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Photochemical reduction of carbon dioxide to formate catalyzed by 2,2′-bipyridine- or 1,10-phenanthroline-ruthenium(II) complexes *

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Abstract

Formate is photogenerated by visible light irradiation of systems containing either the $[Ru(bpy)_3]^{2+}$ $2Cl^-$ (bpy = 2,2′-bipyridine) complex alone, or a mixture of two ruthenium(II) complexes. The former system produces the active catalytic species by photolabilisation of a bpy ligand. The latter system consists of a mixture of $[Ru(L)_3]^{2+}$ (L = bpy derivatives or 1,10-phenanthroline (phen)) as photosensitizer and *cis*-$[Ru(bpy)_2(CO)(X)]^{n+}$ (X = Cl, H, $n = 1$ or X = CO, $n = 2$) or *cis*-$Ru(bpy)(CO)_2(Cl)_2$ as homogeneous catalysts which mediate carbon dioxide reduction to formate. The efficiency of formate production is dependent on the presence of water and excess ligand but is independent of CO_2 pressure. A maximum quantum yield of 15% was measured for the mixed $[Ru(bpy)_3]^{2+}$/*cis*-$[Ru(bpy)_2(CO)(H)]^+$ system. The photochemical process consumed triethanolamine as electron donor and was studied by ^{13}C NMR using labelled carbon dioxide in order to determine the origin of the formate. This CO_2 photoreduction system consists of two catalytic cycles: a photochemical one for the ruthenium-trischelate and a dark-reaction pathway for the ruthenium bis- or mono-bpy complex. The reaction involves reductive quenching of the $[Ru(L)_3]^{2+}$ excited state by the tertiary amine to the corresponding ruthenium(I) complex which reduces the carbon dioxide activation catalyst to Ru^I and further to Ru^0.

Introduction

Artificial photochemical systems for the generation of reduced carbon compounds from carbon dioxide have been extensively studied in the past decade [1]

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* Dedicated to Professor Günther Wilke on the occasion of his 65th birthday.

using different methods (electrochemistry, photoelectrochemistry and photochemistry). However few efficient catalytic systems are known at present. Electrochemical and photoelectrochemical systems, involving the direct reduction of carbon dioxide at an electrode or in presence of soluble transition-metal catalysts have been reviewed [1c,2].

Purely photochemical systems are classified as either heterogeneous, making use of semi-conductor suspensions [3], or as homogeneous employing aqueous solutions of metal ions [4], organic dyes [5], or transition-metal complexes. Examples of transition-metal catalysts for the photo- or electro-reduction of CO_2 comprise: (i) macrocyclic cobalt and nickel complexes [6]; (ii) soluble phthalocyanines [7] or porphyrin complexes [8]; (iii) metal clusters [9]; (iv) rhodium [10] and palladium [11] phosphine complexes; (v) polyimine complexes of cobalt [12], rhenium [13,14], rhodium and iridium [15], ruthenium [15a,16–18] and osmium [1c,19]. The use of this latter group of complexes has recently attracted much attention. We first achieved the photochemical reduction of carbon dioxide with a system containing $[Ru(bpy)_3]^{2+}$ (as photosensitizer) and $[Co(bpy)_3]^{2+}$ or Co^{II} ions (as electron mediator and as H_2O and CO_2 reduction catalysts) and generated catalytic amounts of both H_2 (6.5% quantum yield) and CO (1.2% conversion) [12]. In a second system based on the single *fac*-$[Re(bpy)(CO)_3Cl]$ complex (acting both as photosensitizer and as carbon dioxide activation catalyst in its reduced state), high yields of CO (14% quantum yield) and traces of *fac*-$[Re(bpy)(CO)_3(HCOO)]$ have been produced photochemically [13].

We report here our results and mechanistic investigations of a third type of system which we described earlier in preliminary form [16]. It is based on the ruthenium(II) complexes (**1**–**12**) among which the $[RuL_3]^{2+}$ species (L = bpy, phen or derivatives thereof) act as photosensitizers and the ruthenium-bisbipyridine species as both electron mediators and homogeneous carbon dioxide reduction catalysts. The ruthenium(II)-bisbpy complex was either generated in situ by photolabilisation of a bpy from the starting $[Ru(bpy)_3]^{2+}$ or added as starting material. High yields of formate and traces of CO were obtained by photoreduction of carbon dioxide with visible light. A related mechanistic study of such a system has been reported recently [17].

$[Ru(bpy)_3]^{2+}\ 2Cl^-$ (**1**)
cis-$[Ru(bpy)_2(CO)(Cl)]^+\ PF_6^-$ (**2**)
cis-$[Ru(bpy)_2(CO)(H)]^+\ PF_6^-$ (**3**)
cis-$[Ru(bpy)_2(py)(Cl)]^+\ Cl^-$ (**4**)
cis-$[Ru(bpy)_2(CO)_2]^{2+}\ 2PF_6^-$ (**5**)
cis-$[Ru(bpy)_2(CH_3CN)_2]^{2+}\ 2PF_6^-$ (**6**)

cis-$[Ru(bpy)_2(DMF)_2]^{2+}\ 2PF_6^-$ (**7**)
cis-$Ru(bpy)_2Cl_2$ (**8**)
cis-$Ru(bpy)(CO)_2(Cl)_2$ (**9**)
$[Ru(phen)_3]^{2+}\ 2Cl^-$ (**10**)
$[Ru(bpy\text{-}R_2)_3]^{2+}\ 2Cl^-$ (**11**)
$[Ru(bpy\text{-}R_4)_3]^{2+}\ 2Cl^-$ (**12**)
$(R = CH_3)$

Visible-light CO_2 photoreduction experiments

Our studies were carried with two different active solutions. The first contained at the start only the ruthenium(II) complex $[Ru(bpy)_3]^{2+}$, both as photosensitizer and as CO_2 reduction catalyst precursor. The solvent was either organic DMF/DMF-d_7/TEOA (3/1/1) or an aquo-organic mixture DMF/DMF-d_7/TEOA/

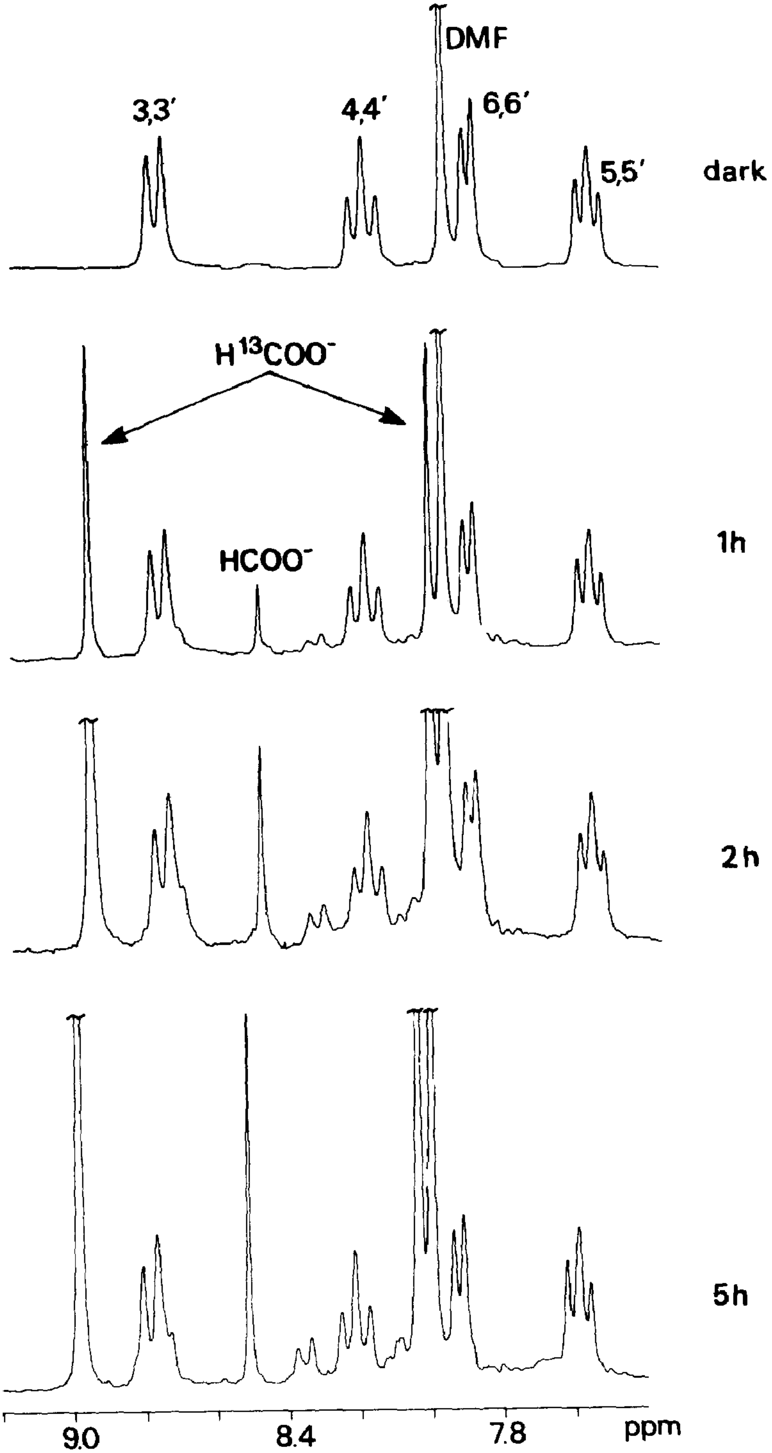

Fig. 1. ^{1}H NMR spectra (9.2 to 7.4 ppm) of a solution containing DMF-d_7/TEOA/H_2O (3/1/1), $^{13}CO_2$ and $[Ru(bpy)_3]^{2+}$, in the dark and after 1, 2 and 5 h irradiation with visible light (250 W non focused halogen lamp).

H_2O (3/1/1/1), containing 1 mmol of labelled carbon dioxide in a sealed 10 mm NMR tube (DMF = dimethylformamide; DMF-d_7 perdeuteriated-dimethylformamide; TEOA = triethanolamine). The second contained two starting ruthenium(II) complexes: $[Ru(bpy)_3]^{2+}$ or $[Ru(phen)_3]^{2+}$ and a ruthenium bis- or mono-bipyridine species in the same conditions as in the previous case. Irradiation of both solutions with visible light ($\lambda > 400$ nm) catalytically produced formate and traces of CO and H_2. Comparing to authentic samples, ^{13}C NMR studies did not reveal other reduction products such as formaldehyde, methanol or coupling products like oxalate. The conversion of carbon dioxide into formate was followed by ^{13}C NMR spectroscopy [16] which showed the disappearance of the $^{13}CO_2$ signal (δ 125 ppm) and the simultaneous increase of the formate resonance, as irradiation was continued (δ 167.4 ppm, J(CH) 187 Hz). The ^1H NMR spectra also agreed with these results (Fig. 1) giving a singlet at 8.52 ppm for $HCOO^-$ and a doublet (J(CH) 187 Hz) for $H^{13}COO^-$. The electron donor (TEOA) was consumed in the process. Oxidation products were identified as glycolaldehyde and diethanolamine by comparison with the ^{13}C NMR spectrum of authentic samples. *N,N*-Bis(2-hydroxyethyl)carbamic acid (zwitterionic form) was formed by reaction of diethanolamine with carbon dioxide [13] giving the appropriate spectral peaks. A series of control experiments were performed to confirm that the presence of each component was essential. Both systems showed no activity when either the light, $^{13}CO_2$, the ruthenium complex or the tertiary amine were omitted. To confirm the catalytic nature of the processes, to improve empirically the efficiency and selectivity, and to investigate the mechanism, various studies have been carried out on the influence of some of the system's parameters as well as on the nature of the catalytic species.

Formate generation by the system using $[Ru(bpy)_3]^{2+}$ alone

Using 1.1×10^{-2} molar solutions of $[Ru(bpy)_3]^{2+}$, formate production remained linear over 6 h irradiation with $^{13}CO_2$ added every 1 or 2 h so as to maintain its initial concentration (i.e. constant $^{13}CO_2$ pressure). This showed that the catalytic system was stable on this time scale (540 μmol of $H^{13}CO_2^-$ were generated after 6 h irradiation, giving 40 turnovers on the starting $[Ru(bpy)_3]^{2+}$ complex, Fig. 2 [16]). When constant $^{13}CO_2$ pressure was not maintained, formate generation was not linear versus time, indicating that carbon dioxide might play an important role in the rate limiting step of this process; in addition some decomposition of the starting ruthenium(II) complex may occur (700 μmol of $H^{13}CO_2^-$ were produced after 24 h photolysis giving 54 turnovers, Fig. 2 [16]).

The effect of solvent composition, $[Ru(bpy)_3]^{2+}$ concentration, $^{13}CO_2$ pressure, addition of water and excess bpy ligand on the efficiency of formate photogeneration are listed in Table 1.

As previously observed [12a,13] the DMF/TEOA solvent mixture gave the most efficient photochemical reduction of carbon dioxide. Triethylamine/DMF or TEOA/acetonitrile mixtures were less active.

At very low concentrations of $[Ru(bpy)_3]^{2+}$, the photogeneration of formate decreased by one order of magnitude (compare expt. 2, 5 and 6 in Table 1). Under these conditions, photosubstitution of the tris(2,2-bipyridine)-ruthenium(II) complex, probably depletes the concentration of the photosensitizer, thus giving a low efficiency for the photoreduction of carbon dioxide to formate [20–24].

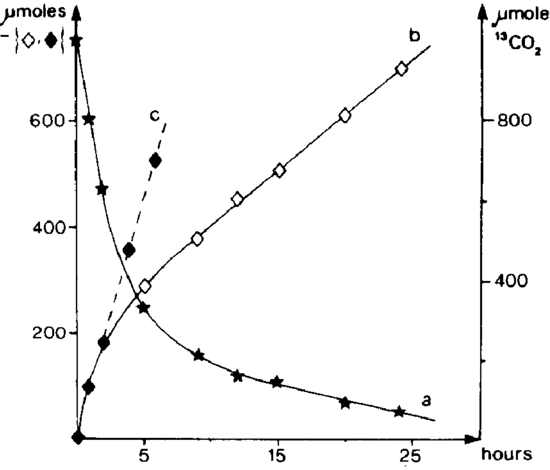

Fig. 2. Photogeneration of $H^{13}COO^-$ (curves b and c) by photoreduction of $^{13}CO_2$ (curve a) as a function of time. At constant volume (curve b) and at constant pressure (curve c) of $^{13}CO_2$; the solution contains $[Ru(bpy)_3]^{2+}$, DMF/DMF-d_7/TEOA/H_2O (3/1/1/1).

Almost no $^{13}CO_2$ pressure effects were observed between 0.5 and 2 atm, under short time photolysis (exp. 5, 12, 13). At a $^{13}CO_2$ pressure of 7 atm (expt. 14), formate generation decreased by a factor of three. This could be due to a pH effect

Table 1

Generation of $H^{13}COO^-$ by photoreduction of $^{13}CO_2$ in presence of different concentrations of $[Ru(bpy)_3]^{2+}$, H_2O, $^{13}CO_2$ and excess bipyridine [a]

Experiment	$[Ru(bpy)_3]^{2+}$ conc. (*M*)	% water added	$^{13}CO_2$ in mmol [b] (pressure in atm)	$H^{13}CO_2^-$ [c] μmol	Turnover number [d]
1 [e]	1.1×10^{-2}	15	1 (1.8)	–	–
2	1.1×10^{-2}	15	1 (1.8)	186	19
3 [f]	1.1×10^{-2}	15	1 (1.8)	374	38
4 [f]	1.1×10^{-2}	15	1 (1.8)	422	43
5	1.9×10^{-3}	15	1 (1.8)	118	69
6	7.5×10^{-5}	15	1 (1.8)	12	185
7	1.9×10^{-3}	0	1 (1.8)	<1	–
8	1.9×10^{-3}	5	1 (1.8)	66	40
9	1.9×10^{-3}	30	1 (1.8)	97	58
10	1.9×10^{-3}	40	1 (1.8)	68	41
11	1.9×10^{-3}	50	1 (1.8)	37	22
12	1.9×10^{-3}	15	0.3 (0.5)	98	59
13	1.9×10^{-3}	15	0.5 (1)	103	62
14	1.9×10^{-3}	15	3.9 (7.2)	36	22

[a] 1.8 ml of a degassed mixture of DMF $(0.9-x)$ + DMF-d_7 (0.3) + TEOA (0.3) + H_2O (x) ml containing $Ru(bpy)_3Cl_2 \cdot 6\,H_2O$ were irradiated during 2 h in a sealed 10 mm NMR tube with a non-focused 250 W halogen lamp (slide projection) fitted with a 400 nm cut-off filter under non thermostated conditions (~ 35 °). [b] Total volume of the sealed tube 1.3×10^{-2} l. Pressure was calculated using $p=(n\times0.082\times293)/(1.3\times10^{-2})$, n = number of $^{13}CO_2$ mol at 20 °C. [c] Formate concentration was determined by ^{13}C NMR spectroscopy (± 10%). [d] Obtained by dividing the number of mol of $H^{13}CO_2^-$ produced in 2 h by the number of mol of the Ru complex, multiplied by a factor two for the photosensitizer (2 electrons are involved during the reduction). [e] Blank experiment carried out without $^{13}CO_2$. [f] 25 and 100 equiv. excess 2,2′-bipyridine were added respectively in expt. 3 and 4.

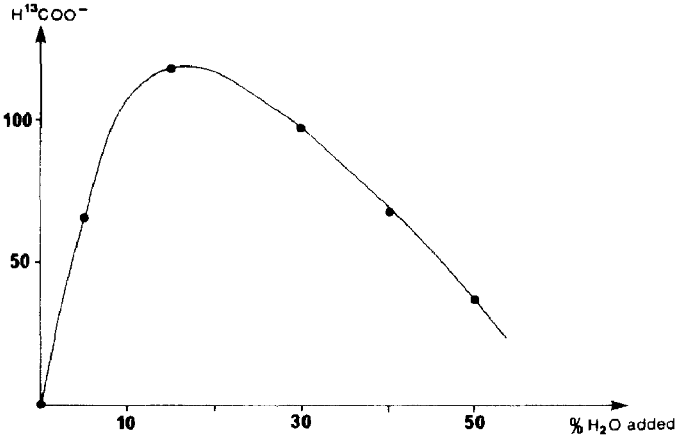

Fig. 3. Amount of $H^{13}COO^-$ produced from $^{13}CO_2$ after 2 h catalysis, as a function of the amount of H_2O added; the solution contains $[Ru(bpy)_3]^{2+}$, DMF/DMF-d_7/TEOA/H_2O (3/1/1/1).

(3.9 mmol $^{13}CO_2$ and 2.2 mmol TEOA were used), slowing down the rate of the excited state quenching reaction.

Effect of the addition of water. The presence of water * enhanced the reaction with an optimum concentration around 0.015 *M* (~ 15%, Fig. 3). In the absence of water no formate was detected (expt. 7), while in the presence of a large excess (50%), formate production was three times less efficient. With large amounts of water significantly more hydrogen and carbon monoxide were produced: in conditions of expt. 11, 0.28 ml CO and 3.1 ml H_2 were produced while only < 0.01 ml CO and 0.29 ml H_2 were formed in conditions of expt. 2 **. Water might play a role in the photolabilisation of a bpy ligand from $[Ru(bpy)_3]^{2+}$ [20–24] to generate the active catalytic species.

Addition of bipyridine ligand. A marked increase in formate generation was observed on addition of 25 equiv. (exp. 3) and 100 equiv. (expt. 4) of bipyridine. This could be due, at least in part, to a favourable shift in the proportions of tris-bpy complex (photosensitizer) and bis-bpy complex (carbon dioxide reduction catalyst) present in solution as the reaction proceeds.

During the course of the photolysis, the colour of the solution changed from orange to red, while the aromatic region of the proton NMR spectra showed (Fig. 1) the formation of small new peaks (the area of the doublet at 8.36 ppm being ca 15% of the triplet at 8.22 ppm of the starting $[Ru(bpy)_3]^{2+}$ complex), indicating the formation of new species. These observations, along with previous studies on the substitutional photolabilisation of ruthenium(II)-trischelate complexes in water [20], dimethylformamide [21], dichloromethane [22] and various other solvents [23] led us to suppose that a Ru^{II} bis-bpy species was produced by photolabilisation of a bpy ligand from the starting Ru^{II} tris-bpy complex, and that this new complex was the active catalytic species. Since, due to ligand rigidity, Ru^{II} tris-phen complexes are

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* It should be noted that there will always be some water present (< 1%) in the system, coming from either triethanolamine or water of recrystallization of the complexes.

** These experiments were performed in a Schlenk flask using 5 ml of solution under one atmosphere of carbon dioxide (see experimental section).

more photostable than their bpy analogues [23], the loss of photocatalytic activity when $[Ru(phen)_3]^{2+}$ was used in place of $[Ru(bpy)_3]^{2+}$ (expt. 34 in Table 3) is in agreement with this hypothesis. The photochemical quantum yields for the labilisation of a bpy ligand are low in dimethylformamide or water (of the order of 0.001 [21]), but they are markedly enhanced in less polar solvents like dichloromethane ($0.06 < \phi < 0.10$ [22,23]). The small quantum yield in dimethylformamide is ap-

Table 2

Generation of $H^{13}COO^-$ by photoreduction of $^{13}CO_2$ in the presence of both $[Ru(bpy)_3]^{2+}$ (**1**), and bis(2,2'-bipyridine)ruthenium(II) complex (**2**–**9**) [a]

Experiment	Ruthenium(II) complex	Irradiation times (h) /% H_2O added	$^{13}HCOO^-$ (μmol)	Turnover number [b]
15 [c]	$[Ru(bpy)_2(CO)(Cl)]^+$	2/15	<1	–
16	**1**/$[Ru(bpy)_2(CO)(Cl)]^+$	1/15	67	42
		2/15	133	83
17	**1**/$[Ru(bpy)_2(CO)(Cl)]^+$	1/0	322	200
		2/0	525	326
18 [d]	$[Ru(bpy)_2(CO)(H)]^+$	24/15	39	3
19 [d]	$[Ru(bpy)_2(CO)(H)]^+$	21/0	<1	–
20 [a]	**1**/$[Ru(bpy)_2(CO)(H)]^+$	1/15	73	42
21 [e]	**1**/$[Ru(bpy)_2(CO)(H)]^+$	1/0	335	200
		2/0	537	322
22	**1**/$[Ru(bpy)_2(CO)(H)]^+$ + 100 equiv. bpy	1/0	256	153
		2/0	410	245
23	$[Ru(bpy)_2(py)(Cl)]^+$	2/0	<1	–
24 [e]	**1**/$[Ru(bpy)_2(py)(Cl)]^+$	1/15	27	16
		2/15	40	24
25 [e]	**1**/$[Ru(bpy)_2(py)(Cl)]^+$	1/0	135	80
		2/0	200	120
26	$[Ru(bpy)_2(CO)_2]^{2+}$	2/0	<1	–
27 [e]	**1**/$[Ru(bpy)_2(CO)_2]^{2+}$	2/15	51	30
		4/15	64	38
28 [e]	**1**/$[Ru(bpy)_2(CO)_2]^{2+}$	1/0	142	85
		2/0	178	107
29	**1**/$Ru(bpy)_2Cl_2$	1/0	50	30
		2/0	85	51
30	**1**/$[Ru(bpy)_2(CH_3CN)_2]^{2+}$	1/0	73	43
		2/0	152	91
31	**1**/$[Ru(bpy)_2(DMF)_2]^{2+}$	1/0	110	66
		2/0	220	132
32 [e]	**1**/$Ru(bpy)(CO)_2(Cl)_2$	1/15	38	23
		2/15	79	47
33 [e]	**1**/$Ru(bpy)(CO)_2(Cl)_2$	1/0	258	156
		2/0	425	255

[a] The same experimental and analytical conditions as in Table 1 were used: 1.8 ml (15% water) or 1.5 ml (0% water added) solution of DMF/DMF-d_7/TEOA and/or H_2O (3/1/1 or 3/1/1/1) contained 3.3 μmol of $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 3.3 μmol of complexes **2** to **9** and 1 mmol of $^{13}CO_2$. [b] Calculated for complex **1**; for complexes **2**–**9** these numbers should be divided by two, because two mol of $[Ru(bpy)_3]^{2+}$ are required for one catalytic cycle but only one mole of complexes **2**–**9** is needed (see mechanistic section). [c] The solution was yellow before irradiation and turned deep-red during photolysis. [d] 1.12×10^{-2} *M* of $[Ru(bpy)_2(CO)(H)]PF_6$ were used. [e] A deep-blue insoluble precipitate was formed during the photolysis while the solution remained orange-red.

Table 3

Generation of $H^{13}COO^-$ by photoreduction of $^{13}CO_2$ in the presence of a $[RuL_3]^{2+}$ complex as photosensitizer and a *cis*-bis(2,2′-bipyridine)ruthenium(II) complex as catalysts [a]

Experiment	Photosensitizer/CO_2 activation catalyst	%H_2O added	$H^{13}CO_2^-$ (μmol)	Turnover [b]
34	$Ru(phen)_3^{2+}$	0 or 15	<1	–
35	$Ru(phen)_3^{2+}/[Ru(bpy)_2(CO)(Cl)]^+$	15	57	34
36	$Ru(phen)_3^{2+}/[Ru(bpy)_2(CO)(Cl)]^+$	0	121	72
37	$Ru(phen)_3^{2+}/[Ru(bpy)_2(CO)(H)]^+$	15	62	37
38	$Ru(phen)_3^{2+}/[Ru(bpy)_2(CO)(H)]^+$	0	142	86
39	$Ru(phen)_3^{2+}/[Ru(bpy)_2(CO)_2]^{2+}$	15	43	25
40	$Ru(phen)_3^{2+}/[Ru(bpy)_2(CO)_2]^{2+}$	0	98	57
41	$Ru(bpy\text{-}R_2)_3^{2+}$	0	<1	–
42	$Ru(bpy\text{-}R_2)_3^{2+}/[Ru(bpy)_2(CO)(H)]^+$	0	115	70
43	$Ru(bpy\text{-}R_4)_3^{2+}$	0	<1	–
44	$Ru(bpy\text{-}R_2)_3^{2+}/[Ru(bpy)_2(CO)(H)]^+$	0	82	50

[a] Same experimental and analytical conditions as in Tables 1 and 2 using 3.3 μmol of $[RuL_3]^{2+}$ and 3.3 μmol of $[Ru(bpy)_2(CO)(X)]^{n+}$ ($X = Cl$, H, $n = 1$; $X = CO$, $n = 2$). 1 mmol of $^{13}CO_2$. Solutions were irradiated during 3 h. [b] Calculated for the photosensitizer, see note [b] in Table 2.

parently sufficient to generate the catalytically active species in our system, the reduction of carbon dioxide to formate being by far the most efficient process (quantum yield > 0.1). Unfortunately attempts to isolate the active species failed for reasons due to its low concentration and to the complexity of the solvent mixture used (DMF, H_2O, TEOA and oxidation products of TEOA). In order to increase the efficiency and to gather more mechanistic information, we have studied the photoreduction of carbon dioxide to formate in the presence of ruthenium(II)bis-bpy or mono-bpy complexes, photosensitized by $[Ru(bpy)_3]^{2+}$ (see Table 2) and $[Ru(phen)_3]^{2+}$ (see Table 3) complexes.

Formate generation by the mixed system using tris-bipyridineruthenium and bis-bpy- or mono-bpy-ruthenium complexes

In the absence of the photosensitizer (under the conditions described in Table 2) none of the ruthenium bis-bpy or mono-bpy complexes **2**–**9** produced any formate. However, long term photolysis of complex **3** led to decomposition and formation of small amounts of formate; at the end of the experiment the hydride signal (δ −11.3 ppm) in the proton NMR spectrum was no longer observable.

The highest efficiency was observed when a CO group was coordinated to either a Ru^{II}bis-bpy **2**–**3** or a Ru(II) mono-bpy **9** unit. The addition of water decreased the efficiency of the reaction, whereas $[Ru(bpy)_3]^{2+}$ itself did not generate formate in the absence of water (see above and expt. 7 in Table 1 and Fig. 3). In the presence of 15% water the efficiency decreased by a factor of three and gave less stable photosystems (compare Fig. 4 and 5). Under these conditions water might competitively react with the reduced complex to form carbon monoxide and hydrogen: e.g. in the presence of 15% water, the mixed system containing $[Ru(bpy)_3]^{2+}$ and *cis*-$[Ru(bpy)_2(CO)(H)]^+$, produced 2.9 ml H_2 and 0.5 ml CO (in conditions of expt. 20), while in the absence of added water the same mixture gave only 0.48 ml H_2 and 0.03 ml CO (in conditions of exp. 21). Using $[Ru(bpy)_3]^{2+}$ as photosensitizer and

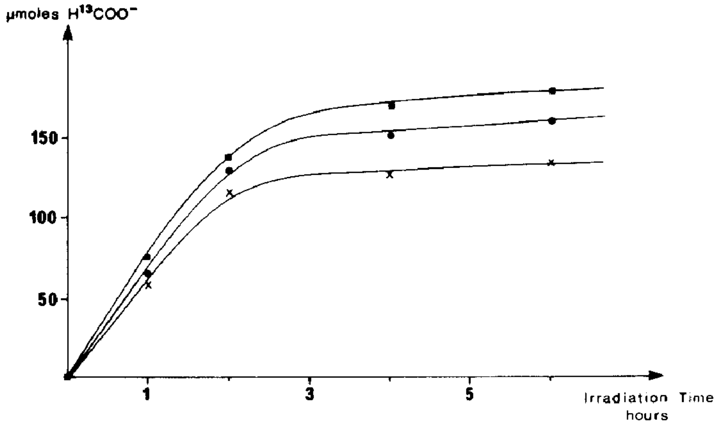

Fig. 4. Photogeneration of $H^{13}COO^-$ from $^{13}CO_2$ as a function of time, using $[Ru(bpy)_3]^{2+}$ alone (X), $[Ru(bpy)_3]^{2+}$ + *cis*-$[Ru(bpy)_2(CO)(H)]^+$ (■), $[Ru(bpy)_3]^{2+}$ + *cis*-$[Ru(bpy)_2(CO)(Cl)]^+$ (●), in a DMF/DMF-d_7/TEOA/H_2O (3/1/1/1) solution.

cis-$[Ru(bpy)_2(CO)(H)]^+$ as catalyst, almost 70% of the carbon dioxide present in the system was converted to formate giving respectively 410 and 205 turnovers for the ruthenium complexes, after three hours irradiation with visible light (Fig. 5).

Kinetic studies showed formate generation to be non-linear with respect to time. This might be attributed to (i) the consumption of CO_2 (closed systems containing 1 mmol CO_2) and (ii) some decomposition of the photosensitizer and/or of the active catalytic species.

When carbonyl or pyridine complexes were used, a deep blue precipitate formed (note [e] in Table 2), probably due to cluster formation [25]. Most of this insoluble material disappeared when a 100 fold excess of bpy was added to the reaction mixture (expt. 22). A slow decrease in catalytic activity was observed under these conditions. *cis*-$[Ru(bpy)_2(CO)_2]^{2+}$ (5) has also been used in the photochemical [17a]

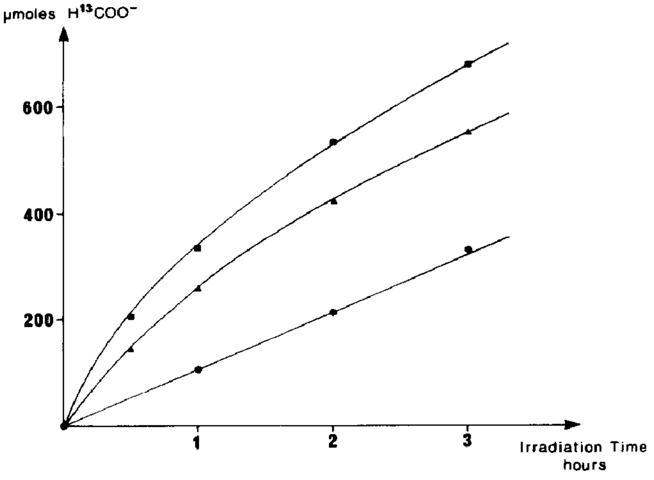

Fig. 5. Photogeneration of $H^{13}COO^-$ from $^{13}CO_2$ as a function of time, using $[Ru(bpy)_3]^{2+}$ (as photosensitizer), and *cis*-$[Ru(bpy)_2(DMF)_2]^{2+}$ (●), *cis*-$Ru(bpy)(CO)_2(Cl)_2$ (▲), or *cis*-$[Ru(bpy)_2(CO)(Cl)]^+$ (■) (as carbon dioxide reduction catalysts) in a DMF/DMF-d_7/TEOA (3/1/1) solution.

and electrochemical [17b] reduction of carbon dioxide to formate. The chloro complex **2**, the synthetic precursor of complex **3**, showed almost the same efficiency as the hydrido species **3** (expt. 17 and 21).

In order to gain more information on the chemical stability of the system, the infrared and proton NMR spectra of the irradiated solutions were recorded. The carbonyl band of *cis*-$[Ru(bpy)_2(CO)(Cl)]^+$ at $\nu(CO)$ 1970 cm^{-1} [27] was still present after 3 h irradiation (expt. 17). However the characteristic hydride NMR resonance at δ -11.3 ppm [27] and the carbonyl vibration at $\nu(CO)$ 1930 cm^{-1} of *cis*-$[Ru(bpy)_2(CO)(H)]^+$ had disappeared after 3 h irradiation (expt. 21). Furthermore, a new $\nu(CO)$ band was observed at $\nu(CO)$ 1980 cm^{-1}, a value very close to that of the chloro complex, possibly indicating that the hydride had photochemically reacted with a proton source to give molecular hydrogen [26]. A solvent molecule (DMF) might coordinate to the ruthenium forming a new species, such as a *cis*-$[Ru(bpy)_2(CO)(DMF)]^{2+}$ complex.

These results, and others obtained under similar conditions (no hydride signal was observed in any of the catalytic systems studied) have important mechanistic implications and suggest that a hydride species is not needed for the reduction of carbon dioxide to formate. Similar results have also been obtained recently [17]. Replacing a carbonyl ligand by a coordinated pyridine led to a decrease in efficiency by a factor of two (expt. 24, 25).

cis-Bpy complexes having two coordinated solvent molecules (complexes **6** and **7**) or two coordinated chloride anions (complex **8**) also gave catalytic reduction of carbon dioxide to formate (expt. 29–31). A high efficiency was obtained using the bis-DMF complex 7, despite its strong deep red colour (λ 499 nm; ε 6500 l mol^{-1} cm^{-1}) which causes an important filter effect. This result is important, because the complex 7 could be generated in situ in the single complex system, by photolabilisation of bpy and coordination of two DMF solvent molecules.

An efficiency comparable to that of complexes **2** and **3** was obtained using the red *cis*-$Ru(bpy)(CO)_2(Cl)_2$ complex **9** (expt. 32, 33, Fig. 5). No *cis/trans* isomerisation of this complex was observed by UV-VIS and IR spectroscopy, after 3 h irradiation under the standard catalytic conditions ($\nu(CO)$ 1970 and 2030 cm^{-1}; λ_{max} 510 nm [28]).

Effect of the photosensitizer

Different photosensitizers $[Ru(L)_3]^{2+}$ with L = phen, 4,4′-dimethyl-2,2′-bipyridine (bpy-R_2) and 4,4′,5,5′-tetramethyl-2,2′-bipyridine (bpy-R_4) were used in order to investigate the influence of variations in excited state lifetime, redox potential of ground and excited states, and complex stability. None of the photosensitizers tested produced any detectable amount of formate when photolysis was conducted in absence of an active Ru-bis-bpy species (expt. 34, 41, 43 in Table 3). In the presence of complex **3** three photosensitizers gave approximatively the same activity producing 71 μmol (exp. 38), 57 μmol (expt. 42), 41 μmol (expt. 44) $H^{13}COO^-$ per hour. No correlation was found between the excited-state life-time and the efficiency of the process: $[Ru(L)_3]^{2+*}$ L bpy, τ_0 0.78 μs; L bpy-R_2, τ_0 0.33; L bpy-R_4, τ_0 0.77; L phen, τ_0 0.81 [12a].

The reactive ruthenium(I) form of the photosensitizer may be obtained by reductive quenching of the excited state by triethanolamine. All three photosensitizers in their reduced form are powerful enough reducing agents to reduce the carbon dioxide activation catalysts. The redox potentials for $[Ru(L)_3]^{2+*/+}$ are very close to that of TEOA. Increasing the number of methyl groups on the bpy ligand decreases the corresponding $Ru^{2+*/+}$ redox potential, so that the efficiency of the reductive quenching reaction is lower. Hence less $[Ru(L)_3]^+$ complex was photogenerated and the overall efficiency of the photochemical system decreased. Indeed the highest efficiency was observed with $[Ru(bpy)_3]^{2+}$ (expt. 2, Table 2) when used in the same conditions as in Table 3. Compared to $[Ru(bpy)_3]^{2+}$ no improved photostability of the system has been observed during long term photolysis experiments.

Quantum yield determinations

Using Reinecke's salt as actinometer (see experimental section), a quantum yield of 15% ($\lambda = 440 \pm 21$ nm) was determined using the mixed system $[Ru(bpy)_3]^{2+}$ + *cis*-$[Ru(bpy)_2(CO)(H)]^+$ in the absence of added water (same conditions as expt. 21 in Table 2).

A quantum yield of 4.9% was determined using $[Ru(bpy)_3]^{2+}$ alone, in the presence of 15% water (same conditions as expt. 2 in Table 1). When a 100 fold excess of bpy was added, the quantum yield rose to 9.6% (same conditions as expt. 4 in Table 1).

The efficiency of this photochemical system compares well with the 14% quantum yield obtained with the single *fac*-$[Re(bpy)(CO)_3Cl]$ complex system, for the catalytic reduction of CO_2 to CO [13].

Mechanistic components of the photoreduction process of CO_2 to formate

As stated above, the photochemical CO_2 reduction process is catalytic with respect to the ruthenium(II) complexes present in the medium. It consumes triethanolamine which provides the electrons required for reduction. The protons involved come from either the oxidized amine or from water. The net reaction may be expressed as in eq. 1:

$$CO_2 + 2\,TEOA + H^+ \rightarrow HCOO^- + 2\,TEOA^{+\cdot} \qquad (1)$$

The overall process, schematically represented in Fig. 6, comprises two interconnected catalytic cycles: a photochemical one involving $[Ru(bpy)_3]^{2+}$ and a thermal one based on a bis-bpy or mono-bpy-ruthenium complex.

Photogeneration of the reduced complex. Thermodynamic constraints rule out oxidative quenching of the $[Ru(bpy)_3]^{2+*}$ excited state by complexes having a redox potential ($E^{\circ\prime}$ $Ru^{3+/2+*}$) more negative than −0.83 V * [12]. No decrease of the Ru-bpy luminescence at 607 nm, was observed in the presence of either carbon dioxide, a bis-bpy- or a mono-bpy-ruthenium(II) complex.

However, it has previously been observed that the luminescence of the $[Ru(bpy)_3]^{2+*}$excited state is quenched by TEOA with a rate constant of 1.7×10^5 M^{-1} s^{-1} (eq. 2) [12].

$$[Ru(bpy)_3]^{2+*} + TEOA \rightarrow [Ru(bpy)_3]^+ + TEOA^{+\cdot} \qquad (2)$$

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* All redox potentials listed in the present work are given vs. the normal hydrogen electrode (NHE).

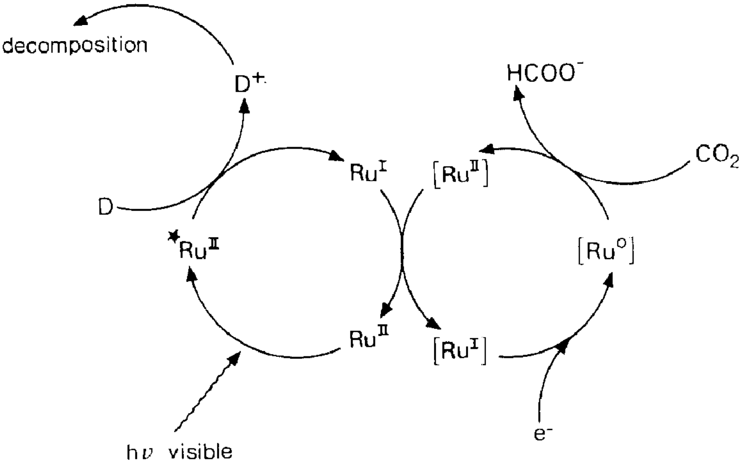

Fig. 6. Schematic representation of the processes occurring in the generation of formate by photoinduced reduction of carbon dioxide using the mixed catalytic system and following a pathway of reductive quenching of the excited state of the ruthenium photosensitizer; it involves a photosensitizer cycle (ruthenium-trischelate) (left) and a CO_2 catalytic reduction cycle (ruthenium bis- or mono-chelate) (right); D represents TEOA (electron donor); the ligands of the metal ions are not indicated.

Flash photolysis experiments on $[Ru(bpy)_3]^{2+}$ in the presence of a tertiary amine have indicated the formation of $[Ru(bpy)_3]^+$ [29]. However, with 25% water present, a fast reaction with water occurred yielding hydrogen [30].

Generation of the reduced catalytically active species. $[Ru(bpy)_3]^+$ is a powerful monoelectronic reducing agent ($E^{\circ\prime}$ $Ru^{2+/+}$ -1.23 [31]) able to reduce $[Co(bpy)_3]^{2+}$ to the Co^I species [12], or *cis*-$[Ru(bpy)_2(CO)(Cl)]^+$ to the ruthenium(I) complex ($E^{\circ\prime}$ $Ru^{2+/+}$ -1.19 V [26,27]). However it is not possible to reduce directly carbon dioxide, the monoelectronic reduction of carbon dioxide requiring at least -2 volts [32]. In photo- and electro-chemical studies on *cis*-$[Ru(bpy)_2(CO)_2]^{2+}$ catalysed carbon dioxide reduction, it has recently been proposed that this complex was reduced stepwise by two moles of $[Ru(bpy)_3]^+$ to give a coordinatively unsatured, formally Ru^0, complex after the release of one CO molecule [17]. Similarly in the present system the same active species could be generated by double reduction of the starting Ru-bis-bpy species **2** and release of a chloride anion (eq. 3):

$$[Ru(bpy)_2(CO)(Cl)]^+ + 2[Ru(bpy)_3]^+ \rightarrow [Ru(bpy)_2(CO)]^0 + 2[Ru(bpy)_3]^{2+} + Cl^- \quad (3)$$

The analogous process for the hydride complex **3** can also be envisaged.

$$[Ru(bpy)_2(CO)(H)]^+ + H^+ + 2[Ru(bpy)_3]^+ \rightarrow [Ru(bpy)_2(CO)]^0 + 2[Ru(bpy)_3]^{2+} + H_2 \quad (4)$$

The following observations are compatible with reaction 4: (i) the chloro- and the hydrido-complexes **2** and **3** have almost the same activity in the photochemical process; (ii) proton NMR spectroscopy shows the rapid disappearance of the hydride species during photolysis.

Thermal reduction of carbon dioxide to formate. Addition of 26.7 μmol of electrogenerated $[Ru(bpy)_3]^+$ (in 2 ml DMF) to 24.1 μmol of *cis*-$[Ru(bpy)_2(CO)$-

(Cl)]$^+$, under $^{13}CO_2$ and in the absence of added water, yielded an average of 12 μmol of formate (45% with respect to the ruthenium(I) complex). Likewise, addition of $[Ru(bpy)_3]^+$ (26.7 μmol) to *cis*-$[Ru(bpy)_2(CO)(H)]^+$ (25.5 μmol) under the same conditions yielded 10 μmol of formate (38%). In the absence of the bis-bpy complex, $[Ru(bpy)_3]^+$ gave no detectable amount of formate, even in the presence of 15% added water.

These observations suggest that two mol of $[Ru(bpy)_3]^+$ produce one mol of the reduced active complex (eq. 3, 4) which reacts with CO_2 to give one mol of formate (eq. 5).

$$[\mathrm{Ru(bpy)_2(CO)}]^0 + \mathrm{Cl^-} + \mathrm{CO_2} + \mathrm{H^+} \rightarrow [\mathrm{Ru(bpy)_2(CO)(Cl)}]^+ + \mathrm{HCOO^-} \tag{5}$$

Under catalytic conditions. Using sixteen time less *cis*-$[Ru(bpy)_2(CO)(Cl)]^+$ (1.7 μmol, catalytic species) then $[Ru(bpy)_3]^+$ (26.7 μmol, reductant), $H^{13}COO^-$ (12.5 μmol) was obtained with a turnover of 7 with respect to the catalyst and a 47% yield of formate with respect to the $[Ru(bpy)_3]^+$.

The mechanism of carbon dioxide reduction to formate is unknown but might proceed through protonation of bound CO_2 to a carboxylic complex followed by rearrangement to a formate complex (eq. 6a), or protonation of bound CO_2 directly to a formate complex (eq. 6b); either would be followed by substitution by chloride with release of formate, regenerating the starting ruthenium-bis-bpy complex (eq. 7). A complex $[Ru(bpy)_2(CO)(COOH)]^+$ has been prepared and postulated as an intermediate in the water-gas shift reaction catalyzed by $[Ru(bpy)_2(CO)(Cl]^+$ [34]; since it apparently did not rearrange to a formate complex, this would favour path (eq. 6b).

$$[\mathrm{Ru(bpy)_2(CO)}]^0 + \mathrm{CO_2} \longrightarrow$$

$$[\mathrm{Ru(bpy)_2(CO)(CO_2)}]^0 \xrightarrow{H^+} [\mathrm{Ru(bpy)_2(CO)(COOH)}]^+ \tag{6a}$$

$$\xrightarrow{H^+} [\mathrm{Ru(bpy)_2(CO)(HCOO)}]^+ \tag{6b}$$

$$[\mathrm{Ru(bpy)_2(CO)(HCOO)}]^+ + \mathrm{Cl^-} \rightarrow [\mathrm{Ru(bpy)_2(CO)(Cl)}]^+ + \mathrm{HCOO^-} \tag{7}$$

Monomethoxycarbonylruthenium complexes have been obtained by reaction of ruthenium(0) clusters with methoxide anion in methanol [35]. Hydroxy-carbonyl complexes of platinum were obtained by nucleophilic attack of OH^- on a carbonyl ligand [36] or insertion of CO into a hydroxyplatinum complex [37]. Hydroxy-carbonyl-bpy complexes of ruthenium [17] and iridium- or rhodium-CO_2 complexes [15b] have been proposed as intermediates in the reduction of carbon dioxide to formate.

Conclusion

The present work describes a photochemical catalytic system performing the dielectronic reduction of carbon dioxide to formate with high efficiency and selectivity, giving a maximum quantum yield of 15%. The $[Ru(bpy)_3]^+$ complex obtained by a reductive quenching pathway in the photochemical system or prepared electrochemically, reduced a ruthenium bis-bpy complex acting as catalyst to a ruthenium(0) species, which in turn coordinated and reduced carbon dioxide to formate. Further investigations are directed towards the use of related polynuclear metal carbonyl complexes of ruthenium and osmium in order to develop new photo- and electro-catalytic systems for the reduction of carbon dioxide.

Experimental

(1) General. All operations were carried out under an atmosphere of argon or ^{13}C-labelled carbon dioxide (90.5% isotopic enrichment) using standard Schlenk or vacuum-line techniques unless otherwise specified. Dimethylformamide was dried over P_2O_5, distilled from solid KOH pellets at room temperature under argon and stored in the dark. $RuCl_3 \cdot 3H_2O$ (35% Ru) was purchased from Roth Chemical Co. Triethanolamine (Fluka), pyridine (Fluka), 2,2′-bipyridine (Fluka), and trimethylamine oxide (Fluka) were used as received. The gases (CO, H_2) produced photochemically were analyzed by gas chromatography (GC), at room temperature, using a Varian-Aerograph-700 apparatus equipped with a 5Å molecular sieve column (13X mesh 42/10) and using methane as the carrier gas. Solutions of the labelled-formate were analysed by both ^{13}C and ^1H NMR spectroscopy and their concentrations were determined ($\pm 10\%$) either by comparison with a standard solution (0.193 mmol of 90% enriched $H^{13}COO^- NMe_4^+$ in 1.8 ml of DMF/DMF-d_7/TEOA/H_2O (3/1/1/1) under 1 mmol $^{13}CO_2$), or by addition of a known quantity of solid $H^{13}CO_2^- NMe_4{}^+$ salt into the solutions.

^1H and ^{13}C NMR spectra: 200-MHz Bruker-SY-200 and 400-MHz Bruker-SY-400 spectrometers at 50.3 MHz (^{13}C), 100.654 MHz (^{13}C) and or 200.1 MHz (^1H). UV/VIS spectra: Cary-219 spectrophotometer, quartz cell mounted on a Schlenk tube; molar extinction coefficients were obtained from absorbance measurements of solutions of at least two different concentrations of complex. IR spectra: Perkin Elmer 597 spectrometer in Nujol mull (KBr disk), or in DMF solutions. Cyclic voltammetry: EDT-ECP 133 potentiostat, pilot scanner, current potential converter, and IF-3802 Ifelec-XY recorder. Continuous electrolysis experiments PRT-100-IX Tacussel potentiostat and IG5-LN current integrator. Solutions of $[Ru(bpy)_3]^+$ [33] were prepared coulometrically using an Hg working electrode, and a saturated calomel electrode (SCE) as a reference.

(2) Photochemical generation of $H^{13}CO_2^-$. All experiments were performed in sealed NMR tubes (10 mm in diameter, total volume ca. 13 ml), under an atmosphere of $^{13}CO_2$. The quantities of each component used in the experiments are given in Tables 1 to 3. The compounds were dissolved in 1.5 ml DMF/DMF-d_7/TEOA (3/1/1) and vacuum-degassed by three freeze-thaw cycles. $^{13}CO_2$ (1 mmol) was generated by acidic treatment (1*M* HCl) of barium carbonate (200 mg, 90% enriched) and was trapped, in the NMR tube, together with some water (0.3 ml), by cooling with liquid nitrogen (90 s). Alternatively, dry $^{13}CO_2$ purchased from CEA-ORIS, was measured volumetrically on a vacuum line, and was trapped in the same manner.

Blank experiments were carried out in the absence of $^{13}CO_2$, under vacuum. For analysis of CO and H_2, the compounds were dissolved in the same solvent and placed in a round-bottomed Schlenk tube (ca. 16 ml volume) which was vacuum-degassed, and a quantity of CO_2 (measured volumetrically and of gas purity 99.8%) was dissolved in the reaction mixture. After irradiation, the internal pressure was brought to atmosphere pressure by cooling the flask in dry ice and by introducing NaOH (ca. 1*M*) into the reaction vessel. A sample of the gas present in the flask was removed by syringe and analyzed by GC. Samples were irradiated with a non-focused 250 W halogen lamp (slide projector) fitted with a 400 nm cut-off-filter (Schott GG420), having 0% transmission at 395 nm. For quantum yield determinations, a 1000-W Hg lamp fitted with a Choffel, model GM 250, monochromator was used as light source ($\lambda = 440 \pm 21$ nm). Incident intensity was determined using an aqueous solution of $KCr(NH_3)_2(NCS)_4$ (Reinecke's salt) as a chemical actinometer [38]; the experiments were conducted at pH = 5.2 under low (ca. 9%) photoaquation conditions.

(3) Generation of formate in electrochemical experiments. Solutions of the electrochemically generated $[Ru(bpy)_3]^+$ complex were prepared under argon and were volumetrically transferred into NMR tubes containing the complexes **2** or **3**. The solutions were degassed by three freeze-thaw cycles and allowed to react with dry $^{13}CO_2$. The solutions were then analysed for formate by ^{13}C NMR spectroscopy. The concentration of $[Ru(bpy)_3]^+$ was determined by current integration [33].

(4) Materials. All complexes used during these studies were carefully purified by chromatography on alumina followed by two recrystallizations. Their purity was checked by ^1H NMR spectroscopy to ensure the absence of impurities that might catalyze the photochemical reaction.

$Ru(bpy)_3Cl_2 \cdot 6H_2O$ (**1**) [39], *cis*-$[Ru(bpy)_2(CO)(Cl)]PF_6$ (**2**) [40], *cis*-$[Ru(bpy)_2(CO)(H)]PF_6$ (**3**) [41], *cis*-$[Ru(bpy)_2(py)(Cl)]Cl$ **4** [42], *cis*-$[Ru(bpy)_2(CO)_2] \cdot 2PF_6$ (**5**) [28], *cis*-$[Ru(bpy)_2(CH_3CN)_2]2PF_6$ (**6**) [43], *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ (**8**) [44], *cis*-$Ru(bpy)(CO)_2(Cl)_2$ (**9**) [28], $Ru(phen)_3Cl_2 \cdot 6H_2O$ (**10**) [39], $Ru(bpy\text{-}R_2)_3Cl_2$ (**11**) [39] and $Ru(bpy\text{-}R_4)_3Cl_2$ (**12**) [39] were prepared and purified according to literature procedures.

cis-$[Ru(bpy)_2(DMF)_2]2PF_6$ (**7**). To a solution of 200 mg (0.38 mmol) of $Ru(bpy)_2Cl_2 \cdot 2H_2O$ [44] in 30 ml of Ar-degassed DMF, 24 mg (0.85 mmol, 2.2 equiv.) of $AgPF_6$ were added. After heating under reflux for 3 h, the deep-red suspension was filtered through celite. To the red solution, a few drops of water saturated NH_4PF_6 were added and the solvent was slowly evaporated at 60° C, under vacuum to ca. 10 ml. When kept at 4° C, complex **7** crystallised out (320 mg, 53%). UV-Vis (DMF) λ_{max}, nm (ϵ, 1 mol^{-1} cm^{-1}): 248 (15000), 296 (43200), 350 (6100), 499 (6500). IR (2–3% in KBr): 1640 cm^{-1} (vs, DMF). ^1H NMR (methanol-d_4, 200 MHz): δ 9.35 (d, 2H), 8.68 (d, 2H), 8.48 (d, 2H), 8.26 (t, 2H), 7.93 (m, 4H), 7.65 (d, 2H), 7.30 (s, 2H, DMF), 7.19 (t, 2H), 2.90 (s, 6H), 2.89 (s, 6H). ^{13}C NMR (DMF-d_7, 100.654 MHz): δ 168.35 (C=O, DMF), 160.80 (CC), 158.65 (CC), 154.59 (CH), 151.99 (CH), 137.69 (CH), 136.14 (CH), 127.70 (CH), 126.67 (CH), 124.28 (CH), 124.18 (CH), 37.96 (CH_3, DMF), 32.83 (CH_3, DMF). FAB^+: 705.1 (M^+ for $[Ru(bpy)_2(DMF)_2 \cdot PF_6]^+$) with the expected isotope abundance at 699 (14.60%), 700 (4.68), 701 (5.76), 702 (35.27), 703 (44.37), 704 (57.49), 705 (100.00), 706 (29.46), 707 (54.26), 708 (16.42), 709 (2.71). Anal. Found: C, 36.70; H, 3.48; N, 9.61. $C_{26}H_{23}N_6O_2P_2F_{12}Ru$ calcd.: C, 36.76; H, 3.56; N, 9.89%.

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