduced five-coordinate
anion \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (5) began to form,\(^{25}\) accompanied by the production of free formate, as evidenced by the \(\nu_{\text{as}}(\text{CO})\) band at 1604 cm\(^{-1}\) (eq 11).

It is clear from these results that the reduction of \([\text{Re(bpy)(CO)}_3\text{(O}_2\text{CH})]\) (9) leads to an essentially stable radical anion, in contrast to \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (1), since none of the dimer \([\text{Re(bpy)(CO)}_3\text{Cl}]_2\) (6) and hence no five-coordinate radicals are produced. The production of \([\text{Re(bpy)(CO)}_3\text{(O}_2\text{CH})]^+\) (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 \(\text{CO}_2\) reduction: In \(\text{CH}_3\text{CN}\), the one-electron (radical) and two-electron (anionic) \(\text{CO}_2\) reduction pathways can run simultaneously at the potential required to initiate the one-electron reduction of \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (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 concentration of \(\text{CH}_3\text{CN}\) (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 \(\text{IR}\) OTTLE experiments performed in the presence of \(\text{CO}_2\) are described below.

5. Reduction of \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (1) in THF Solution with Excess \(\text{Cl}^-\) in the Presence of \(\text{CO}_2\) (Figure 5). The one-electron reduction of \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (1) under the title conditions initially leads, as expected,\(^{7,11,24}\) to the radical anion \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (2). Initially \(\text{CO}_2\) 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 \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (2) alone is not sufficient to catalyze \(\text{CO}_2\) reduction. This observation disproves the assumption\(^{8,9}\) that \(\text{CO}_2\) reacts directly with 2. \(\text{CO}_2\) reduction was considerably accelerated at the point when, according to the blank experiment in the absence of \(\text{CO}_2\) (see part 2 above), the dimer \([\text{Re(bpy)(CO)}_3\text{Cl}]_2\) (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 \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (2). This new species has very similar \(\nu(\text{CO})\) stretching frequencies to the radical anion and can be most easily identified by the changes in the low-frequency \(\nu(\text{CO})\) region toward the end of the reduction of 1 where it is clear that the two \(\nu(\text{CO})\) bands due to \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (2) are changing to one broad band. This band, along with one that is coincident with the high-frequency band of \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (2) at 1996 cm\(^{-1}\), can be assigned to the stable radical anion \([\text{Re(bpy)(CO)}_3\text{(O}_2\text{CH})]^+\) (10) (Table 2), along with the shoulder appearing at 1628 cm\(^{-1}\) due to coordinated formate (see part 4 above). The reduction of \([\text{Re(bpy)(CO)}_3\text{(O}_2\text{CH})]\) (9) to the radical anion 10 at the reduction potential of \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (1) is certainly possible (see Table 1), and the inherent stability of \([\text{Re(bpy)(CO)}_3\text{(O}_2\text{CH})]^+\) (10) at the reduction potential of the parent complex, \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (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 \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (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 \(\text{CO}_2\) 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 \(\text{CO}_2\) in the form of an ion pair,\(^{31,27}\) as shown in part 4 above, the shoulder at 1628 cm\(^{-1}\) belongs to the coordinated \(\text{O}_2\text{CH}^-\) ligand in \([\text{Re(bpy)(CO)}_3\text{(O}_2\text{CH})]^+\) (10). The band at 1680 cm\(^{-1}\), which grows independently of the band at 1640 cm\(^{-1}\) and possesses a comparable intensity with the latter peak (particularly at the beginning of the \(\text{CO}_2\) reduction), might be assigned to some other organic carboxylato product or its salt (i.e. not to a ligand coordinated to the \(\text{Re(bpy)(CO)}_3\) unit since no \(\nu(\text{CO})\) bands of some

\(^{25}\) The reduction of \([\text{Re(bpy)(CO)}_3\text{(O}_2\text{CH})]\) is well separated from that of \([\text{Re(bpy)(CO)}_3\text{Cl}]^-\) (see Table 1). As shown in part 4 above, the shoulder at 1628 cm\(^{-1}\) belongs to the coordinated \(\text{O}_2\text{CH}^-\) ligand in \([\text{Re(bpy)(CO)}_3\text{(O}_2\text{CH})]^+\) (10). The band at 1680 cm\(^{-1}\), which grows independently of the band at 1640 cm\(^{-1}\) and possesses a comparable intensity with the latter peak (particularly at the beginning of the \(\text{CO}_2\) reduction), might be assigned to some other organic carboxylato product or its salt (i.e. not to a ligand coordinated to the \(\text{Re(bpy)(CO)}_3\) unit since no \(\nu(\text{CO})\) bands of some

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 (1) is well separated from those of [Re(bpy)(CO)3(O2CH)]1− (10) and [Re(bpy)(CO)3Cl]− (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 CO2 reacts directly with the radicals [Re(CO)3(bpy)]•− (a), as was spectroscopically observed for [Re(CO)3(dmbpy)]•−.11 On the other hand, it seems that CO2 does not react directly with [Re(bpy)(CO)3Cl]•− (2) as this product was formed at the same transient concentration with respect to the parent complex as observed in the absence of CO2 (see part 2 above).

6. Reduction of [Re(bpy)(CO)3(Otf)]11 THF Solution in the Absence and Presence of CO2 (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-catalyzed14 formation of [Re(bpy)(CO)3(THF)]1 (8) and its subsequent reduction. Since the reduction of [Re(bpy)(CO)3(THF)]1 (8) lies 170 mV more positive than [Re(bpy)(CO)3Cl]1 (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]1− (5) prior to the complete reduction of [Re(bpy)(CO)3(THF)]1− (8). Moreover, the radical [Re(bpy)(CO)3(THF)]1•− (b) is much less stable than [Re(bpy)(CO)3Cl]1•− (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 CO2 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]• (a). This was not completely possible for [Re(bpy)(CO)3Cl]1 (1) in CO2-saturated THF (see part 5 above).

The data from the IR OTTLE experiment under the title conditions in CO2-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)1 (8). The reduction of this cation then initiated the electrocatalytic reduction of CO2. 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(O2CH)]1•− (10). The IR spectra reveal that, under these specific conditions given by the rather positive reduction potential of [Re(bpy)(CO)3(THF)]1 (8), the neutral formato complex [Re(bpy)(CO)3(O2CH)]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 CO2− (1640 cm−1), coordinated O2CH− (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]1− (2) as a potential catalyst, the CO2 reduction was initiated only by the formation of the reactive radicals [Re(bpy)(CO)3]• (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 source14 of [Re(bpy)(CO)3]1•− (5) in the absence of CO2.

7. Reduction of [Re(bpy)(CO)3Cl]1 (1) in CH3CN Solution with Excess Cl− in the Presence of CO2 (Figure 7).

Having established that the one-electron pathway involving the five-coordinate radicals could lead to efficient CO2 reduction (see parts 5 and 6 above), an IR OTTLE experiment, using the title conditions,
was performed to see the effect of introducing the two-electron anionic pathway. Figure 7 shows that reduction of approximately 20% [Re(bpy)(CO)3Cl] (1) in CH3CN/Cl- was accompanied by very fast formation of free CO32- (sharp band at 1643 cm$^{-1}$) and CO, together with the unassigned product (band at 1679 cm$^{-1}$) which appeared earlier than the CO32-. The IR spectra in the ν(CO) region revealed the presence of comparably small amounts of [Re(bpy)(CO)3Cl]$^{-}$ (2) and [Re(bpy)(CO)3(CH3CN)]$^{-}$ (3). It is interesting to note that no bands due to the [Re(bpy)(CO)3(O2CH)]$^{-}$ (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 CO2 illustrate that the reduction pathway of [Re(bpy)(CO)3Cl]$^{-}$ (1) in CH3CN 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(CH3CN)]$^{-}$ (3) which could be directly reduced to the anions [Re(bpy)(CO)3]$^{-}$ (5) and the predominant [Re(bpy)(CO)3(CH3CN)]$^{-}$ (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 CO2 reduction in CH3CN much more efficient in comparison with that in THF as demonstrated by the rapid formation of free CO$_2$ and CO (Figure 7).

8. Reduction of [Re(bpy)(CO)3(P(OEt)3)]$^{+}$ (12) in THF Solution in the Absence of CO$_2$ (Figures 8 and 9). As was stated in the Introduction, the stability of [Re(bpy)(CO)3(P(OEt)3)]$^{+}$ affords an excellent opportunity to study the two-electron catalytic pathway in the absence of the one-electron radical route to CO2 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)]$^{+}$ (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).

In the presence of CO2, 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 CO2 nor appearance of its reduction products could be observed, indicating again that CO2 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]$^{+}$ (a), which is not produced here due to the inherent stability of [Re(bpy)(CO)3(P(OEt)3)]$^{+}$ (13). The subsequent reduction of the radical, forming the coordinatively unsaturated anion [Re(bpy)(CO)3]$^{-}$ (5), initiated the CO2 reduction. The reduction of the six-coordinate radical was accompanied by the rapid production of CO32- 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(O2CH)]$^{+}$ (10), which exhibits a very similar reduction potential to that of [Re(bpy)(CO)3(P(OEt)3)]$^{+}$ (13). On shifting of the reduction potential more negative, both [Re(bpy)(CO)3(P(OEt)3)]$^{+}$ (13) and [Re(bpy)(CO)3(O2CH)]$^{+}$ (10) were completely reduced. A number of new unknown complexes were formed in place of [Re(bpy)(CO)3]$^{-}$ (5), of
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 ν(CO) bands due to [Re(bpy)(CO)₃]²⁻ (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]²⁻ (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][Re(bpy)(CO)₃CH₃CN]⁺/[Re(bpy)(CO)₃(CH₃CN)]⁻/[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 CO₂ (Figure 10). Having established the catalytic activity of both [Re(bpy)(CO)₃]⁺ (a) and [Re(bpy)(CO)₃]²⁻ (5), we made an attempt to study the reactivity of the six-coordinate anions [Re(bpy)(CO)₃]L⁻. 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 CO₂, one-electron reduction of [Re(bpy)(CO)₃][P(OEt)₃]⁺ (12) gave, as Figure 9. IR spectral changes following OTTLE cell reduction of [Re(bpy)(CO)₃][P(OEt)₃]⁺ (12) in CO₂ 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 CO₂ leading to the production of CO, CO₃²⁻, 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(O₂CH)]⁻ (10). As the CO₂ concentration decreases, the ν(CO) bands due to [Re(bpy)(CO)₃(O₂CH)]⁻ (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 containing a 100-fold excess of P(OEt)₃ (arrows indicate whether the bands decrease or increase ). (a) In the absence of CO₂, [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]⁻ (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 CO₂ the reaction proceeds as above until [Re(bpy)(CO)₃][P(OEt)₃]⁻ (15) was expected to be produced. At this point rapid CO₂ reduction occurs producing CO, CO₃²⁻, 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 CO₂ reduction is completed (marked *). The small band marked A is possibly due to a very small amount of [Re(bpy)(CO)₂][P(OEt)₃]⁻ (15).
expected, the radical \([\text{Re(bpy)(CO)}_2(P\text{OEt})_3]^-\) (13) (Figure 10a). This radical, however, was readily transformed to the substituted radical \([\text{Re(bpy)}(\text{CO})_2(P\text{OEt})_3]_{2^-}\) (14)\(^{13}\) by reaction with free \(P\text{OEt}_3\). It was hoped that despite this reaction it would still be possible to stabilize a six-coordinate anion, namely \([\text{Re(bpy)}(\text{CO})_2(P\text{OEt})_3]_{2^-}\). 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 \([\text{Re(bpy)}(\text{CO})_3(P\text{OEt})_3]^-\) (15) formed by the reduction of \([\text{Re(bpy)}(\text{CO})_2(P\text{OEt})_3]_{2^-}\) (14) and concomitant substitution reaction of \([\text{Re(bpy)}(\text{CO})_3(P\text{OEt})_3]^-\) with the CO liberated in the initial formation of \([\text{Re(bpy)}(\text{CO})_2(P\text{OEt})_3]_{2^-}\) (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 \([\text{Re(dapac)(CO)}_3(P\text{OMe})_3]^-\), where \(\text{dapac} = 2,6\text{-diacetylpyridinebis(anil)}\) (see Table 2). The complete shift of the equilibrium between \([\text{Re(bpy)}(\text{CO})_3]^-\) (5) and \([\text{Re(bpy)}(\text{CO})_3L]^-\) toward the six-coordinate anion for \(L = P\text{OEt}_3\) in the presence of excess \(P\text{OEt}_3\) is thus in contrast with the situation for \(L = \text{CH}_3\text{CN}\), where \(5\) still forms at room temperature even in neat \(\text{CH}_3\text{CN}\) (see Figure 1). This difference in the stability of \([\text{Re(bpy)}(\text{CO})_3L]^-\) is ascribed to the strong \(\pi\)-acceptor character of the \(\text{PO}_{\text{Et}}\) ligand.

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

The reduction of \([\text{Re(bpy)}(\text{CO})_3(P\text{OEt})_3]^-\) (12) in the presence of \(\text{CO}_2\) is depicted in Figure 10b. The sequence of reactions is identical to that described above up to and including the formation of the radical, \([\text{Re(bpy)}(\text{CO})_2(P\text{OEt})_3]_{2^-}\) (13). This observation illustrates that \(\text{CO}_2\) is not able to react with stable six-coordinate radicals, probably not even with \([\text{Re(bpy)}(\text{CO})_2(\text{CH}_3\text{CN})]^-\) (3) and \([\text{Re(bpy)}(\text{CO})_3\text{Cl}]^-\) (2) (see above) provided the Re--L bond (\(L = \text{CH}_3\text{CN}, \text{Cl}^-\)) is stabilized by the presence of a large excess of \(L\). In contrast to the results in the absence of \(\text{CO}_2\) (see above) further reduction of \([\text{Re(bpy)}(\text{CO})_2(P\text{OEt})_3]_{2^-}\) (13) led to very little or no \([\text{Re(bpy)}(\text{CO})_3(P\text{OEt})_3]^-\) (15). Instead, almost all the \(\text{CO}_2\) was reduced rapidly within 2 min to give again free \(\text{CO}, \text{CO}_2^{2-}\), 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 \(\nu(\text{CO})\) region, bands of unidentified species were found at 1987, 1926.5, 1873, and 1840 cm\(^{-1}\) (marked by \(\ast\) in Figure 10), after the reduction of \(\text{CO}_2\) had been completed. The reduction potential of \([\text{Re(bpy)}(\text{CO})_2(P\text{OEt})_3]_{2^-}\) (14) is in fact very close to that of the reduction of free \(\text{CO}_2\) at a Pt cathode;\(^{27}\) however, the observed transformation of \(\text{CO}_2\) 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 \(\text{CO}_2\) reduction pathway using this catalytic system. The unsaturated anion \([\text{Re(bpy)}(\text{CO})_3(P\text{OEt})_3]^-\) (d)\(^{28}\) is more electronically rich than its \([\text{Re(bpy)}(\text{CO})_3]^-\) (5) derivative and will probably be trapped by \(\text{CO}_2\) rather than by the CO liberated from \([\text{Re(bpy)}(\text{CO})_3(P\text{OEt})_3]^-\) (13) (see above), since \(\text{CO}_2\) is present in the solution at much higher concentration than the CO. It therefore seems likely that in this case \(\text{CO}_2\) reacts readily with the unsaturated transient five-coordinate anion \([\text{Re(bpy)}(\text{CO})_2(P\text{OEt})_3]^-\) (d) rather than with the six-coordinate anion \([\text{Re(bpy)}(\text{CO})_3(P\text{OEt})_3]^-\) (15), which would otherwise be formed in the absence of \(\text{CO}_2\) (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 \([\text{Re(bpy)}(\text{CO})_3(\text{CH}_3\text{CN})]^-\) (3) in \(\text{CH}_3\text{CN}\) which introduces the two-electron pathway for the electrocatalytic reduction of \(\text{CO}_2\). Having studied \(\text{CO}_2\) reduction mediated by \([\text{Re(bpy)}(\text{CO})_3(\text{Cl})]^+\) (1) in \(\text{CH}_3\text{CN}\), we provide for the first time spectroscopic evidence that \(\text{CO}_2\) does not interact directly with the radical anion \([\text{Re(bpy)}(\text{CO})_3(\text{Cl})]^-\) (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 \([\text{Re(dmbpy)}(\text{CO})_3(\text{Cl})]^+\) since it readily decomposes to give the \(\text{CO}_2\)-catalyst \([\text{Re(dmbpy)}(\text{CO})_3]^-\) instead of the stable solvent radical \([\text{Re(dmbpy)}(\text{CO})_3(\text{CH}_3\text{CN})]^-\). The reduction of parent \([\text{Re(dmbpy)}(\text{CO})_3(\text{Cl})]^-\) in the presence of \(\text{CO}_2\) hence leads instantaneously to the formation of \(\text{CO}, \text{CO}_2^{2-}\), and formate complexes, making it impossible to confirm or disprove the catalytic activity of \([\text{Re(dmbpy)}(\text{CO})_3(\text{Cl})]^-\) itself. In contrast to this pathway, the secondary chemical reaction of 2 in \(\text{CH}_3\text{CN}\) leads to the 18e radical \([\text{Re(bpy)}(\text{CO})_3(\text{CH}_3\text{CN})]^-\) (3) and does not produce a detectable amount of the dimer \([\text{Re(bpy)}(\text{CO})_3]_{2^-\text{Br}}\) (6). This spectroelectrochemical result seems to be in disagreement with the cyclic voltammetric studies\(^{9}\) of \([\text{Re(bpy)}(\text{CO})_3]_{2^-\text{Br}}\) in \(\text{CH}_3\text{CN}\), which is reduced in the absence of \(\text{CO}_2\) to give both the radical 3 and the dimer 6. However, Stor et al. have shown\(^{14}\) that the primary

\(^{28}\) The anion \([\text{Re(bpy)}(\text{CO})_2(P\text{OEt})_3]^-\) (d) can be produced\(^{14}\) smoothly by stepwise two-electron reduction of \([\text{Re(bpy)}(\text{CO})_2(P\text{OEt})_3]_{2^-}\) in the absence of excess \(P\text{OEt}_3\).
The reaction of CH₃CN with the radical anion [Re(bpy)(CO)₃Br]⁻ produces a large amount of [Re(bpy)(CO)₃]⁺ (12), which then dimerizes to give the dimer [Mn(bpy)(CO)₃]₂. This reaction may take place even in CH₃CN, where the slow replacement of Cl⁻ by CH₃CN in the case of 2, especially in the presence of excess Cl⁻, may therefore be viewed as an associative process where CH₃CN reacts directly with [Re(bpy)(CO)₃Br]⁻ (12), i.e., the dissociative X⁻-loss pathway considered by Sullivan, Meyer, et al.8 Instead, CO₂ attacks the coordinatively unsaturated [Re(bpy)(CO)₃]⁺ (12) 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 CO₂, 5 has been found to exist in an equilibrium with the six-coordinate anion [Re(bpy)(CO)₃(CH₃CN)]⁻ (4) which is probably not capable of CO₂ coordination.

The two-electron catalytic pathway also applies to the complex [Re(bpy)(CO)₃(PCy₃)]⁺ (13) with respect to 3, makes the electrocatalytic CO₂ reduction more efficient in comparison with the catalyst precursor 1 in CH₃CN. The same conclusion can probably be drawn also for the chemically reversible redox couples [Re(bpy)(CO)₃(PR₃)]⁺⁻, e.g., with R = Ph.14

The dissociative one-electron catalytic pathway is always indicated in the absence of CO₂ 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]⁺ (a). This pathway becomes dominant in solvents like THF or DMF that cannot stabilize the 18e radicals [Re(bpy)(CO)₃(solvent)]⁺ due to their weaker coordination as compared with CH₃CN. The same situation probably applies also to related radical complexes with a strongly basic α-dimine ligand like 1,1O-phenanthroline and 2,2'-bipyridine with electron-releasing substituents11 or with pyridine ligands.29

The one-electron pathway in Scheme 6 might be linked to the two-electron one via a fast one-electron reduction of the radical intermediate [Re(bpy)(CO)₃(solvent)]⁺, 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(CO₂H)]⁺ (10) becomes largely suppressed in the case of a very efficient two-electron catalytic pathway, for example using [Re(bpy)(CO)₃(PCy₃)]⁺ (12) or [Re(bpy)(CO)₃Cl] (1) in CH₃CN 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 both in THF and CH₃CN to give at room temperature exclusively [Mn(bpy)(CO)₃]₂ and subsequently [Mn(bpy)(CO)₃]⁺⁻, shows no catalytic activity toward CO₂ reduction.31 The absence of the one-electron 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]⁺⁻ 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-dimine)(CO)₃(halide)] with basic α-dimine ligands, as it was also observed for the related compound [Mn(iPr-DAB)-(CO)₂Br] (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-DAB)(CO)₃]⁻ (M = Mn, Re),31,33 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.

(31) Hartl, F. Unpublished results.
by considering a decreasing diffusion character of their frontier d orbitals in the same order, which are involved in the π-bonding with the formally doubly-reduced α-dimine ligand.32 The better matching of the d orbitals with the lowest π* orbital of the reduced α-dimine in the same order then results in a stronger π-back-bonding from the reduced α-dimine toward the metal center. The stronger the delocalized π-bonding over the M(α-dimine) chelate ring, the higher is the electron density on the metal center and the more stable is its five-coordinate geometry.14 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(α-dimine)(CO)3]n− remain inert with respect to the CO2 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 d6-metals: [M11(triphos)(DBCat)]+ (M = Co, Rh, Ir),34 [M(L)n(CO)3(DBCat)]n− (M = Mn, n = 0; M = Re, n = 1),35,36 and [M(CO)4(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-dimines like 2,2′-bipyrimidine (bpym) or azo-2,2′-pyridine (apy) leads to facile coordination of a sixth ligand, producing stable [Re(α-dimine)(CO)3]− (L = e.g. THF or PPh3).14,15 Electrocatalytic reduction of CO2 was also not observed in this case.31 The relatively low electron density on the Re center in the six-coordinate anions [Re(α-dimine)(CO)3]−, as documented14 by their significantly higher ν(CO) frequencies in comparison with those of five-coordinate [Re(α-dimine)(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 CO2 reduction with these complexes forbidden.

In conclusion, availability of a free coordination site is a necessary prerequisite of the Re(bpy) catalysts for the CO2 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)]+ is sufficiently electronically poor to allow coordination of Lewis bases like phosphines or CH2CN instead of rapid dimerization, but it is still electronically rich enough to coordinate and reduce CO2 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 (CH2CN, P(OEt)3). However, coordination and efficient reduction of CO2 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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