212. Photochemical and Electrochemical Reduction of Carbon Dioxide to Carbon Monoxide Mediated by (2,2'-Bipyridine)tricarbonylchlororhenium(I) and Related Complexes as Homogeneous Catalysts[1])

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[*fac*-Re(bpy) $(CO)_3Cl$] (bpy = 2,2'-bipyridine) is an efficient homogeneous catalyst for the selective and sustained photochemical or electrochemical reduction of CO_2 to CO. A quantum yield of 14% and a faradic efficiency of 98% were measured in the presence of excess Cl^- ions.The photochemical process took place under visible-light irradiation and consumed a tertiary amine as electron donor. A formato-rhenium complex was isolated in the absence of excess Cl^- ions. Substitution by Cl^- ion generated free formate, but no CO was detected. Luminescence measurements showed that the tertiary amine quenches the metal-to-ligand charge-transfer excited state of the rhenium complex *via* a reductive mechanism, with a rate constant of $3.4 \times 10^7 \text{M}^{-1}\text{s}^{-1}$. The 19e-complex $[Re(bpy)(CO)_3X]^-$ produced either photochemically or electrochemically appears to be the active precursor in the CO-generation process. Detailed spectroscopic studies on ^{13}C-enriched carbonyl-rhenium and formato-rhenium complexes derived from ^{13}C-enriched CO_2 were performed in order to confirm the origin of the products and to study the exchange of the ligands. A mechanism for the present CO_2 photoreduction process is presented; it involves separate pathways for CO and formate generation, in which the [Re(bpy) $(CO)_3X$] complex plays the role of *both the photoactive and the catalytic center*.

Introduction. – Natural photosynthesis involves the photogeneration of reduced carbon compounds from CO_2 and H_2O. CO_2 is an abundant source of raw material in nature. Accordingly, a great deal of attention has been devoted recently to systems capable of activating CO_2 [1]. Few catalytic systems are known, despite the development of a number of different strategies (electrochemical, photoelectrochemical, and photochemical).

Electrochemical systems using an electrode to either directly reduce CO_2 or to reduce a transition-metal complex which further reacted with CO_2 have been reported to produce high yields of formic acid [2–6], appreciable formation of oxalic acid [4] [6–10] or CO [4] [8] [9] [11], low yields of methanol and methane [12], and traces of glyoxylate, glycolate, and tartrate [4]. In some electrocatalytic systems, electrodes were modified with an insoluble transition-metal complex such as phthalocyaninato-cobalt or -nickel [13], with a viologen-based polymer into which metallic Pd was dispersed [14], or with a polymerized Re complex [15]. Other materials used as homogeneous catalysts in electrocatalytic systems included soluble phthalocyanines [16] or porphyrin complexes [17] [18], ironsulfur clusters [19], Ni and Co complexes of macrocyclic polyamines [20] [21], as well as

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[1]) Communicated in part at the 5ème Atelier de Photochimie et de Photophysique des Composés Organométalliques et de Coordination, Société Française de Chimie, Paris, 21–22 June, 1984; for a preliminary communication, see [38]; taken in part from *J. Hawecker*, Ph.D. thesis, Université Louis Pasteur, Strasbourg, 1984.

[2]) UA 422 of the *CNRS*.

Re [22] or Rh [23] complexes. High current efficiency and long term stability (high overall turnover) were obtained using [*fac*-Re(bpy) $(CO)_3Cl$] (bpy = 2,2'-bipyridine) [22] or nickel (II)-cyclam [20b]. In both cases, the average current efficiency was 98 %.

Most of the *photoelectrochemical* systems described were heterogeneous and involved single-crystal semi-conductor eletrodes [24]. In two cases, a semi-conductor has been used in association with an electron relay. The first contained a tetraazamacrocyclic Ni or Co complex [25] and in the second, methylviologen was coupled with a formate dehydrogenase enzyme [26]. Numerous studies concerned the direct reduction of CO_2 in semi-conductor-based photoelectrochemical cells such as p- or n-GaP [27] [28], p- or n-GaAs [12a] [12b] [29], p-CdTe [30], p-InP [12a] [31], and p-Si [25] [31]. Most of these processes were inefficient and frequently unstable [28]. UV irradiation of a clean single crystal of strontium titanate in the presence of H_2O and CO_2 has been reported to yield stoichiometric quantities of methane [32].

The purely *photochemical* systems may be classified as either heterogeneous involving the use of semi-conductor suspensions [33] [34] or as homogeneous involving the use of aqueous solutions of metal ions [35], organic dyes [36], or of transition-metal complexes [37–40]. We have recently developed three systems for visible-light-driven catalytic reduction of CO_2 [37–40]. In the first, which contained $[Ru(bpy)_3]^{2+}$ (as photosensitizer) and $[Co(bpy)_3]^{2+}$ or Co(II) ions (as electron mediator and as H_2O- and CO_2-reduction catalysts), catalytic amounts of both H_2 and CO were produced [37]. In the second system based on *fac*-[Re(bpy) $(CO)_3Cl$], high yields of CO were obtained [38]. In the third system, based on Ru complexes, catalytic amounts of formate were formed [39].

We describe here our results and mechanistic investigations for the system based on rhenium complexes **1**–**9** [38], in which the complex used acts both as photosensitizer and as homogeneous CO_2-reduction catalyst for the efficient and selective photoreduction of CO_2 to CO. A related mechanistic study of this system has been performed recently [41].

[*fac*-Re(bpy)$(CO)_3Cl$] (**1**)
[*fac*-Re(bpy)$(CO)_3Br$] (**2**)
[*fac*-Re(bpy)$(^{13}CO)_3Cl$] (**3**)
[*fac*-Re(bpy)$(^{13}CO)_3(H^{13}COO)$] (**4**)
[*fac*-Re(bpy)$(CO)_3(HCOO)$] (**5**)
[*fac*-Re(bpy)$(CO)_3(CH_3CN)]^+ BF_4^-$ (**6**)
[μH-{*fac*-Re(bpy)$(CO)_3\}_2]^+ Cl^-$ (**7**)
[*fac*-Re(bpy)$(CO)_3(H_2O)]^+ BF_4^-$ (**8**)
[*fac*-Re(bpy)$(CO)_3(OClO_3)$] (**9**)

Visible-Light CO_2 Photoreduction Experiments. – Visible-light ($\lambda > 400$ nm) irradiation of a dimethylformamide nitrilotriethanol (DMF/NTE 5:1)[3]) solution containing [Re(bpy) $(CO)_3Cl$] (**1**), excess Et_4NCl, and CO_2 yielded catalytically and exclusively CO [38]. No trace of H_2 (less than 1µl by GC) could be detected. When 90.5 % enriched $^{13}CO_2$ was used, 88 % of ^{13}CO was obtained as determined by GCMS (*Fig. 1*). Control experiments carried out in the absence of either CO_2, NTE, or light did not generate CO. However, in absence of CO_2 but in presence of the electron donor, traces of H_2 were detected when formal pH of the solution was adjusted with AcOH to that in the presence of CO_2. Continuous photolysis of **1** in the absence of CO_2 caused bleaching of the solution due the photolabilization of the organic ligand; the presence of free bpy was determined by ^{13}C-NMR spectroscopy (in (D_7) DMF/DMF/NTE: 155.6 (C(2,2')); 149.1, 136.9, 123.9, 120.5 ppm (C(3,3'), C(4,4'), C(5,5'), C(6,6')) and by UV spectroscopy ($\lambda_{max} = 280 \pm 2$ nm). No bleaching of the solution was observed in the presence of CO_2, indicating that irradiation yielded a reduced species which then reacted immediately with CO_2 to regenerate the starting complex. In a study of the chemical stability of the

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[3]) NTE stands for $N(CH_2CH_2OH)_3$.

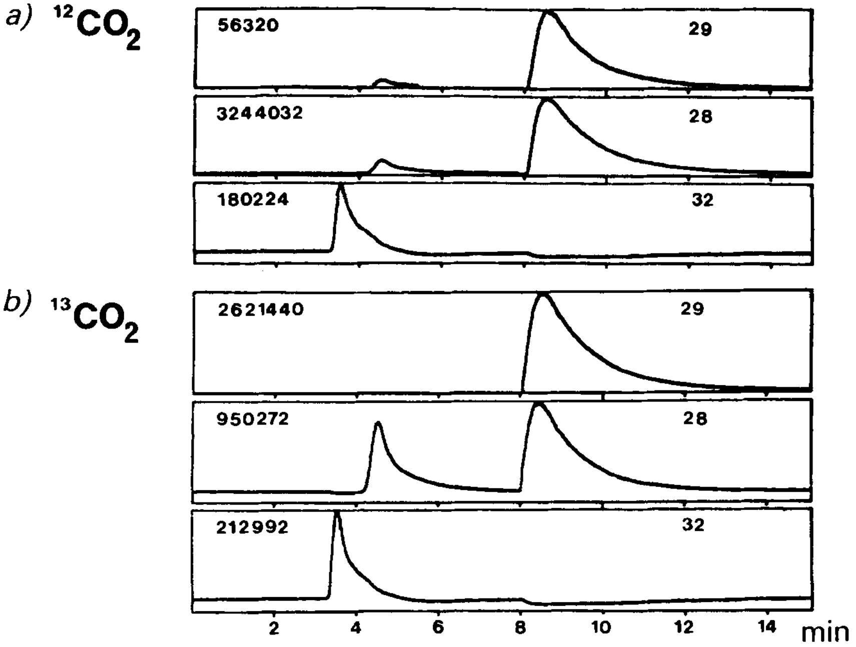

Fig. 1. *GC/MS analysis of photogenerated CO.* Gas obtained from photoreduction of *a)* $^{12}CO_2$ and *b)* $^{13}CO_2$. The mass peaks are recorded at very different sensitivities as indicated by the height of the strongest peak (numbers given at left); for example, CO at mass 29 in *Fig. 1a* is natural abundance ^{13}CO. Abscissa: GC retention time.

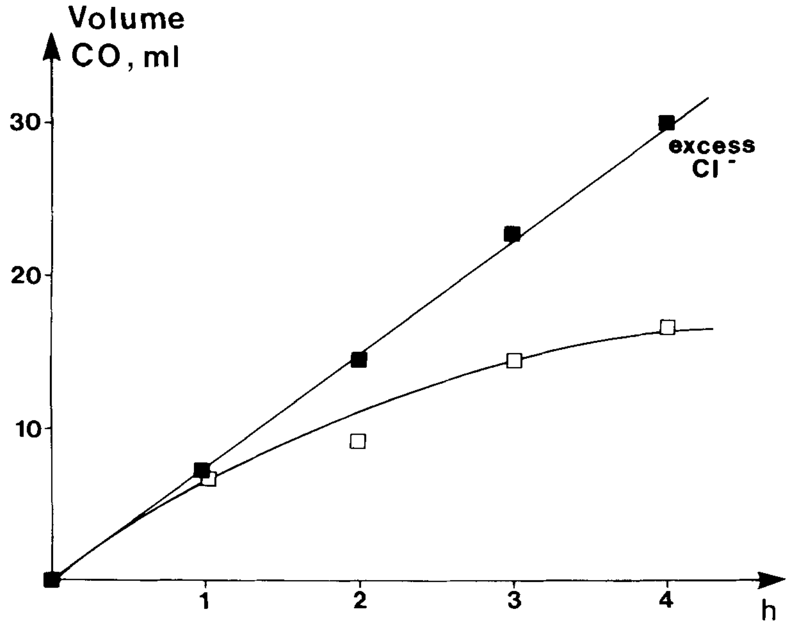

Fig. 2. *Photogeneration of CO from CO_2 as a function of time, using [Re(bpy)(CO)$_3$Cl]* (**1**) *as catalyst in the presence* (■) *or absence* (□) *of excess Et_4NCl*

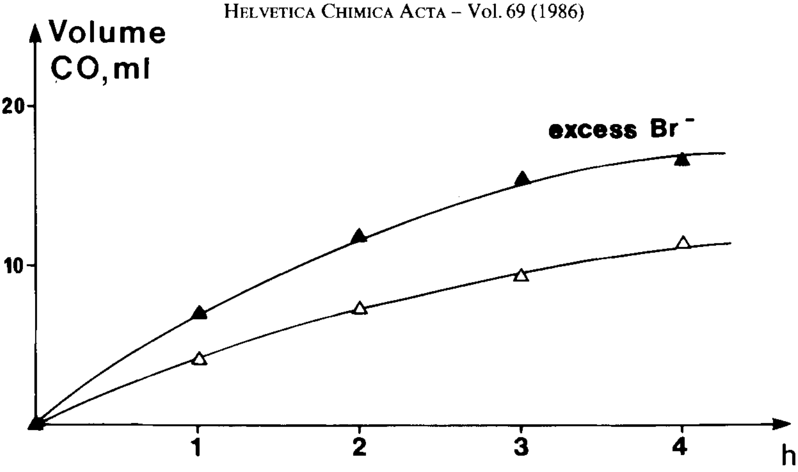

Fig. 3. *Photogeneration of CO from CO_2 as a function of time, using [Re(bpy)(CO)$_3$Br]* **2** *as catalyst in the presence* (▲) *or absence* (△) *of excess Bu_4NBr*

photochemical system, two different photosentitizers [Re(bpy) (CO)$_3$X], X = Cl or Br (**1** and **2** resp.), were used. The results obtained are shown in *Figs. 2* and *3*. The following trends were observed: *i*) the chloro complex was more efficient than the bromo one, *ii*) in both cases, in the absence of an additive, the photogeneration of CO was not linear with respect to time, and the chloro complex **1** appeared to be more stable than the bromo complex **2**. The consumption of CO_2 in the course of the reaction (*ca.* 10% after 4 h irradiation) was unlikely to be the major reason for this loss of efficiency. In order to investigate if it could be due to partial decomposition of the catalyst, different substances were added to the reaction mixture. Addition of 20 equiv. of free bpy caused no observable change in the photochemical generation of CO. Addition of 25 equiv. of Bu_4NBr to the [Re(bpy) (CO)$_3$Br] system increased only slightly the rate of CO generation and did not stabilize its continuous formation *(Fig. 3)*. However, an interesting effect was observed in the presence of a 23-fold excess of Et_4NCl; both the efficiency and stability of complex **1** were significantly improved *(Fig. 2)*. In the case of **1**, the addition of both 23 equiv. of a chloride salt and 200 equiv. of bpy did not change the behaviour of the photochemical system. Photolabilization of coordinated CO, which requires UV irradiation of the ligand-field bond did not seem to occur. No free CO was detected in the gas phase after photolysis of **1** in the absence of CO_2. No CO exchange was observed on placing the chloro-rhenium complex **1** under a ^{13}CO atmosphere in the dark or under continuous photolysis in the absence of a tertiary amine.

Influence of the Halo Ligand. Since an important factor was apparently the labilization of the halo ligand, we studied the reactivity of [Re(bpy)(CO)$_3$Cl] (**1**) and [Re(bpy)(CO)$_3$Br] (**2**) towards Br$^-$ and Cl$^-$ ions both in the dark (15 h) and under irradiation (12 h) in DMF/NTE 5:1. Analysis of the products by TLC (silica, AcOEt/MeOH 4:1; R_f = 0.4 for **1** and 0.56 for **2**) gave the following qualitative results: in presence of 20 equiv. Et_4NBr, **1** afforded a mixture of complexes **1** and **2** under irradiation, but no reaction in the dark; in presence of 20 equiv. of Et_4NCl, **2** gave a mixture of **2** and **1** both in light and in the dark. This indicated that *i*) [Re(bpy) (CO)$_3$Cl] (**1**) was more stable than its bromo analogue **2**, *ii*) labilization of the anionic ligand occurred more readily in the presence of an electron donor and light, suggesting a greater reactivity of the reduced complex $[Re(bpy)(CO)_3X]^-$ towards ligand exchange. This agrees with the fact that irradiation of complex **2** in the absence of NTE did not significantly accelerate the Br exchange (only traces of the chloro-rhenium complex **1** were detected), although the large excess of chloride should clearly favour the starting complex **1**. These observations together with the carbonyl exchange described below have important mechanistic implications, since CO_2 reduction requires coordination to the metal centre [1].

Quantum-Yield Determinations. The measurements performed (see *Exper. Part*) showed that 14% of the light (λ = 385 ± 20 nm) absorbed by $[Re(bpy)(CO)_3Cl]$ (**1**) was converted into CO, in the presence of a 23-fold excess of Et_4NCl in DMF/NTE 5:1. The quantum yield was 8.7% in the absence of excess Cl^- ions. A quantum yield $\Phi = 0.15$ was determined using the bromo complex **2** [41]. The high quantum yields determined for this system represent a remarkable increase of efficiency as compared to the first experiments reported for catalytic reduction of CO_2 to CO ($\Phi_{CO} = 0.012$ for a system based on trisbipyridine-ruthenium and 2,9-dimethyl-1,10-phenanthroline-cobalt(II) complexes [37b]).

Experiments with ^{13}C-Labelled CO_2. Generation of the Formato-rhenium Complex [*fac*-Re(bpy)(CO)$_3$(HCOO)] (5). – When $[Re(bpy)(CO)_3Cl]$ (**1**) was irradiated in a sealed NMR tube under a 90.5%-enriched $^{13}CO_2$ atmosphere without adding excess Et_4NCl, the intensity of the ^{13}C-NMR peak (No. 6, *Fig. 4b*) corresponding to free $^{13}CO_2$ (125 ppm) decreased markedly, and simultaneously a new peak (No. 3, *Fig. 4b*) due to free ^{13}CO appeared (184 ppm, identified by comparison with authentic samples of ^{13}CO in DMF/NTE). This confirmed that the CO originated from the photochemical reduction of CO_2. Furthermore, the relative intensities of the carbonyl-rhenium peaks at 197 and 189 ppm (No. 1, *Fig. 4b*) were enhanced in comparison with the bpy signals, indicating that exchange of the two types of carbonyl groups coordinated to the Re center occurred during the photochemical reduction of CO_2. The carbonyl group in the axial position gives a signal at higher field than those in the bpy plane due to the π-donor effect of the coordinated chloro ligand which leads to shielding of the carbonyl in the *trans*-position [42a]. New carbonyl peaks at 198 and 194 ppm and splitting of the peaks at 153, 140, 128, and 124 ppm corresponding to the signals of C(3,3'), C(4,4'), C(5,5'), and C(6,6') of the coordinated bpy showed that a new Re complex was formed. In addition, a new intense ^{13}C-signal at 167 ppm (No. 4, *Fig. 4b*) which split into a *d* (J(C,H) = 197 Hz) in absence of ^{1}H-decoupling suggested the generation of a formate species from $^{13}CO_2$. Isolation and characterization of the product showed that it was the ^{13}C-labelled complex $[Re(bpy)(^{13}CO)_3(H^{13}COO)]$ (**4**) in which formato is coordinated to the Re-atom. The peaks corresponding to the solvent (D$_7$)DMF and DMF (162.4 ppm for the C=O group, 35 and 30 ppm for the 2 CH_3 groups) and to the excess NTE (59 and 57 ppm) were unchanged after irradiation. New signals due to oxidation of the electron donor (NTE) were, however, detected after irradiation at 91.4 and between 50 and 65 ppm (No. 7, *Fig. 4b*). The corresponding products were identified as glycolaldehyde (=2-hydroxyethanol; at 91.4 and 62 ppm) and iminodiethanol by comparison with authentic samples *(Table 1)*. Iminodiethanol also gave peaks due to the formation of *N,N*-bis(2-hydroxyethyl)carbamic acid (zwitterionic form); their chemical shifts were in good agreement with those obtained in H_2O at pH 8–10 [43] *(Table 1)*.

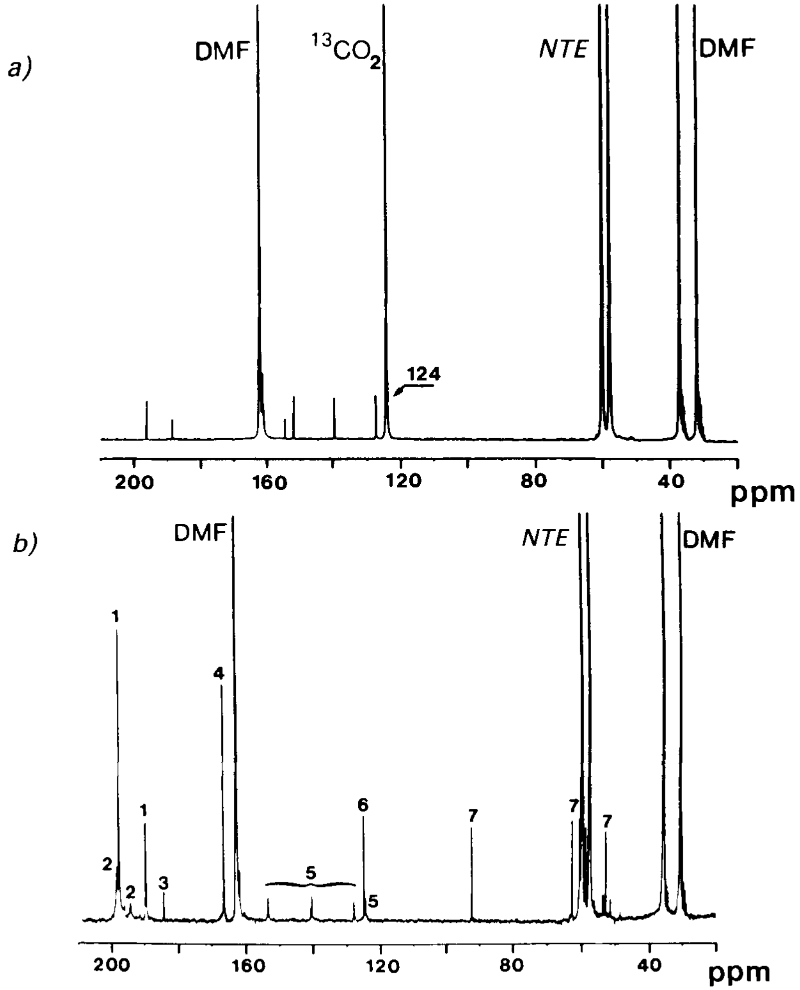

Fig. 4. *^{13}C-NMR spectra of a solution containing DMF/(D_7)DMF/NTE, $^{13}CO_2$ and [Re(bpy)(CO)$_3$Cl]* (**1**). a) In the dark; b) after 4 h visible-light irradiation; for labelling of the peaks, see text.

Table 1. *^{13}C-NMR Chemical Shifts of Iminodiethanol and its Carbamate in Organic and Aqueous Media*[a])

C-Atom	Chemical shifts [ppm]		
	aq. medium pH 8–10 [43]	DMF/NTE[b])	DMF/NTE medium[c])
$HN(CH_2\mathit{C}H_2OH)_2$	56.5–59.5	57.6	57.9
$HN(\mathit{C}H_2CH_2OH)_2$	49.2–49.8	50.4	52.1
$^-OO\mathit{C}{-}NH^+(CH_2CH_2OH)_2$	164.3	161.8[d])	162.4
$^-OOC{-}NH^+(\mathit{C}H_2CH_2OH)_2$	60.8	60.9[d])	59.7
$^-OOC{-}NH^+(CH_2\mathit{C}H_2OH)_2$	50	50.4[d])	

[a]) Shifts are given with respect to the DMF C=O signal at 162.4 ppm.

[b]) Authentic samples of iminodiethanol and glycolaldehyde were used in this experiment.

[c]) As in a photochemical experiment; values obtained from the irradiation experiment shown in *Fig. 4* containing [Re(bpy)(CO$_3$)Cl] (**1**), $^{13}CO_2$, and DMF/NTE 5:1 as solvent.

[d]) Same samples as in *Footnote b*, but kept under $^{13}CO_2$ in a sealed NMR tube.

When the same experiment was carried out in a sealed ^{13}C-NMR tube with **1** and $^{13}CO_2$ in presence of 25 equiv. of Et_4NCl, the peaks corresponding to the formato-rhenium complex were not observed. Only consumption of CO_2, carbonyl exchange, and CO formation took place.

The complexes present after irradiation of [Re(bpy) $(CO)_3Cl$] (**1**) in DMF/NTE under $^{13}CO_2$ and in the absence of Et_4NCl were extracted, separated by chromatography, and recrystallized (see *Exper. Part*) giving as the two main products [*fac*-Re(bpy) $(^{13}CO)_3Cl$] (**3**) and [*fac*-Re(bpy) $(^{13}CO)_3$ $(H^{13}COO)$] (**4**) in good yield.

The IR carbonyl stretching frequencies [44] for **3** and the unlabelled starting complex **1** are given in *Table 2*. A complete exchange of the 3 carbonyl ligands was observed. The isotope shift of 45 cm^{-1} is in good agreement with the calculated theoretical value. The ^{1}H-NMR spectrum *(Fig. 5a)* as well as the ^{13}C-NMR spectrum *(Fig 5b)* of **4** showed the presence of a coordinated formato group. The CH coupling constant of 197 Hz as well as the chemical shift (167.4 ppm) are in good agreement with the values reported for $[Cr(CO)_5(HCOO)]^-$ [42] $[W(CO)_5(HCOO)]^-$ [42] [45a], $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(HCOO)]$ [45b], $[Re(HCOO)(diphos)_2]$ [46], and $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(HCOO)]$ [47]. The weak peak observed at 7.8 ppm *(Fig. 5a)* corresponds to the presence of a small amount of unlabelled formato-rhenium complex.

Table 2. *IR Carbonyl Stretching Frequencies* [cm^{-1}] *for Complexes* **1** *and* **3**[a])

	[*fac*-Re(bpy)$(CO)_3Cl$] (**1**) before irradiation[b])	[*fac*-Re(bpy)$(^{13}CO)_3$ Cl] (**3**) after irradiation	Calculated values
$\tilde{\nu}_1$	2020	1975	1975
$\tilde{\nu}_2$	1920	1875	1877
$\tilde{\nu}_3$	1900	1855	1858

[a]) CH_2Cl_2 solution.

[b]) These values are in good agreement with those published [44].

[c]) Values calculated using $\tilde{\nu} = (2\pi)^{-1}(k/m)^{1/2}$.

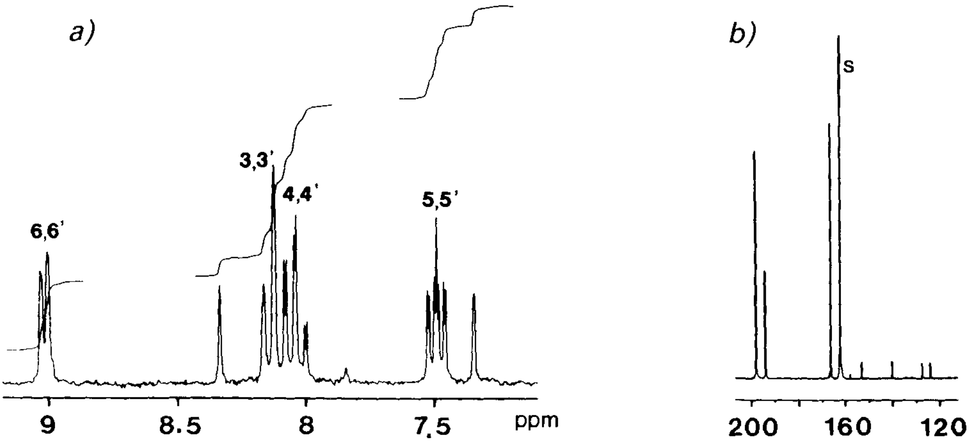

Fig. 5. *NMR spectra of [*fac*-Re(bpy)$(^{13}CO)_3(H^{13}COO)$]* (**4**). *a)* ^{1}H-NMR in CD_2Cl_2; *b)* ^{13}C-NMR in (D_7)DMF/DMF, S = solvent.

Table 3. *IR Stretching Frequencies* [cm^{-1}] *in the Carbonyl and Formate Regions for Complexes* **4** *and* **5**[a])

	[*fac*-Re(bpy)(CO)$_3$(HCOO)][b]) (**5**) before irradiation[b])	[*fac*-Re(bpy)(^{13}CO)$_3$(H^{13}COO)] (**4**) after irradiation	Calculated values
$\tilde{\nu}$(CO)	2020	1975	1975
$\tilde{\nu}$(CO)	1920	1875	1877
$\tilde{\nu}$(CO)	1880	1855	1838
$\tilde{\nu}_{asym}$(COO)	1630	1585	1594
$\tilde{\nu}_{sym}$(COO)	1280	1235	1251
$\tilde{\nu}$(HCO$_2$Re)	2790	2780	2782

[a]) In nujol mull.

[b]) Complex **5** was synthetized using [Re(bpy)(CO)$_3$(CH$_3$CN)]$^+$ BF$_4^-$ and Me$_4$N$^+$HCOO$^-$.

[c]) Values calculated using $\tilde{\nu} = (2\pi)^{-1} (k/m)^{1/2}$.

When the same experiment (with **1**, no Et$_4$NCl) was carried out under unlabelled CO$_2$, the complex [*fac*-Re(bpy) (CO)$_3$(HCOO)] (**5**) was isolated. In the ^{1}H-NMR, resonance at 7.8 ppm due to Re-OOC*H* was observed, besides the bpy signals. IR spectroscopy *(Table 3)* showed that the formato ligand was monodentate: $\tilde{\nu}_{asym}$(HCOORe) 1630 and $\tilde{\nu}_{sym}$(HCOORe) 1280 cm^{-1}. Reported stretching frequencies for a monodentate formato group are $\tilde{\nu}_{asym}$(COO) 1640–1600 and $\tilde{\nu}_{sym}$(COO) 1320–1290 cm^{-1}, whereas those for a bidentate formato are $\tilde{\nu}_{asym}$(COO) 1570–1550 and $\tilde{\nu}_{sym}$(COO) 1360–1340 cm^{-1} [1] [44–48]. Usually, the $\tilde{\nu}$(CH) vibration of a formato-metal is observed between 2700 and 2900 cm^{-1}; $\tilde{\nu}$(CH) of the formato ligand in complexes **4** and **5** were observed at 2780 and 2790 cm^{-1}, respectively. An isotope effect of 45 cm^{-1} (carbonyl) and 10 cm^{-1} (formato C–H bond) were obtained for the formato-rhenium complexes **4** and **5**. The absence of a $\tilde{\nu}$(ReCl) vibration around 280 cm^{-1} indicated that the formato had replaced the chloro ligand. The structure of the formato-rhenium complex has been confirmed by X-rays crystallography of complex **5** *(Fig. 6)* [49a].

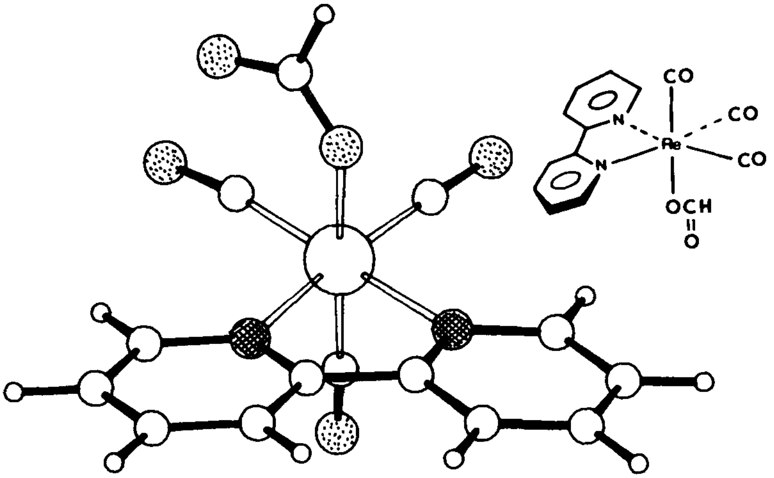

Fig. 6. *X-Ray crystal structure of [*fac*-Re(bpy)(CO)$_3$(HCOO)]* (**5**) [49a]

The carbonyl exchange of the starting complex **1** and the generation of the formato-rhenium complex **4** (or **5**) suggested that two active sites were present on the initial complex for the reduction of CO_2 either to CO or to the coordinated formato group. Formato production was suppressed in the presence of excess Cl^- ion resulting in linear formation of CO *vs.* time, whereas in the absence of excess Cl^- ions, non-linear formation of CO and accumulation of complex **5** in solution occured *(Fig. 2)*.

Carbonyl-Ligand Exchange. When [Re(bpy)$(CO)_3$Cl] (**1**) was kept under a ^{13}CO atmosphere in the dark for 50 h in the same medium as that used in the photochemical reaction, no CO exchange was observed by ^{13}C-NMR and IR spectroscopy. After 2 h irradiation ($\lambda > 400$ nm), exchange was complete. When the same complex was irradiated under ^{13}CO in the absence of NTE, no exchange occurred, excluding direct photolabilization of a CO ligand. This set of experiments suggested that the CO exchange proceeded *via* a photoproduced species which could be the reduced complex [Re(bpy)$(CO)_3$Cl]$^-$. Labilization of the CO ligands would represent one way to create, on the metal center, the vacant sites necessary for CO_2 fixation and reduction (see below). Unfortunately, because of experimental difficulties (different solubilities and different ^{13}C-NMR relaxation times for the two gases), we could not determine whether CO exchange was faster in the presence of $^{13}CO_2$ or of ^{13}CO, nor if the exchange proceeded during the reduction of CO_2 to CO or subsequently.

Studies of the Formato-rhenium Complexes (4 and 5). – *Photochemical Experiments.* In order to analyze the mechanism involved, it is important to know whether the formato-rhenium complex is an intermediate in the photoreduction of CO_2 to CO or whether it is formed from CO_2 *via* an independent pathway. Complex **5** was synthetized in good yield by two different methods. Irradiation of [Re(bpy)$(CO)_3$Cl] (**1**) in DMF/NTE in the presence of a large excess of $Me_4N^+HCOO^-$ followed by extraction with CH_2Cl_2, purification on a silica column, and recrystallization yielded compound **5** (*Eqn. 1*).

$$\mathbf{1} + Me_4N^+HCOO^- \xrightarrow[\text{DMF/NTE}]{h\nu} \underset{\mathbf{5}}{[Re(bpy)(CO)_3(HCOO)]} + Me_4NCl \qquad (1)$$

Abstraction of the chloro ligand from complex **1** using $AgBF_4$ in CH_3CN gave complex **6** (see also [50] [51]) (*Eqn. 2*) which by displacement of the coordinated solvent by formate ions also afforded complex **5** (*Eqn. 3*).

$$\mathbf{1} \xrightarrow[CH_3CN]{AgBF_4} \underset{\mathbf{6}}{[Re(bpy)(CO)_3(CH_3CN)]^+BF_4^-} + AgCl \qquad (2)$$

$$\mathbf{6} \xrightarrow{Me_4N^+HCOO^-} \underset{\mathbf{5}}{[Re(bpy)(CO)_3(HCOO)]} + Me_4NBF_4 \qquad (3)$$

The main results obtained when compound **5** was used as a photosensitizer are listed in *Table 4* and compared with those for complex **1**. In the presence of CO_2 and in the absence of other additives, **5** was only half as active in the photochemical reduction of CO_2 to CO as its chloro analogue **1** (*Exper. 1* and *3*). When Et_4NCl was added, the volume of CO produced was similar in both cases (*Exper. 2* and *4*). This suggests that the active species was the same in both experiments. This assumption was confirmed by studies of

Table 4. *Photochemical Generation of CO and H_2 Using [*fac-*Re(bpy)(CO)$_3$Cl]* (**1**) *or [*fac-*Re(bpy)(CO)$_3$(HCOO)]* (**5**) *as Photosensitizer*[a]

Exper.	Complex	Irradiation time [h]	Additive[b]	Volume of CO_2 [ml] (or pH)	Volume of CO produced [ml]	Volume of H_2 produced [ml]
1	**1**	2	–	160	9.7	–[e]
2	**1**	2	Cl^-	160	14.5	–[e]
3	**5**	2	–	160	4.1	–[e]
4	**5**	2	Cl^-	160	10.7	–[e]
5	**5**	2	$HCOO^-$	(8.4)[c]	0.1	1.5
6	**1**	4	$HCOO^-$	(11)[d]	0.1	1.5
7	**5**	1	Cl^-	(11)[d]	0.05	0.7
8	**5**	4	–	(11)[d]	0.01	0.5

[a] In DMF/NTE 5:1 (30 ml) containing 8.7×10^{-4} M of **1** or $8.5\ 10^{-4}$ M of **5**.

[b] Et_4NCl (2×10^{-4} M) or Me_4NHCOO (2.8×10^{-4} M).

[c] Experiment carried out in absence of CO_2; the formal pH was adjusted to the desired value using HCOOH.

[d] Experiment carried out in absence of CO_2, the formal pH was not adjusted.

[e] Less than 1 µl of H_2 produced (limit of detection).

the thermal displacement of the formato ligand by chloride anion *(vide infra)*. If the formato-rhenium complex were an intermediate in the photochemical reduction of CO_2 to CO, replacement of CO_2 by formate (which coordinates to the Re center under irradiation: see preparation of compound **5** above) should generate CO. Only traces of CO were in fact detected (*Exper. 5* and *6, Table 4*). When a large excess of free formate was used, a dark-orange species accumulated in the solution. This highly air-sensitive complex may be formulated as $[Re(bpy)(CO)_3(HCOO)]^-$ by analogy with the species generated electrochemically from **1** in the absence of CO_2 [22]; attempts to isolate it were unsuccessful. In the presence of formate, but in the absence of CO_2, some H_2 was obtained (*Exper. 5–8, Table 4*). It may result from the decomposition of the formato complex, yielding free CO_2 and a hydrido-metal complex which on protonation would give H_2, following the reverse reaction of the insertion reaction of CO_2 into a Re–H bond. The formation of hydridometal complexes by elimination of CO_2 from complexes of Mo, W [52], Os [53], and Re [46] [54] has been reported. In several cases, carbonyl-hydrido complexes were prepared by decomposition of formato-metal complexes [55]. Decomposition of free formate yielded CO_2 and H_2 but not CO in either heterogeneous [56] or homogeneous system [57]. In some cases, carbonyl-metal species were formed, but such reactions were not cyclic with respect to the metal [46] [58]. Recently, formic acid was found to reduce the excited states of several porphyrins with formation of CO_2 [59]. Only strong acids decomposed formic acid to CO and H_2O [60]. When $[Re(bpy)(CO)_3(HCOO)]$ (**5**) was irradiated in DMF/NTE under a ^{13}CO atmosphere, only the 3 carbonyl ligands underwent rapid exchange.

Quantitative Exchange of the Formato Ligand. Quantitative formato exchange occurred when compound **4** was dissolved in CH_2Cl_2 and treated with NEt_4Cl at room temperature in the dark giving the labelled chlorido-rhenium complex **3** and free $H^{13}COO$ (analyzed by ^{13}C-NMR and GC). Most literature reports on the reactivity of the formato ligand in transition-metal complexes [45–47] concern decarboxylation by heating, with formation of the corresponding hydrido-metal complex and free CO_2. This result confirms that no formato-rhenium complex can accumulate in solution in the presence of excess Cl^- ions, which appears to block the generation of a vacant site by labilization of the anion and thus inhibits reduction of CO_2 to formate.

Simultaneous Photogeneration of ^{13}CO *and [*fac-*Re(bpy)(*$^{13}CO)_3$*(H*^{13}COO*)]* (**4**). The simultaneous photogeneration of ^{13}CO and **4** was followed by GC and ^{13}C-NMR, respectively. The rates of both reactions were linear with respect to time *(Fig. 7)*. Complex **4** may be considered a minor product, the quantity of CO produced being *ca.* 150 times greater. After 4 h irradiation, only 7% of the starting chloro complex **1** was converted to the formato complex **4**. The formation of both products was simultaneous and not consecutive; both products accumulated, and a stationary concentration of the formato complex was not observed. Thus, the latter is not an intermediate in the photochemical formation of CO.

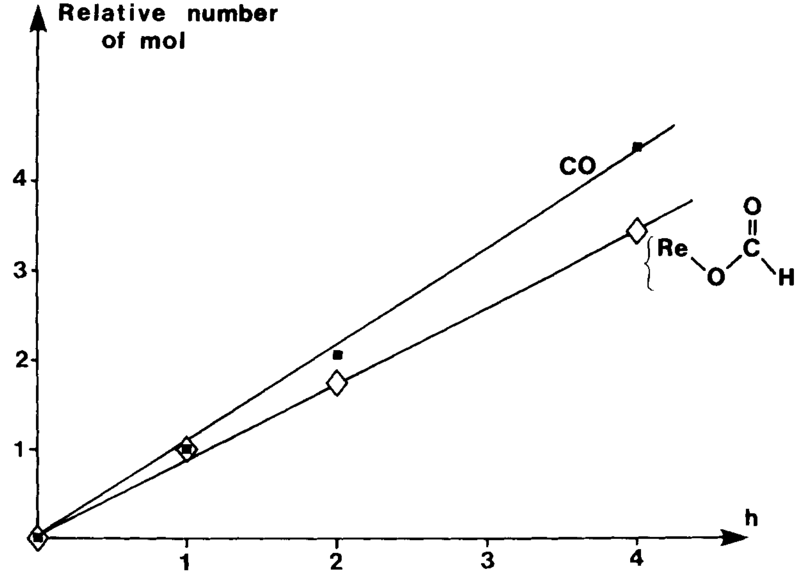

Fig. 7. *Photogeneration of* ^{13}CO (■) *and [Re(bpy)(*$^{13}CO)_3$*(H*^{13}COO*)]* (**4**; ◇) *as a function of time.* The number of mol formed after 1 h is arbitrarily fixed to 1 for each component; in reality, CO generation is 150 times more efficient.

*Preparation and Reactivity of the Bridged Hydride [*μ*H-{*fac-*Re(bpy)(CO)*$_3$*}*$_2$*]*$^+$*Cl*$^-$ (**7**). The formation of a formato ligand from CO_2 by insertion into a hydrido-metal bond is well documented [1]. The small amount of formato complex **5** produced here along with CO in the course of CO_2 photoreduction may result from CO_2 insertion into a hydridorhenium complex formed in the photochemical reaction as suggested previously [38]. Indeed CO_2 insertion into Re—H bonds has been shown to yield formato complexes [54]. CO_2 insertion into a hydrido-metal bond may involve precoordination of CO_2 to the metal centre [1]; in the present case, a vacant site might be created by labilization of a CO ligand or of a single pyridine group of the Re complex (see [61] [62]). The synthesis of the hydrido complex $[Re(bpy)(CO)_3H]$ and its reaction with CO_2 to give the formato complex **5** have been recently reported [63].

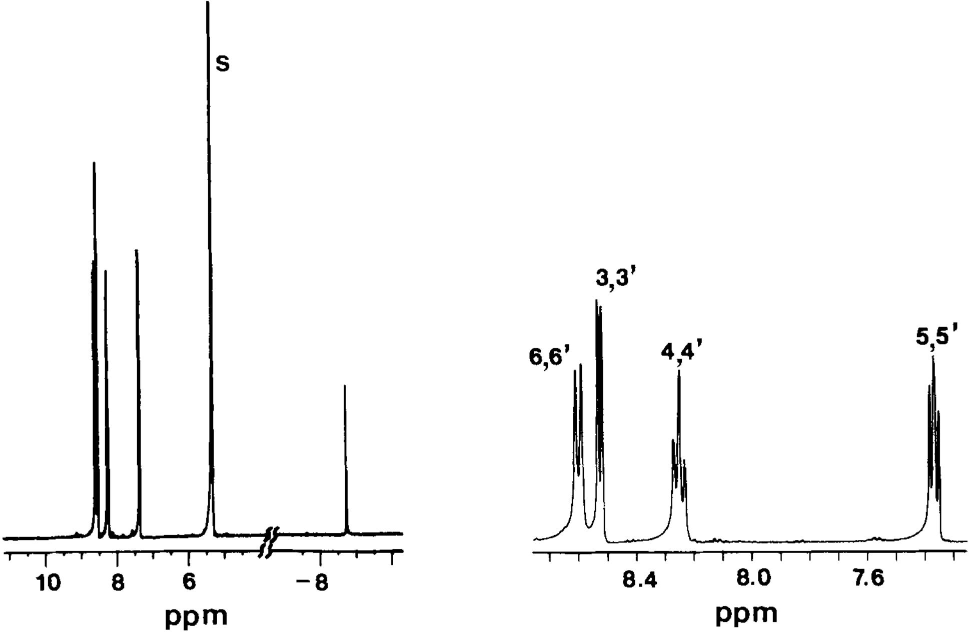

Fig. 8. *^{1}H-NMR spectrum of [μH-{*fac-*Re(bpy)(CO)$_3$}$_2$]$^+$Cl* (**7**) *in CD_2Cl_2* (=S)

A bridged hydrido complex [μH-{*fac*-Re(bpy)(CO)$_3$}$_2$]$^+$Cl$^-$ has been obtained in the present studies by reaction of $AgBF_4$ with [Re(bpy)(CO)$_3$Cl] (**1**; *Eqn. 4*), followed by addition of $NaBH_4$ as hydride source *(Eqn. 5)*.

$$\mathbf{1} \xrightarrow{AgBF_4} [Re(bpy)(CO)_3]^+ BF_4^- + AgCl \tag{4}$$

$$[Re(bpy)(CO)_3]^+ \xrightarrow{NaBH_4} 1/2[\mu H\text{-}\{fac\text{-}Re(bpy)(CO)_3\}_2]^+ \tag{5}$$

7

Fig. 8 shows the ^{1}H-NMR spectrum of this complex, isolated as the chloride of **7**, with a characteristic signal for the hydride at − 8.8 ppm. The nature of **7** has been unambiguously demonstrated by a crystal structure determination [49b].

No insertion was observed when complex **7** was kept under $^{13}CO_2$ in DMF in the dark nor when the same solution was irradiated (λ > 400 nm) during 60 h. Irradiation in the presence of NTE gave free CO, exchange of the 3 carbonyl ligands, and formato-rhenium complex **4**. After short periods of irradiation (15 min), the quantity of **4** obtained was no more than that found in an experiment carried out with [Re(bpy)(CO)$_3$Cl] (**1**) in the absence of excess Cl$^-$. Irradiation of complex **7** in DMF/NTE under $^{13}CO_2$ followed by extraction of the Re compounds and workup showed the absence of the starting **7** and the formation of a complicated mixture of Re complexes, one of them being **4** (identified by ^{13}C-NMR spectroscopy and TLC).

Electrocatalytic Reduction of CO_2 to CO. – If in the previous photochemical system light absorption serves to generate a rhenium-to-bipyridine charge-transfer excited state

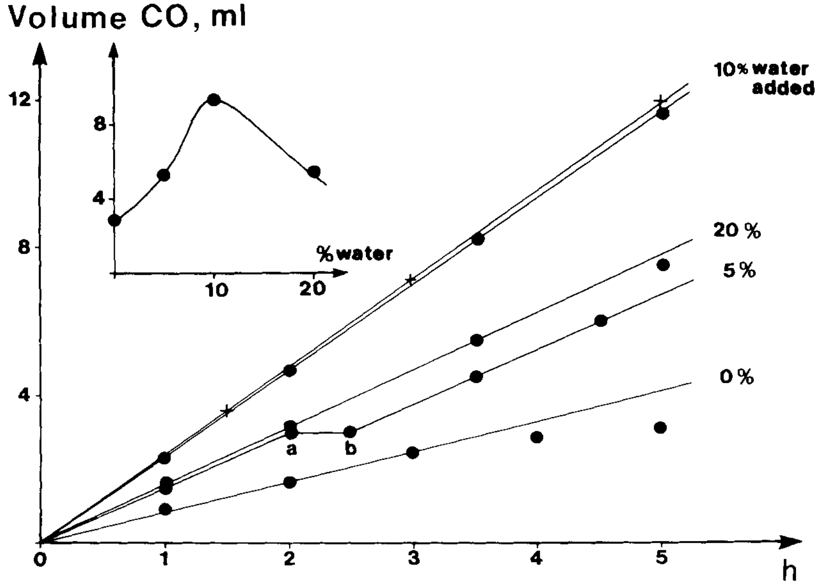

Fig. 9. *Volume of CO generated electrochemically as a function of percentage water added and time;* supporting electrolyte: Et_4NCl (●) or Bu_4NClO_4 (+). The electrolysis cell was flushed and kept under N_2 during 30 min (point a) and then N_2 was replaced by CO_2 (point b). Insert: volume of CO produced, after 4 h electrolysis, as a function of the amount of H_2O added.

which is reductively quenched by the tertiary amine to form $[Re(bpy)(CO)_3X]^-$ (see below), it should also be possible to set up an electrocatalytic system in which the starting Re complex would be reduced on an electrode. Recently, we showed that $[Re(bpy)(CO)_3Cl]$ (**1**) was a highly efficient (98% faradic yield) and selective electrocatalyst for the reduction of CO_2 to CO, at a potential of 1.25 V *vs.* NHE [22].

This system showed a marked dependence on the *amount of H_2O* present in the solution *(Fig. 9)*. When no H_2O was added to the medium, the electrogeneration of CO *vs.* time was non-linear. After 5 h electrolysis, all the residual H_2O had probably been consumed and a plateau was observed; at the same time a light-orange complex accumulated in the solution. Addition of traces of H_2O to this medium caused the disappearance of the reduced complex and an electroformation of CO which was linear with respect to time. This indicated that no degradation of the catalyst occurred even after electrolysis in the absence of H_2O. An optimum efficiency was obtained using approximately 10% of H_2O (see insert in *Fig. 9*). When 20% or more H_2O was present, the electrosystem was less efficient, and the formation of a green precipitate *(vide infra)* led to a decrease in catalytic activity. When Bu_4NClO_4 was used as supporting electrolyte, optimum efficiency was also observed using 10% of water. Perchlorate is able to bind to the Re center as shown by the isolation of a neutral species, the perchlorato-rhenium complex **9**, on reaction of the cation **8** (prepared from **1** *via* treatment of $[Re(bpy)(CO)_3][BF_4]$ (*Eqn. 5* with H_2O; see *Exper. Part*) with excess ClO_4^- *(Eqn. 6)*.

$$\underset{\mathbf{8}}{[Re(bpy)(CO)_3(H_2O)]^+ BF_4^-} \xrightarrow{ClO_4^-} \underset{\mathbf{9}}{[Re(bpy)(CO)_3(OClO_3)]} + BF_4^- \qquad (6)$$

Complex **9** was also isolated from the electrochemical mixture containing **1** as starting complex, Bu_4NClO_4, CO_2, and DMF. The same electrochemical activity was found starting with complex **9** and Et_4NCl as supporting electrolyte (10% of H_2O present), indicating that **1** and **9** had similar properties.

No accumulation of a reduced species was observed during electrolysis under CO_2. When the cell was flushed with N_2 after 2 h electrolysis (*Fig. 9*, domain a–b), a new orange species accumulated in solution; CO was no longer formed, and the electron consumption decreased drastically. When CO_2 was readmitted after 30 min under N_2, the orange colour disappeared instantaneously, restorting the yellow colour of complex **1**, and the electrocatalytic CO_2 reduction resumed with the same efficiency as before (*Fig. 9*, domain after point *b*). In the absence of CO_2, the reduction of **1** was quantitative, the ratio of electrons consumed to the concentration of complex present being 0.95. The resultant orange species was probably the active precursor in our system and may be formulated as $[Re(bpy)(CO)_3Cl]^-$.

When a similar electrolysis was carried out in the presence of 10% of H_2O but in the absence of CO_2, the same orange species accumulated in solution, but electrocatalysis was slow. H_2 was generated with a faradic yield of 85% (4.5 ml in 5 h), whereas only a small amount was obtained in absence of complex (< 0.1 ml in 5 h). In the presence of CO_2, reduction of H_2O was totally inhibited, showing that the reduced species $[Re(bpy)(CO)_3Cl]^-$ was less reactive towards H_2O than towards CO_2. The same behaviour was observed photochemically. Under optimal conditions (10% H_2O with NH_4Cl as supporting electrolyte), no formato-rhenium species could be detected (by TLC and ^1H-NMR spectroscopy) in the organometallic material extracted from the electrolysis medium. Thus, *[Re(bpy)(CO)$_3$Cl]* (**1**) *is a highly specific photo- or electrocatalyst for the reduction of CO_2 to CO.*

Table 5. *Electrochemical Generation of CO or H_2 by Reduction of CO_2 or H_2O in Presence of [Re(bpy)(CO)$_3$Cl]* (**1**) *as Catalyst*[a])

Electrolyte	Electrolysis time [h]	Volume of CO produced [ml][b])	Volume of H_2 produced [ml][b])	Number of coulomb consumed	Faradic yield [%][c])
Et_4NCl	1	2.4	–	20.5	
	2	4.7	–	40.6	94
	5	11.7	–	100.1	
NH_4PF_6[d])	1	–	4.6	38.5	
	2	–	8.8	74.1	96
	5	–	20.0	168.0	
Bu_4NPF_6	1	4.0	0.15	33.7	
	2	7.5	0.55	65.4	99
	6	23.0	1.7	200.6	
	8	27.9	2.2	244.1	

[a]) A CO_2-saturated solution (60 ml of DMF/10% H_2O) containing 25 mg of $[Re(bpy)(CO)_3Cl]$ (**1**; 9×10^{-4} M) and supporting electrolyte (0.1 M) was placed in a gas-tight electrolysis cell; working electrode was glassy carbon (*ca.* 10 cm^2); for other experimental details, see *Exper. Part.*

[b]) Measured by GC: detection limit < 1 µl for H_2 and 2–3 µl for CO.

[c]) Averaged over the total duration of the experiment; since the reduction product requires two electrons for its formation, 2 equiv. of electrons passed through the electrolysis cell to afford 1 mol of CO or H_2.

[d]) Results shown after substraction of the values obtained in the blank runs (*i.e.* absence of catalyst); a green product **10** precipitated during electrolysis.

When NH_4PF_6 was used as supporting electrolyte, no CO was detected, but near quantitative amounts of H_2 were formed *(Table 5)*. During electrolysis the solution turned green, and a green solid precipitated. Traces of the formato-rhenium complex **5** were detected (TLC) in the resulting solution. The air-stable green complex was subsequently isolated and characterized as the rhenium(0) dimer $[\{fac\text{-Re(bpy)(CO)}_3\}_2]$ (**10**). A recent study carried out in CH_3CN with Bu_4NPF_6 as supporting electrolyte agrees with this formulation [64]. Reaction of this complex with HCl gave H_2 and $[Re(bpy)(CO)_3Cl]$ (**1**; starting complex). No $[Re(bpy)(CO)_3(H\,^{13}COO)]$ was detected when the green rhenium dimer **10** was kept under $^{13}CO_2$ in a $(D_7)DMF/DMF$ medium. In the presence of the non-coordinating anion PF_6^-, labilization of the chloro ligand from the reduced complex provides a vacant site on the metal center *(Eqn. 7)*.

$$[Re(bpy)(CO)_3Cl]^- \longrightarrow [Re(bpy)(CO)_3] + Cl^- \qquad (7)$$

This may be followed by: *i)* the formation of a hydrido complex by addition of an electron and a proton *(Eqn. 8)*

$$[Re(bpy)(CO)_3] \xrightarrow{e,\,H^+} [Re(bpy)(CO)_3H] \qquad (8)$$

and further reaction of this complex with H_2O or NH_4^+ to yield H_2 and a Re(I) complex which may regenerate the starting complex **1** by reaction with Cl^- (*Eqn. 9*);

$$[Re(bpy)(CO)_3H] \xrightarrow{H^+,\,Cl^-} \underset{\mathbf{1}}{[Re(bpy)(CO)_3Cl]} + H_2 \qquad (9)$$

ii) dimerization of the reduced complex with formation of the green species *(Eqn. 10)*.

$$2\,[Re(bpy)(CO)_3] \longrightarrow \underset{(\mathbf{10})}{[\{fac\text{-}Re(bpy)(CO)_3\}_2]} \qquad (10)$$

These electrochemical studies clearly showed that the nature of the supporting electrolyte, in particular whether its anion was ligating (Cl^- or ClO_4^-) or not (PF_6^-), played a major role in the electrocatalytic processes observed (CO_2 reduction, H_2O reduction, dimerization). When the vacant site on the metal was blocked by excess anion, the only process observed was the electrochemical reduction of CO_2 to CO (98% faradic yield) in agreement with photochemical experiments. When anion dissociation was promoted (in the presence of PF_6^-), the major processes observed were dimerization and proton reduction, the latter process being in fact favoured by the presence of NH_4^+.

Studies on the Reaction Mechanism. – As pointed out in the preceding sections, the photochemical or electrochemical reduction of CO_2 to CO is catalytic with respect to the Re complex. In the photochemical system, the electron donor NTE is consumed, whereas in the electrochemical system, electrons provided by an electrode are consumed. Catalytic quantities of formate were not obtained in these systems. However, under certain conditions, formato complexes were isolated. The overall process for photogeneration of CO and formate is schematically represented in *Fig. 10*. It comprises a photochemical cycle in which a reduced species is generated and a dark cycle in which CO_2 is reduced to CO and formate.

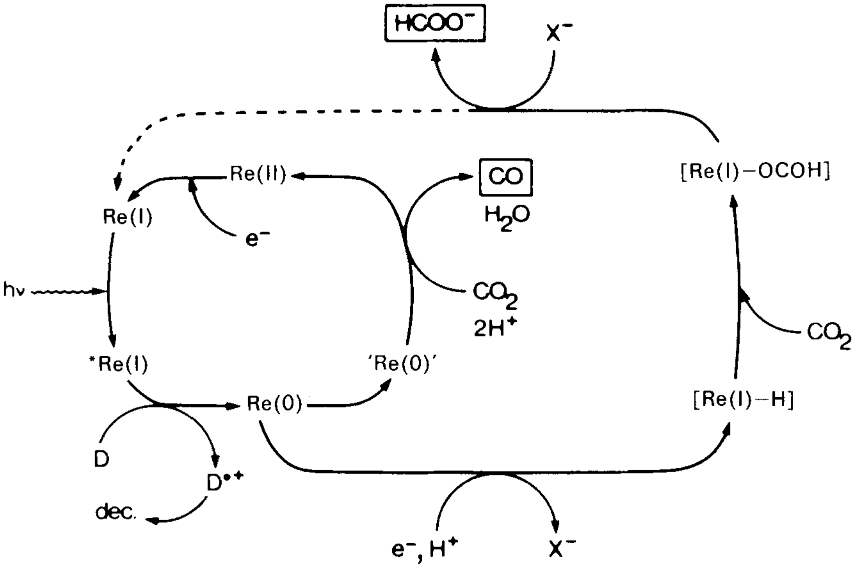

Fig. 10. *Schematic representation of the photochemical CO and $HCOO^-$ generation process by CO_2 reduction with the system [Re(bpy)(CO)$_3$X]/NTE/CO_2 in DMF.* The internal and external loops lead to CO and HCO_2^-, respectively; the ligands of the Re complex are omitted for clarity; Re(0) represents the reduced complex; 'Re(0)' represents the complex with a vacant site (see text).

Generation of the Reduced Species in the Photochemical System. Reductive quenching of the rhenium-to-bipyridine charge-transfer (MLCT) excited state, which has substantial triplet character [65], by NTE was indicated by luminescence studies. A *Stern-Volmer* plot of the emission intensity (λ_{em} = 610 nm) on addition of increasing concentrations

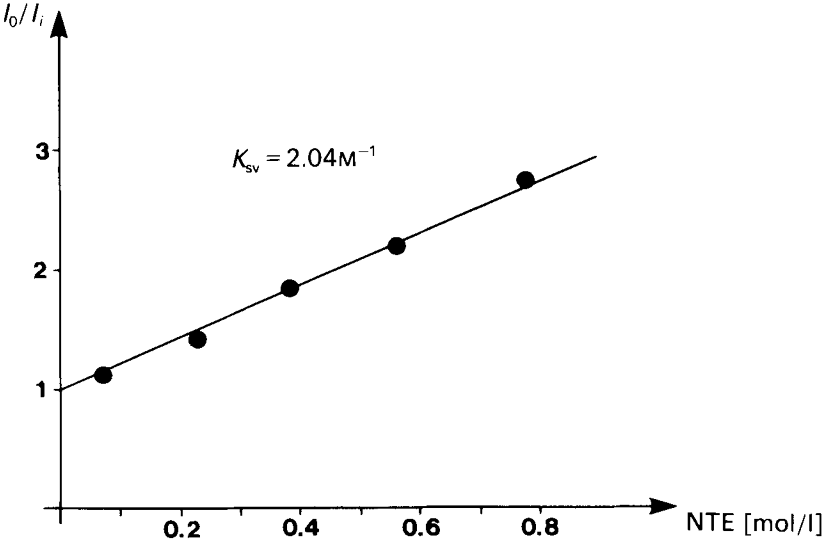

Fig. 11. Stern-Volmer *plot for the quenching of the luminescence of [Re(bpy)(CO)$_3$Br]* (**2**) *by NTE at 25° in DMF under Ar.* $K_{sv} = k_q\tau_o, k_q$ = quenching constant and τ_o = 60 ns for excited-state lifetime of the Re complex.

of NTE *(Fig. 11)* gave the rate constant for the quenching reaction *(Eqn. 11)* $k_q = 3.4 \times 10^7 \text{M}^{-1}\text{s}^{-1}$[4]) with X = Br.

$$\underset{\mathbf{2}^*\ (X = Br)}{[Re(bpy)(CO)_3X]^*} + NTE \xrightarrow{k_q} [Re(bpy)(CO)_3X]^- + NTE^{+\cdot} \qquad (11)$$

A similar value has been reported recently [41]. The excited state of the Re complex has an estimated reduction potential of at least 1.0 V *vs.* NHE[5]) and is thus thermodynamically capable of oxidizing NTE ($E°$ (NTE$^+$/NTE) = 0.82 V *vs.* NHE [66]). The quenching-rate constant was the same in the presence or absence of CO_2, indicating that there was no direct interaction between CO_2 and the photoexcited Re complex. The 19-electron product of a bipyridine-based reduction [50] [67], $[Re(bpy)(CO)_3X]^-$, never accumulated in the solution under standard conditions. However, electrochemically in the absence of CO_2 or photochemically under more basic conditions (*e.g.* in the presence of Et_3N or Me_4NOH), the reduced Re complex (orange species) was formed and reacted within seconds on introduction of CO_2. Unfortunately, attempts to isolate the reduced complex were not successful. One may assume that $[Re(bpy)(CO)_3X]^-$ obtained by a one-electron reduction is the active precursor in the two-electron reduction of CO_2 to CO *(Eqn. 12)*.

$$CO_2 + H_2O + 2e^- \longrightarrow CO + 2OH^- \qquad (12)$$

The $2OH^-$ ions generated are neutralized by $2H^+$ resulting from the oxidative decomposition of NTE [68] which delivers the 2 electrons.

Mechanism of Carbon-Monoxide Formation. A schematic representation of a possible mechanism is depicted in *Fig. 12.* In the presence of excess Cl^- ions, we may assume that the Re-Cl site is never vacant and no formato ligand is obtained in this case. Reductive quenching of the excited state of the Re complex by the tertiary amines gives an unstable 19-electron species in which a coordination site may become available by labilization of a CO group (see section on CO exchange above) or of a pyridine unit to give a sesqui-bipyridine ligand [61] [62]. Only the former of these two processes is represented in *Fig. 12.* The contribution of pyridine labilization may be related to the significantly lower efficiency of the $[Re(Br\text{-}phen)(CO)_3Br]$ complex in which the bpy ligand has been replaced by 5-bromophenanthroline [38]. The resulting 17-electron Re complex contains a vacant site available for the fixation and reduction of CO_2 initiated by formation of a metallocarboxylic complex *via* nucleophilic attack of the formally zero valent Re center on the electrophilic C center of the CO_2 molecule. The carboxylic group may be either *cis* or *trans* with respect to the chloro ligand. Several carboxylato-metal complexes of Ir [69] [70], Pt [71], Fe [72], and Re [73] [74] have been isolated, characterized, and their reactivity towards decarboxylation studied. Most are formed by direct attack of H_2O [69] [70] or NaOH [72] [73] on coordinated CO. A hydroxycarbonyl complex of Pt(II) is obtained on insertion of CO into a metal–hydroxo bond [71]. Decomposition of the carboxylato-rhenium intermediate by protonation would give H_2O and a (2,2′-bipyridine)tri-

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[4]) Quenching experiments were carried out under a CO_2 atmosphere. k_q has been calculated, assuming that the life-time of the excited state in DMF is 60 ns, as determined by Dr. *A. Harriman* (Royal Institution, London).

[5]) This value has been calculated, using $E°(Re(I/0)) = -1.15$ V *vs.* NHE for complex **2** and an excited-state energy estimated from the emission spectrum of 2.3 eV [50].

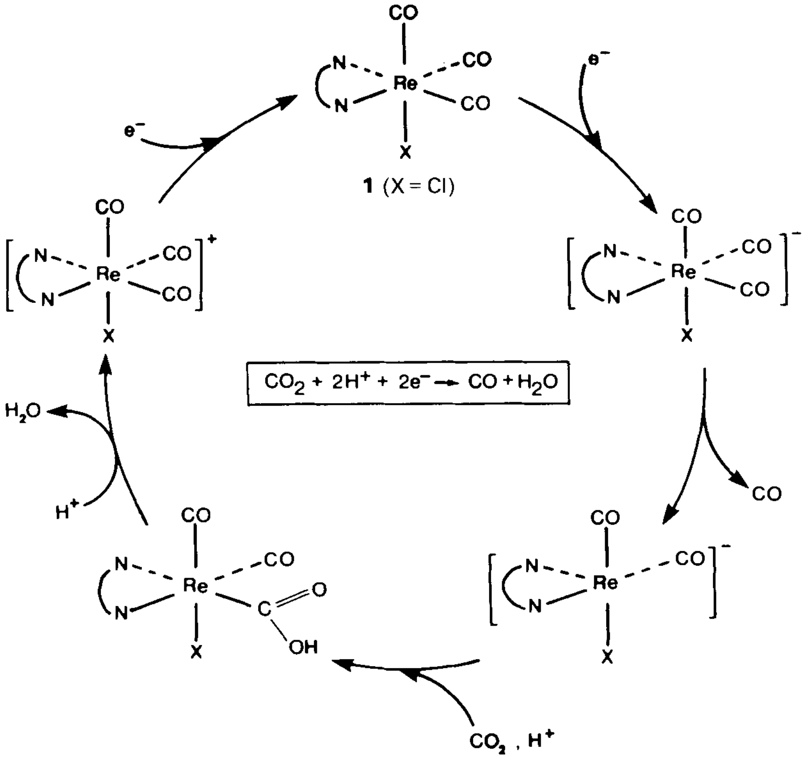

Fig. 12. *Schematic representation of a possible catalytic Re cycle for the reduction of CO_2 to CO, in the presence of excess ligating anion;* only the pathway in which the vacant site on Re is generated by loss of a CO ligand is represented; another pathway might involve labilization of a pyridine group (see text); since the exact steps at which electron and proton uptake occur are not known, the sequence of events indicated is only tentative. N⌒N represents the bpy ligand; X = coordinating anion.

carbonylchlororhenium(II) complex which by reduction regenerates the starting complex **1** *(Fig. 12)*. This second electron is globally provided by the oxidative decomposition of the donor NTE which yields 2 electrons overall [68].

The final O-atom acceptor in the reduction of CO_2 to CO is the proton in the present conditions. No labelled CO_3^{-2} or HCO_3^- was detected in the ^{13}C-NMR spectrum obtained after a photoreduction experiment using $^{13}CO_2$ *(Fig. 4b)*, although these species might be intermediates [63].

Light is used only to generate the reduced $[Re(bpy)(CO)_3X]^-$ complex *via* a reductive quenching pathway. This was confirmed by the fact that in the electrocatalytic system, 98% current efficiency was obtained for the production of CO. Thus, the mechanism of CO formation in both the photochemical and the electrochemical systems should be the same. Unfortunately, no direct evidence for the presence of $[Re(II)(bpy)(CO)_3Cl]^+$ was found in either case.

Mechanism of Formato-Complex Generation. In the absence of excess Cl^- ions, the labilization of Cl^- from the 19-electron complex formed by reductive quenching may provide a 17-electron species, which may pick up a second electron and a proton to give the hydrido complex [Re(bpy)(CO)$_3$H]. Insertion of CO$_2$ [63] would then yield the formato complex **5**. Quantitative displacement of the formato by a chloro ligand would regenerate the starting chloro-rhenium complex. Only non-catalytic amounts of formato complex were produced, and no free formate was detected although this might occur.

Conclusion. – The present work describes a homogeneous catalytic system which is *both* photochemically and electrochemically active for the reduction of CO$_2$ to CO with high efficiency and selectivity, giving a quantum yield of 14% and a faradic efficiency of 98%. A formato-rhenium complex was formed non-catalytically under certain conditions. The [Re(bpy)(CO)$_3$Cl]$^-$ complex obtained by a reductive quenching pathway in the photochemical system or by a direct one-electron reduction in the electrochemical system seems to be the precursor in this CO$_2$ activation system. Further investigations are directed towards the exploitation of the unique properties of these and related metal complexes in order to develop new photo- and electrocatalysts for the reduction of CO$_2$, in particular beyond CO and formate.

Experimental Part

1. *General.* For photochemical experiments, samples were irradiated using a 250-W halogen lamp (slide projector) fitted with a 400-nm-cut-off filter *(Schott GG 420)*, having 0% transmission at 395 nm. The light beam was concentrated by a converging lens and its width was adjusted so that the entire solution was irradiated. The gases produced photochemically were analysed by gas chromatography (GC), at r.t., with a *Varian-Aerograph-700* apparatus equipped with a 5 Å molecular sieve column (13X mesh 42/60) from *Applied Science Laboratories Inc.*, using methane as the carrier gas. When labelled CO$_2$ was used, the gas was analysed by GC/MS with a *R10/10 Ribermag* GC/MS apparatus. Measurements of emission intensity were performed at r.t. and in the absence of air, using a *Perkin-Elmer model MPF-3*, spectrofluorimeter equipped with a 150-W Xe lamp. For quantum yield determinations, a 1000-W Hg lamp in combination with a *Choffel*, model *GM 250*, monochromator was used as a monochromatic (385 ± 20 nm) light source. Incident-light intensity was determined with an aq. soln. of KCr(NH$_3$)$_2$(NCS)$_4$ (*Reinecke*'s salt) as a chemical actinometer [75] and was typically $5.77 \cdot 10^{-5}$ einstein $\cdot$ sec^{-1} $\cdot$ cm^{-2}. Cyclic voltammetry: *PRT-20-2X-Tacussel* potentiostat, *GSA-TP2-Tacussel* pilot scanner, *ADT-P3-Tacussel* current potential converter, and *IF-3802-Ifelec-XY* recorder. Continuous electrolysis experiments: *PRT-100-1X-Tacussel* potentiostat and *IG5-LN Tacussel* current integrator. Electrochemical measurements were determined with the saturated calomel electrode (SCE) as reference, at r.t., and are uncorrected for junction potential effects. UV/VIS spectra: *Cary-219* spectrophotometer, quartz cell mounted on a *Schlenk* tube; molar extinction coefficients were obtained from absorbance measurements on at least two different concentrations of complex. IR spectra: *Perkin-Elmer-597* spectrometer, CH$_2$Cl$_2$ solution, in nujol mull, or KBr disk. ^{1}H- and ^{13}C-NMR spectra: 200-MHz-*Bruker-SY-200* spectrometer at 50.3 MHz (^{13}C) or 200.1 MHz (^{1}H) or 400-MHz-*Bruker-SY-400* spectrometer at 100.654 MHz (^{13}C) or 400.135 MHz (^{1}H) with the solvent as an internal standard.

2. *Photochemical CO and H$_2$ Generation Experiments.* The nature and concentration of the various components used in each experiment are listed in *Table 4*. Compounds dissolved in 30 ml of soln. were placed in a round-bottomed *Schlenk* tube (*ca.* 60 ml volume). This was vacuum degassed, and a volumetrically measured quantity of CO$_2$ (gas purity 99.8%) was dissolved in the reaction mixture. Blank experiments were carried out under vacuum, in the absence of CO$_2$. After irradiation, the internal pressure was brought to atmosphere pressure by cooling the flask in dry ice and by introducing NaOH (1M) into the reaction vessel. The gas present in the flask was sampled by syringe and analysed by GC.

3. *Electrochemical CO and H$_2$ Generation Experiments.* The Re complex as well as the supporting electrolyte was dissolved in 60 ml of DMF (compositions are given in *Table 5*). The soln. was degassed by purging with CO$_2$ (99.8% purity) for 30 min in a gas-tight electrolysis cell (three-necked, round-bottomed flask equipped with an oil valve). A glassy carbon working electrode (*ca.* 10 cm^2) was used in all experiments. The connection to the working electrode was made by a Pt wire inserted through the lateral part of the flask. The total volume occupied by the

gases in the electrolysis cell was 130 ml. The counter electrode, isolated from the previous soln. by a sintered glass frit, was a Pt wire (*ca.* 50 cm in length). All the solns. were electrolysed at 1.25 V *vs.* NHE, at *ca.* 25°. The gases were analysed by GC.

4. *Materials.* Dirhenium decacarbonyl (*Aldrich*) and nitrilotriethanol (NTE; *Fluka*) were used as received. DMF (*Normapur*) was dried over KOH, distilled under Ar and stored in the dark under Ar. Additives or supporting electrolytes Et_4NCl, Bu_4NBr, NH_4PF_6, and Bu_4NPF_6 were recrystallized twice from $EtOH/H_2O$. [*fac*-Re(bpy)$(CO)_3$X] (X = Br or Cl; **1** and **2**, resp.) were prepared according to a literature procedure [44]. [Re(bpy)$(CO)_3(CH_3CN)]^+$ $[BF_4]^-$ (**6**) was synthesised using $AgBF_4$ rather than $AgCF_3SO_3$ [50] or $AgClO_4$ [51] to remove Cl^- from **1**.

5. fac-*(2,2'-Bipyridine)tri((*^{13}*C)carbonyl)chlororhenium(I)* ([*fac*-Re(bpy)(^{13}CO)$_3$Cl]; **3**). $^{13}CO_2$ (120 ml; 90.5% labelled) was added to a soln. of 146 mg (0.316 mmol) of **1** in 60 ml of DMF/NTE 5:1 (*v/v*) and the mixture was irradiated for 6 h. Then, 120 ml of distilled H_2O were added to the mixture which was extracted using 3 × 100 ml of CH_2Cl_2; the latter was washed 5 times with 100 ml of H_2O in order to eliminate excess NTE. After drying the org. phase with Na_2SO_4, the solvent was removed under vacuum, leaving a yellow powder which showed (TLC) the presence of 2 major products (complexes **3** and **4**). Separation by chromatography on a silica column using AcOEt/MeOH 4:1 gave 120 mg (81%) of **3**, after recrystallisation in CH_2Cl_2/Hexane 1:1. UV (CH_3CN): 367 (3024). IR: *Table 2*. ^{1}H-NMR (CD_2Cl_2, 200.1 MHz): 7.58 (*td*, H–C(5,5')); 8.12 (*td*, H–C(4,4')); 8.25 (*d*, H–C(3,3')); 9.04 (*d*, H–C(6,6')). ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 123.0, 123.0, 127.2, 138.9, 153.3, 155.7, 189.4 (CO), 197.0 (2CO). Anal. calc. for **3**: C 34.22, H 1.72, N 6.03; found: C 34.01, H 1.58, N 5.91.

6. fac-*(2,2'-Bipyridine) tri((*^{13}*C)carbonyl) ((*^{13}*C)formiato)rhenium (I)* ([*fac*-Re(bpy)(^{13}CO)$_3$(H^{13}COO)]; **4**). During the previous workup, a second more polar complex was separated by chromatography. Recrystallisation from CH_3CN/hexane 1:1 gave 23 mg (8%) of **4**. UV (CH_3CN): 362 (3424). IR: *Table 3*. ^{1}H-NMR (CD_2Cl_2, 200.1 MHz); 7.44 (*td*, H–C(5,5')); 7.85 (*d*, *J*(HC=O) = 197, HCOO); 8.05 (*td*, H–C(4,4')); 8.14 (*d*, H–C(3,3')); 9.02 (*d*, H–C(6,6')). ^{13}C-NMR ((D$_7$)DMF, 50.3 MHz): 124.2, 127.3, 140.2, 153.3, 155.9, 167.4 (HC=O), 193.5 (CO), 197.7 (2CO); the undecoupled ^{13}C-NMR gave a *d* for the formato ligand (*J* (C,H) = 197). Anal. calc. for **4**: C 36.20, H 1.89, N 5.89; found: C 36.03, H 1.82, N 5.46.

7. fac-*Aqua (2,2'-bipyridine) tricarbonylrhenium (I) Tetrafluoroborate* ([*fac*-Re(bpy)$(CO)_3(H_2O)]^+$ BF_4^-; **8**). In a typical preparation, 500 mg (1.08 mmol) of **1** and 210 mg (1.08 mmol) of $AgBF_4$ were heated at 40° in 190 ml of freshly distilled (from Na) dimethoxyethylene glycol under Ar for 15 h. To the cooled mixture, 50 ml of degassed H_2O were added. After stirring for 15 min, the suspension was filtered through *Celite* and the yellow soln. was concentrated (to *ca.* 70 ml) by slow evaporation. Addition of a few drops of a sat. aq. soln. of $NaBF_4$ at 0° caused crystallisation of the product. After filtration and washing with Et_2O, 550 mg (96%) of pure **8** were obtained (R_f 0.6 in BuOH/i-PrOH/H_2O 5:1:1 on silica). UV (CH_3CN): 335 (sh, 3976). IR (KBr): 2030, 1940, 1905 (carbonyls). ^{1}H-NMR ((D$_7$)DMF, 200.1 MHz): 6.60 (br. *s*, H_2O); 7.87 (*td*, H–C(5,5')); 8.42 (*td*, H–C(4,4')); 8.82 (*d*, H–C(3,3')); 9.15 (*d*, H–C(6,6')). ^{13}C-NMR ((D$_7$)DMF, 50.3 MHz): 125.0, 128.7, 141.5, 154.5, 157.2. Anal. calc. for **8**: C 29.39, H 1.89, N 5.27; found: C 29.14, H 1.83, N 5.11.

8. fac-*(2,2'-Bipyridine)tricarbonylformiatorhenium (I)* [*fac*-Re(bpy)$(CO)_3$(HCOO)]; **5**). *Photochemical Synthesis.* In a typical preparation, 150 mg (0.325 mmol) of **1** and 630 mg (5.29 mmol, 16 equiv.) of Me_4N^+ $HCOO^-$ were dissolved in 60 ml of DMF/NTE 5:1 and irradiated for 4 h. Then, 60 ml of H_2O were added, and the complexes were extracted into CH_2Cl_2 (3 × 50 ml). The org. phase was washed 3 times with 150 ml of H_2O, dried over Na_2SO_4, and evaporated to dryness under vacuum. Workup on a silica column using AcOEt/MeOH 85:15 gave 50 mg (33%) of **1** and 100 mg (65%) of **5**. UV (CH_2Cl_2): 381 (3470). IR: *Table 3*. ^{1}H-NMR (CD_2Cl_2, 200.1 MHz): 7.57 (*td*, H–C(5,5')); 7.93 (*s*, HCOO); 8.13 (*td*, H–C(4,4')); 8.22 (*d*, H–C(3,3')); 9.10 (*d*, H–C(6,6')). ^{13}C-NMR ($CDCl_3$, 100.654 MHz): 122.7, 127.0, 139.2, 154.0, 155.8, 166.2. Anal. calc. for **5**: C 35.65, H 1.91, N 5.94; found: C 35.68, H 2.20, N 5.44.

Thermal Synthesis. A soln. of 50 mg (0.094 mmol) of **8** and 110 mg (1 mmol, *ca.* 10 equiv.) of Me_4N^+ $HCOO^-$ were dissolved in 30 ml of EtOH/H_2O 2:1 and heated at reflux under Ar for 1 h. Extraction into CH_2Cl_2, purification on a silica column, and recrystallisation from CH_3CN/hexane gave 35 mg (79%) of **5**.

9. fac-*(2,2'-Bipyridine)tricarbonylperchloratorhenium (I)* ([*fac*-Re(bpy)$(CO)_3(OClO_3)$]; **9**). Dropwise addition of 1 ml of aq. $LiClO_4$ (200 mg, 20 equiv.) to 50 mg (0.094 mmol) of **8** in 90 ml of EtOH/H_2O 2:1 caused the precipitation of a yellow complex. Recrystallisation from CH_2Cl_2/hexane 1:1 yielded 38 mg (83%) of **9**. UV (CH_3CN): 345 (sh, 1984). IR (KBr): 2030, 1940, 1910 (carbonyls). ^{1}H-NMR (CD_2Cl_2, 200.1 MHz): 7.66 (*td*, H–C(5,5')); 8.20 (*td*, H–C(4,4')); 8.28 (*d*, H–C(3,3')); 9.08 (*d*, H–C(6,6')). ^{13}C-NMR ((D$_7$)DMF, 100.654 MHz): 124.8, 128.6, 141.7, 154.0, 155.9. Anal. calc. for **9**. C 29.67, H 1.52, N 5.33; found: C 29.10, H 1.77, N 5.22.

10. *µ-Hydrido-bis[*fac*-(2,2′-bipyridine)tricarbonylrhenium(I)] Chloride* ($[\mu H\text{-}\{fac\text{-}Re(bpy)(CO)_3\}_2]^+ Cl^-$; **7**). To a soln. of 200 mg (0.43 mmol) of **1** in 30 ml of Ar-degassed $MeOH/H_2O$ 4:1, 84 mg (0.43 mmol, 1 equiv.) of $AgBF_4$ were added. After heating under reflux for 1 h, the yellow suspension was filtered through *Celite*. To the yellow soln., 82 mg (2.17 mmol, 5 equiv.) of $NaBH_4$ were added under Ar. During stirring (15 h) at r.t., the soln. turned deep orange and then deep green. Then, 60 ml of H_2O were added and the complexes extracted into CH_2Cl_2 (3 × 65 ml). The org. phase was washed 3 times with 150 ml of H_2O, dried over Na_2SO_4, and evaporated. Chromatography on an alumina column using AcOEt/MeOH 4:1 gave a green-yellow fraction (most polar fraction, R_f 0.35). After evaporation, the complex was extracted with acetone and recrystallised from acetone/pentane giving 34 mg (18%) of **7** as green monocrystals (crystal structure, see [49b]). The Cl^- must have been picked up during workup. The same complex was also obtained in similar yield by treating directly **1** with $NaBH_4$ in $EtOH/H_2O$. UV (CH_2Cl_2): 375 (5700). IR (KBr): 2030 (Re-H), 2018, 1940, 1908, 1872 (carbonyls). ^1H-NMR (CD_2Cl_2, 400 MHz): − 8.76 (*s*, hydrido); 7.37 (*t*, H−C(5,5′)); 8.25 (*t*, H−C(4,4′)); 8.52 (*d*, H−C(3,3′)); 8.60 (*d*, H−C(6,6′)). ^{13}C-NMR ((D_7)DMF, 100.654 MHz): 124.7, 128.6, 140.7, 153.3, 155.3. Anal. calc. for C 35.1, H 1.91, N 6.30; found: C 36.24, H 2.05, N 6.46.

11. *Bis[*fac*-(2,2′-bipyridine)tricarbonylrhenium(I)]* ($[fac\text{-}Re(bpy)(CO)_3]_2$; **10**) was synthesized electrochemically in the presence of NH_4PF_6 (see *Exper. Part*, above). The green product was separated by filtration on a sintered glass funnel and washed with Et_2O until the filtrate was colourless. After drying under high vacuum, the product (impure by NMR) was treated with CH_2Cl_2 until the org. soln. was colourless: 38 mg (41%) of **10** were obtained starting with 100 mg of **1**. UV (DMF): 380 (sh, 4812), 446 (4280), 589 (4447), 772 (6579). IR (KBr): 2020, 1940, 1860 (carbonyls). ^1H-NMR ((D_7)DMF, 200 MHz): 7.25 (*t*, H−C(5,5′)); 7.85 (*t*, H−C(4,4′)); 8.13 (*d*, H−C(3,3′)); 8.45 (*d*, H−C(6,6′)). ^{13}C-NMR ((D_7)DMF, 100.65 MHz): 123.8, 124.1, 132.4, 150.3, 153.8. Anal. calc. for **10**: C 36.60, H 1.88, N 6.57; found: C 36.31, H 1.70, N 6.30.

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