

# Inorganica Chimica Acta

## LETTER

### Photochemical production of hydrogen and carbon dioxide from formate using mixed-ligand iridium complexes as catalysts

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(Received February 28, 1992; revised May 15, 1992)

Photochemical activation of small molecules (e.g.  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ) has attracted significant interest in recent years with potential important applications for conversion of raw materials into valuable fuels [1]. Photochemical activation shows important advantages over thermal activation as milder conditions are required, thereby diminishing undesirable side reactions, resulting in cleaner processes [2]. We recently described a photochemical water-gas-shift reaction (WGSR) [3] catalyzed by a new family of mixed-ligand iridium(III) complexes containing, within the same molecule, a 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) chelate, a pentamethylcyclopentadienyl ( $\eta^5\text{-Me}_5\text{C}_5 = \text{Cp}^*$ ) ligand and a chloride or hydride anion [4, 5]. Photocatalytic WGSR involving these complexes was shown not to involve a formate intermediate. However, other Group VI transition metal-carbonyl complexes have shown that hydrido complexes can be generated from the formate anion [6]. These observations prompted us to study the light-assisted decomposition of formate into hydrogen and carbon dioxide, catalyzed by the family of iridium complexes depicted in Fig. 1.

Numerous thermal systems for formate decomposition to hydrogen and carbon dioxide have previously been reported all of which are active only at temperatures in excess of  $100^\circ\text{C}$  [6, 7]. Heterogeneous photocatalytic decomposition of saturated carboxylic acids (the photo-

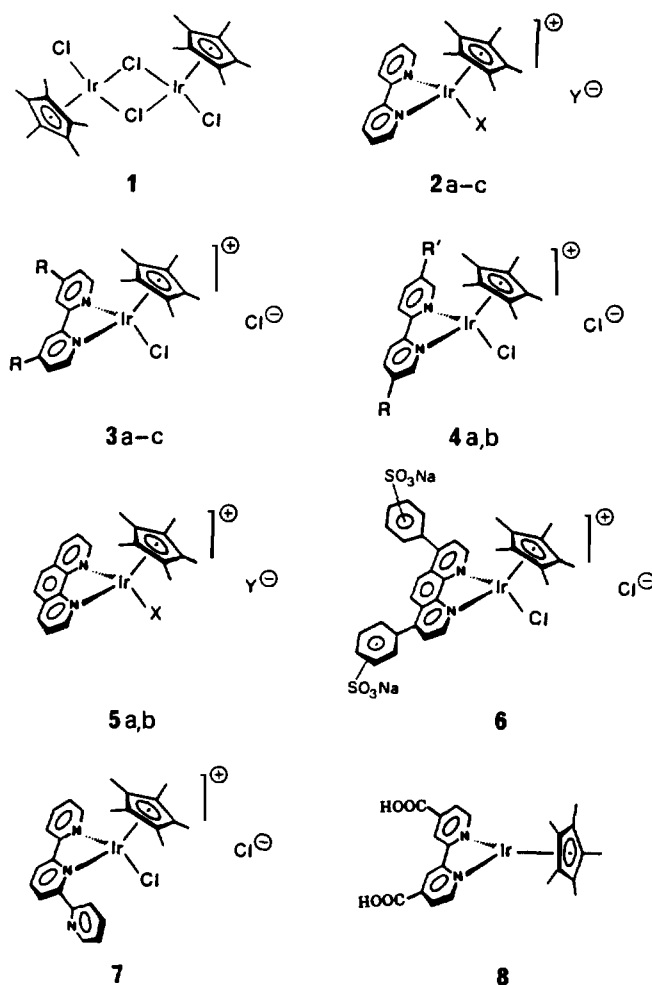


Fig. 1. Structural formulae of the iridium(III) complexes: 2a:  $\text{X}=\text{Y}=\text{Cl}$ ; 2b:  $\text{X}=\text{Y}=\text{CF}_3\text{SO}_3$ ; 2c:  $\text{X}=\text{H}$ ,  $\text{Y}=\text{B}(\text{C}_6\text{H}_5)_4$ ; 3a:  $\text{R}=\text{COOH}$ ; 3b:  $\text{R}=\text{NO}_2$ ; 3c:  $\text{R}=\text{NMe}_2$ ; 4a:  $\text{R}=\text{R}'=\text{COOH}$ ; 4b:  $\text{R}=\text{SO}_3\text{H}$ ,  $\text{R}'=\text{H}$ ; 5a:  $\text{X}=\text{Y}=\text{Cl}$ ; 5b:  $\text{X}=\text{H}$ ,  $\text{Y}=\text{B}(\text{C}_6\text{H}_5)_4$ .

Kolbe reaction) on n-type  $\text{TiO}_2$  semi-conductors has been extensively studied [8]. However, to our knowledge homogeneous photochemical processes for the generation of hydrogen from formate, have not as yet been studied and reported.

We describe here, homogeneous photocatalytic systems, hitherto unknown, for the production of hydrogen and carbon dioxide from formate, based on photoactive mixed-ligand iridium(III) complexes (Fig. 1). In a typical experiment 2 mg of iridium complex were dissolved in 20 ml of aqueous sodium formate (0.5 M) solution, and the pH adjusted to 5.0. The mixture was irradiated with visible light, under vacuum, at room temperature and any gases produced were analyzed by GC. For specific conditions refer to Table 1, where a representative sample of data obtained in these experiments is presented. The following observations can be made from these experiments.

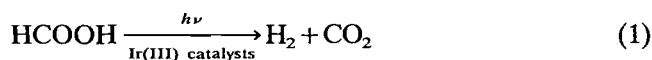
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TABLE 1. Photochemical generation of H<sub>2</sub> catalyzed by iridium complexes 1–8, at room temperature<sup>a</sup>

Expt.	Complex, λ <sub>max</sub> (nm) (ε (M <sup>-1</sup> cm <sup>-1</sup> )) <sup>b</sup>	Volume H <sub>2</sub> <sup>c</sup> (ml)	Overall turnover <sup>d</sup>
1	<b>1</b>	traces	
2 <sup>e</sup>	<b>3a</b> or <b>3c</b>	traces	
3	<b>2a</b> , 351 (2900), 312 sh (8000)	0.09	1
4	<b>2b</b> , 314 (12900)	0.34	5
5 <sup>f</sup>	<b>2c</b> , 428 (3000)	0.07	1
6	<b>3a</b> , 328 (12900), 318 (13000)	0.38	5
7	<b>3b</b> , 487 (790), 394 (5400), 320 (9600)	2.05	26
8	<b>3c</b> , 364 (7700)	3.77	53
9	<b>4a</b> , 326 (17900), 308 (22600)	0.37	5
10	<b>4b</b> , 320 (11500), 301 (14300)	1.15	15
11	<b>5a</b> , 362 (3850), 346 (4000)	0.47	6
12 <sup>f</sup>	<b>5b</b> , 420 (4200)	0.31	3
13	<b>6</b> , 331 (12300)	1.09	15
14	<b>7</b> , 324 (14200), 315 (14200)	0.09	1
15	<b>8</b> , 410 (1300), 328 (12000), 318 (12200)	0.40	5

<sup>a</sup>20 ml of aqueous sodium formate (0.5 M) solution, adjusted to pH=5.0 with HCl (N/10), containing 1.6 × 10<sup>-4</sup> M of complexes 1–8 was irradiated in a 100 ml non-thermostated Schlenk flask, for 2 h, with a 250 W halogen lamp (slide projector). All experiments were performed twice and showed good reproducibility (±10%). <sup>b</sup>Near UV absorption bands assigned to metal perturbed π–π\* transitions involving the diimine ligands. Above 330 nm absorption bands assigned to MLCT transitions (see ref. 9). Measured in CH<sub>3</sub>CN or water solutions (for complexes **3a**, **4b**, **6** neutral pH and for complex **4a** basic pH). <sup>c</sup>The gases H<sub>2</sub> and CO<sub>2</sub> were analyzed by GC. <sup>d</sup>Calculated by dividing the number of moles of H<sub>2</sub> produced in 2 h by the number of moles of Ir(III) complex. <sup>e</sup>Samples were stirred in the dark for 2 h. <sup>f</sup>10 ml of aqueous sodium formate (0.5 M) and 10 ml CH<sub>3</sub>CN were used.

(i) This system provided the first example of a homogeneous light-driven formate decomposition process (eqn. (1)), active under very mild conditions (visible light irradiation, room temperature, pH 5.0).



The dimer **1** [10], precursor of all complexes depicted in Fig. 1, was inactive when irradiated in the presence of formate (expt. 1). Negligible amounts of hydrogen were detected when complexes **3a** or **3c** were kept in the dark, under the above conditions. Most of the complexes showed some catalytic activity, however, surprisingly the highest efficiency observed was for the 4,4'-dinitro (**3b**) and 4,4'-dimethylamino (**3c**) substituted 2,2'-bipyridine iridium(III) complexes. Their catalytic activity being 23 times (expt. 7) and 42 times (expt. 8) enhanced, respectively, compared to the unsubstituted bpy–Ir(III) compound (expt. 3). As previously observed, in the photochemical WGS [3], no change in catalytic activity was observed on changing the carboxylate substitution position on the bpy ligand (4,4'-position (**3a**) to 5,5'-position (**4a**), see expts. 6 and 9). Furthermore, no change in efficiency was observed on changing the oxidation state of the catalyst precursor: (+III) in complex **3a** (expt. 6) and (+I) in complex **8** (expt. 15).

(ii) Kinetic experiments (Fig. 2) show a linear formation of hydrogen with time. When complex **3a** was irradiated in the presence of formate for 16 h a turnover

of 79 was calculated, whilst complex **3b**, after 8 h irradiation gave a turnover of 159 (the gases evolved are collected in an inverted burette on a water reservoir at atmospheric pressure). Some decrease of activity was observed over longer irradiation periods due to saturation with hydrogen and carbon dioxide and/or to some ligand labilization.

(iii) The conversion of H<sup>13</sup>COO<sup>-</sup>NMe<sub>4</sub><sup>+</sup> to <sup>13</sup>CO<sub>2</sub> or <sup>13</sup>CO<sub>3</sub><sup>2-</sup> and H<sub>2</sub> was followed by <sup>13</sup>C NMR spectroscopy, which showed the disappearance of the H<sup>13</sup>COO<sup>-</sup> signal (δ 171.5 ppm) with the simultaneous increase of the <sup>13</sup>CO<sub>2</sub> (δ 125.5 ppm, in acidic media) or <sup>13</sup>CO<sub>3</sub><sup>2-</sup> (δ 160.9 ppm, in basic media) resonances as irradiation was continued\*. Unfortunately no new resonances due to the formation of an iridium formate complex (probable intermediate of the catalytic cycle) could be observed under these conditions, probably due to its high reactivity. This would explain why attempts to isolate [Cp\*Ir(bpy)(HCOO)]<sup>+</sup> from the chloro or triflate analogues have been unsuccessful.

(iv) In order to gain more insight into the mechanism and determine the rate limiting step of this new catalytic process, we studied the effect of temperature (between 15 and 50 °C) on the rate of H<sub>2</sub> formation with two different complexes (**3b** and **3c**). The results are shown

\*This experiment was carried out in a sealed NMR tube containing labelled NMe<sub>4</sub><sup>+</sup>H<sup>13</sup>COO<sup>-</sup> (90% enriched) in distilled water (adjusted to the desired pH), and d<sub>3</sub>-CH<sub>3</sub>CN, as internal standard.

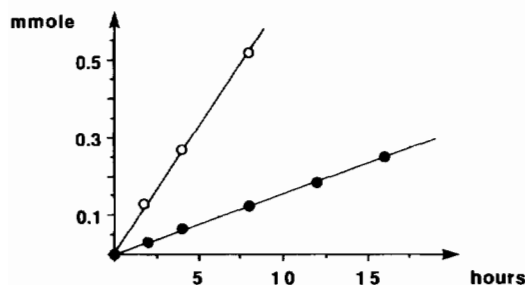


Fig. 2. Continuous photogeneration of  $\text{H}_2$  from formate as a function of time using complexes **3a** (●) or **3b** (○) as catalysts ( $6.5 \times 10^{-4}$  M), at atmospheric pressure.

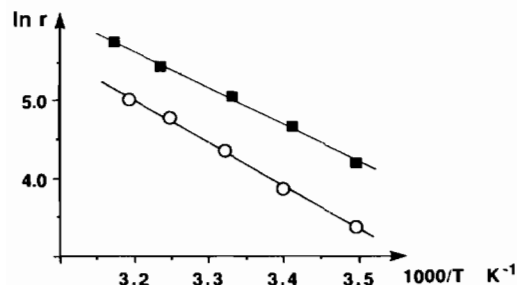


Fig. 3. Effect of temperature on the rate  $r$  ( $\mu\text{mol h}^{-1}$ ) of photochemical generation of  $\text{H}_2$  using complexes **3b** (○) or **3c** (■) as catalysts ( $3.1 \times 10^{-4}$  M), under vacuum.

in the plot of  $\ln r$  versus  $1/T$  in Fig. 3 ( $r$  = rate of  $\text{H}_2$  production). Activation energies,  $E_a$ , of 46.3 and 39.3  $\text{kJ mol}^{-1}$  were found for complexes **3b** and **3c**, respectively. These values are much higher than those determined in the photochemical WGSR (the lowest value measured being 14.6  $\text{kJ mol}^{-1}$  [3]), but much lower than those determined for thermally activated systems for formate decomposition (c. 146  $\text{kJ mol}^{-1}$ ) [11, 12]). More interestingly is the absence of any electron withdrawing/donating effect on the activation energies, due to the various substituents of the 2,2'-bipyridine chelate as previously observed for the photochemical WGSR [3]. The absence of this effect suggests little electronic influence on the rate limiting step of the process. Assuming that the photochemical step (protonation of the hydride [3]) has a very low activation energy [13], the global activation energy values suggest, by comparison with similar values obtained in the literature [14], that decarboxylation of an iridium formate species is the rate-limiting step. The difference in activation energies observed here, compared to the WGSR, could be due to the different mechanism of decarboxylation of a formate complex versus a carboxylate complex. The difference in catalytic activity observed between complexes **3a**, **3b** and **3c** (expts. 6–8 in Table 1) could be due to the formation of an Ir(I) intermediate as previously observed in the photochemical WGSR [15]. Finally, preliminary quantum yield

determinations, using Reinecke's salt as chemical actinometer\*, gave values of 1.7% for **3a**, 9.0% for **3b** and 16.5% for **3c** (conversion of light to hydrogen and carbon dioxide at  $410 \pm 10$  nm).

Further development of this research will include the synthesis of novel mono and dinuclear Ir(III) complexes as well as the study of the mechanism of this unusual photochemical process.

## Acknowledgements

D. Biltz is warmly thanked for help with the preparation of the manuscript. Financial support from the Centre National de la Recherche Scientifique is gratefully acknowledged.

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\*The light intensity was in the order of  $1.79 \times 10^{-6}$  einstein  $\text{min}^{-1} \text{cm}^{-2}$  with 2.2% photolysis in 15 min [16].