

Photocatalysis. Mechanistic Studies of Homogeneous Photochemical Water Gas Shift Reaction Catalyzed under Mild Conditions by Novel Cationic Iridium(III) Complexes

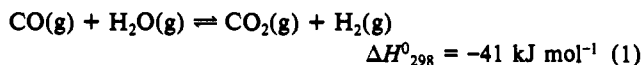
Raymond Ziessel

Contribution from the Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg and the Institut de Physique et de Chimie des Matériaux de Strasbourg, URM 46 du CNRS, 1 rue Blaise Pascal-67008 Strasbourg Cédex, France. Received July 21, 1992

Abstract: The photochemical water gas shift reaction (WGSR) catalyzed, under mild conditions (25 °C, 1 atm CO, visible light, pH = 7), by $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{III}}(\text{bpy})\text{X}]^+$ (bpy = 2,2'-bipyridine, X = H, Cl), $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{III}}(\text{phen})\text{X}]^+$ (phen = 1,10-phenanthroline, X = H, Cl), or $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{III}}(\text{bpyRR}')\text{Cl}]^+$ (R = R' = COOH, COOⁱPr, Br, NO₂, NMe₂ in the 4,4'-positions or R = R' = COOH, R = H and R' = SO₃H in the 5,5'-positions of the bpy ligand) has been investigated. A turnover frequency for H₂ formation of 32 h⁻¹ was obtained in an aqueous phosphate buffer containing $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{III}}(\text{bpy-4,4'-(COOH)}_2)\text{Cl}]^+$ as catalyst, over a 7-h irradiation period at a constant CO pressure of 1 atm. An increase of 1 order of magnitude in catalytic activity was observed for the bpy ligand substituted with two carboxylate groups in the 4,4'- or 5,5'-positions or with one sulfonate group in the 5-position (over the unsubstituted bpy equivalent). Conversely, catalytic activity was lost when the bpy was substituted with two dimethylamino groups. The presence of an electron withdrawing group on the bpy-chelate was shown to decrease the activation energy of the process ($E_a = 14.6 \text{ kJ mol}^{-1}$ for R = COOH, $E_a = 22.2 \text{ kJ mol}^{-1}$ for R = COOⁱPr), cf. the unsubstituted ligand ($E_a = 29.6 \text{ kJ mol}^{-1}$ for R = H). Decarboxylation of the intermediate $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{III}}(\text{bpyRR}')\text{COOH}]^+$ (rate limiting step) seems therefore to be favored by the presence of an electron withdrawing group on the bpy-chelate. Three of the four intermediates involved in the WGS catalytic cycle have been characterized by NMR and FT-IR spectroscopies: (i) the highly reactive $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{III}}(\text{bpyRR}')\text{CO}]^{2+}$ species formed by thermal displacement of the Cl⁻ anion of the starting complex; (ii) the iridium(I) complex $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{I}}(\text{bpyRR}')]$, formed by decarboxylation of the hydroxycarbonyl complex; and (iii) the hydrido complex $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{III}}(\text{bpyRR}')\text{H}]^+$, formed by protonation of $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{III}}(\text{bpyRR}')]$. This latter complex (with R = COOH in the 4,4'-position of the bipyridine) has been characterized by a crystal structure determination. The photochemical step of the cycle was found to be the protonation of the hydride generating H₂ and the starting complex. The global catalytic system (for $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{III}}(\text{bpy-4,4'-(COOH)}_2)\text{Cl}]^+$) has a quantum yield of 12.7% at 410 ± 5 nm, which is independent of light intensity but strongly dependent on the pH of the solution.

Introduction

Pioneering work on the homogeneous water gas shift reaction (WGSR) (eq 1) was performed by German chemists about 60 years ago.¹ It was shown that one of the coordinated carbonyls



of Fe(CO)₅ was oxidized to carbonate and hydrogen was produced, in a second step, by protonation of the HFe(CO)₄⁻ hydride.² Three groups independently reported that homogeneous catalysis of the WGSR was possible.³ Alternative carbonyl complexes were used, notably Ru₃(CO)₁₂^{3a,4} and [Rh(CO)₂Cl]₂ in acidic medium.^{3b,5} Since this seminal work, a large number of homogeneous WGS reactions have been studied, leading to a better understanding of the WGSR mechanism and a gradual improvement in catalytic efficiency. Rhodium(I) phosphine complexes have been used as catalyst either in organic medium⁶ or in aqueous solution using water soluble phosphines.⁷ Iridium phosphine complexes have also been used in both media.⁸ A binuclear "A-frame" rhodium(0) complex proved to be an efficient catalyst for the WGSR.⁹ Platinum complexes have been studied,¹⁰ one

particularly active catalyst precursor being a binuclear complex transformed into a tetranuclear species during the reaction.¹¹ The WGSR catalyzed by platinum(II) associated with SnCl₄ in a mixture of acetic and hydrochloric acids has been reported^{12,13} and a new catalytic cycle for this system has recently been proposed.¹⁴ Among the first-row transition-metal complexes, a dicarbonylnickel(0) complex, containing a diphosphine-pyridine ligand, appears to be the only catalytic precursor leading to activity at low temperature and pressure in water-alcohol solution (22 °C, 0.94 atm).¹⁵

The catalytic system using Fe(CO)₅ has been discussed in detail,^{3c,16,17} and whilst showing no significant catalytic properties under mild conditions, it becomes active at 180 °C, under CO pressure. The reaction mechanism is now well understood, thanks to detailed kinetic analysis.¹⁷ The complexes M(CO)₆ (M = Cr, Mo, W) have also been examined as homogeneous catalysts,^{18,19} but they are of limited use because they catalyze decomposition of formate formed from CO and base, rather than the WGSR

- (1) Hieber, W.; Leutert, F. *Z. Anorg. Allg. Chem.* 1934, 204, 145.
- (2) Reppe, W.; Reindl, E. *Ann. Chem.* 1953, 582, 120.
- (3) (a) Laine, R. M.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* 1977, 99, 252. (b) Cheng, C. H.; Hendriksen, D. E.; Eisenberg, R. *J. Am. Chem. Soc.* 1977, 99, 2791. (c) Kang, H.; Mauldin, C. H.; Cole, T.; Slegier, W.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.* 1977, 99, 8323.
- (4) (a) Ungermann, C.; Landis, V.; Moya, S. A.; Cohen, H.; Walker, H.; Pearson, R. G.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* 1979, 101, 5922. (b) Ford, P. C.; Ungermann, C.; Landis, V.; Moya, S. A.; Rinker, R. C.; Laine, R. M. *Adv. Chem. Ser.* 1979, 173, 81. (c) Ford, P. C. *Acc. Chem. Res.* 1981, 14, 31.
- (5) Baker, E. C.; Hendriksen, D. E.; Eisenberg, R. *J. Am. Chem. Soc.* 1980, 102, 1020.
- (6) (a) Yoshida, T.; Okano, T.; Otsuka, S. *J. Am. Chem. Soc.* 1980, 102, 5966. (b) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* 1981, 103, 3411.
- (7) Nuzzo, R. G.; Feitler, D.; Whitesides, G. *J. Am. Chem. Soc.* 1979, 101, 3683.

- (8) (a) Kaspar, J.; Spogliarich, R.; Mestroni, G.; Graziani, M. *J. Organomet. Chem.* 1981, 208, C15. (b) Kaspar, J.; Spogliarich, R.; Cernogoraz, A.; Graziani, M. *J. Organomet. Chem.* 1983, 255, 371.
- (9) (a) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* 1980, 102, 3637. (b) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* 1982, 21, 2119. (10) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* 1978, 100, 3941.
- (11) Frew, A. A.; Hill, R. H.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* 1982, 198.
- (12) Cheng, C.-H.; Eisenberg, R. *J. Am. Chem. Soc.* 1978, 100, 5968.
- (13) (a) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* 1989, 89, 11. (b) Spencer, A. *In Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1987; Vol. 6, p 292. (c) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* 1978, 28. (d) Clark, H. C.; Jain, V. K. *Coord. Chem. Rev.* 1984, 55, 151.
- (14) Kubota, M. *Inorg. Chem.* 1990, 29, 574.
- (15) Giannoccaro, P.; Vasapollo, G.; Sacco, A. *J. Chem. Soc., Chem. Commun.* 1980, 1136.
- (16) (a) King, R. B.; Frazier, C. C.; Hanes, R. M., Jr.; King, A. D. *J. Am. Chem. Soc.* 1978, 100, 2925. (b) King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* 1980, 102, 1028.
- (17) Pearson, R. G.; Mauerer, H. *J. Am. Chem. Soc.* 1982, 104, 500.

itself.¹⁹ However they do have an advantage over the iron complexes in that they are unaffected by sulfides.¹⁸ This could have important industrial implications for the removal of CO from mixtures of industrial gases.

More recently, systems based on polypyridine compounds of ruthenium(II),²⁰⁻²² rhodium(I),^{23a} and iridium(I)²³ have been shown to efficiently catalyze the *thermal WGS*. An important effect of the substituent ortho to the nitrogen atom of the polypyridine ligand has been demonstrated in the case of Ir(I) leading to one of the most efficient catalysts known today.^{23b} The [Ru(bpy)₂(CO)Cl]⁺ complex has also been studied, and all of the possible intermediates within the catalytic WGS cycle (hydrocarbonyl complex, metal hydride, and aquo intermediates) have been isolated and characterized.^{21b}

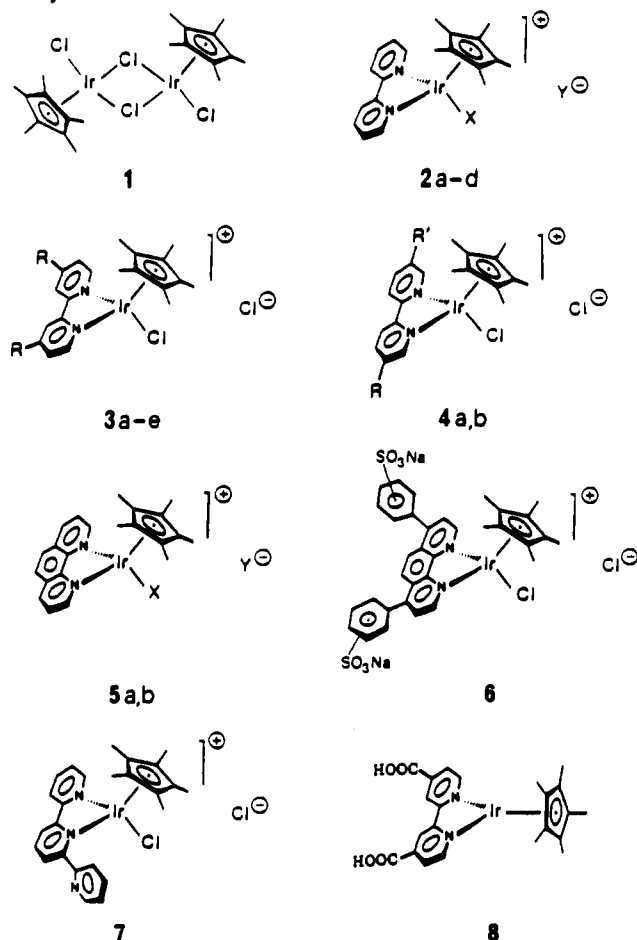
Very little attention has been devoted to *photochemical WGS* reactions. Heterogeneous photoassisted WGS systems have been reported using platinumized TiO₂,^{24,25} rhodium loaded SiC or CdS,²⁶ and ZnS.²⁷ [Ru(bpy)₂(CO)Cl]⁺ has been used in the homogeneous photocatalysis of the WGS;²⁰ however, its activity is only slightly lower in the dark than under light irradiation.²¹

Consideration of the thermodynamics of the WGS makes it important to find catalytic systems active at low temperatures. The negative entropic term of reaction 1, -42 J deg⁻¹, disfavors high temperature in spite of its exergonic character at room temperature (-28 kJ mol⁻¹). An efficient homogeneous catalytic system operating at room temperature would result in large cost savings, through the use of water instead of steam. The use of light energy in order to promote the WGS under ambient conditions is an excellent way to reach this goal. We recently found that a new family of Ir(III) complexes, which coordinate on the same metal center a 2,2'-bipyridine or 1,10-phenanthroline, and a pentamethylcyclopentadienyl ligand provide new catalysts for the homogeneous photoassisted WGS.²⁸ These systems are, to our knowledge, the first examples of a homogeneous light-driven WGS, active under extremely mild conditions (room temperature, ambient pressure, neutral pH, and visible light). We have further investigated these photocatalytic systems with various electron withdrawing or donating substituents on the bpy-chelate and have also isolated the key intermediate of the catalytic cycle. We now report a detailed study of the homogeneous WGS photocatalyzed under a wide range of experimental conditions by a series of new cationic Ir(III) complexes (Scheme I) as well as a straightforward demonstration of the role of thermal processes coupled to photochemical ones.

Experimental Section

General Methods. All operations were carried out under argon using standard Schlenk or vacuum-line techniques unless otherwise specified. Dimethylformamide was dried over P₂O₅, treated with KOH, and distilled at room temperature under argon. Ethanol and water were distilled and degassed under argon. *cis*- and *trans*-2-Bromo-2-butene, acetaldehyde, 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2':6',2''-terpyridine (terpy), and disodium 4,7-diphenyl-1,10-phenanthroline disulfonate (bathophen2Na) were purchased from Aldrich Chemical Co. IrCl₃·3H₂O were obtained from Johnson-Matthey Inc. pentamethylcyclopentadiene;²⁹ bis[(η⁵-pentamethylcyclopentadienyl)dichloroiridium-

Scheme I. Structural Formulas of the Ir^{III} Water-Gas Shift Catalysts^a



^a 2a, X = Y = Cl; 2b, X = Y = CF₃SO₂; 2c, X = H, Y = B(C₆H₅)₄; 2d, X = OH, Y = CF₃SO₂; 3a, R = COOH; 3b, R = COOPr; 3c, R = Br; 3d, R = NO₂; 3e, R = NMe₂; 4a, R = R' = COOH; 4b, R = SO₃H, R' = H; 5a, X = Y = Cl; 5b, X = H, Y = B(C₆H₅)₄.

(III)]₂,³⁰ [(η⁵-Me₅C₅)IrCl₂]₂, 1; [(η⁵-pentamethylcyclopentadienyl)(2,2'-bipyridine)chloroiridium(III)] chloride,^{31,32} [(η⁵-Me₅C₅)Ir(bpy)Cl]Cl, 2a; [(η⁵-pentamethylcyclopentadienyl)(2,2'-bipyridine)hydrido-iridium(III)] tetraphenylborate,^{31,32} [(η⁵-Me₅C₅)Ir(bpy)H]BPh₄, 2c; [(η⁵-pentamethylcyclopentadienyl)(1,10-phenanthroline)chloroiridium(III)] chloride,^{31,32} [(η⁵-Me₅C₅)Ir(phen)Cl]Cl, 5a; [(η⁵-pentamethylcyclopentadienyl)(1,10-phenanthroline)hydrido-iridium(III)] tetraphenylborate,^{31,32} [(η⁵-Me₅C₅)Ir(phen)H]BPh₄, 5b; 4,4'-dibromo-2,2'-bipyridine;³³ 4,4'-bis(isopropoxycarbonyl)-2,2'-bipyridine;³⁴ 4,4'-dibromo-2,2'-bipyridine;³⁵ 4,4'-dinitro-2,2'-bipyridine;³⁶ 4,4'-bis(dimethylamino)-2,2'-bipyridine;^{35,37} 5,5'-dicarboxy-2,2'-bipyridine,³⁸ and 5-sulfo-2,2'-bipyridine³⁹ were prepared according to the literature procedures.

Preparation and Characterization of [(η⁵-Me₅C₅)Ir(bpy)CF₃SO₂]-CF₃SO₂, 2b. To a hot solution of [(η⁵-Me₅C₅)Ir(bpy)Cl]Cl (560 mg, 1.0 mmol) in acetonitrile (50 mL) was added AgCF₃SO₂ (540 mg, 2.1 mmol) as a solid under argon. After 3 h reflux, the suspension was cooled to room temperature and filtered over Celite. The resulting light yellow solution was concentrated to ca. 5 mL by solvent distillation under vacuum and filtered again over Celite. Addition of diethyl ether (75 mL) resulted in the precipitation of the complex (700 mg, 90%): ¹H NMR

(18) King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Chem. Soc., Chem. Commun.* **1980**, 529.

(19) King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1981**, *103*, 2699.

(20) (a) Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1213.

(b) Choudhury, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1885.

(21) (a) Tanaka, K.; Morimoto, M.; Tanaka, T. *Chem. Lett.* **1983**, 901. (b) Ishida, H.; Tanaka, K.; Morimoto, M.; Tanaka, T. *Organometallics* **1986**, *5*, 724.

(22) Taqui Khan, M. M.; Halligudi, S. B.; Shukla, S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1735.

(23) (a) Marnot, P. A.; Ruppert, R. R.; Sauvage, J.-P. *Nouv. J. Chim.* **1981**, *5*, 543. (b) Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *Nouv. J. Chim.* **1985**, *9*, 395.

(24) (a) Sato, S.; White, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 7306. (b) Sato, S.; White, J. M. *J. Catal.* **1981**, *69*, 128. (c) Fang, S.-M.; Chen, B. H.; White, J. M. *J. Phys. Chem.* **1982**, *86*, 3126.

(25) Tsai, Sh.-Ch.; Kao, Ch.-Ch.; Chung, Y.-W. *J. Catal.* **1983**, *79*, 451.

(26) Thewissen, D. H. M. W.; Tinnemans, A. H. A.; Euwhorst-Reinten, M.; Timmer, K.; Mackor, A. *Nouv. J. Chim.* **1983**, *7*, 73.

(27) Kisch, H.; Schlamann, W. *Chem. Ber.* **1986**, *119*, 3483.

(28) Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 844.

(29) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1.

(30) Kong, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(31) Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1988**, 16.

(32) Youinou, M.-T.; Ziessel, R. *J. Organomet. Chem.* **1989**, *363*, 197.

(33) Launikonis, A.; Lay, P. A.; Mau, A. W.-H.; Sargeson, A. M.; Sasse, W. H. F. *Aust. J. Chem.* **1986**, *39*, 1053.

(34) Bos, K. D.; Kraaijkamp, J. G.; Noltes, J. G. *Synth. Commun.* **1979**, *9*, 497.

(35) Maerker, G.; Case, F. H. *J. Am. Chem. Soc.* **1958**, *80*, 2745.

(36) Wenkert, D.; Woodward, R. B. *J. Org. Chem.* **1983**, *48*, 283.

(37) Jones, R. A.; Roney, B. D.; Sasse, W. H. F.; Wade, K. O. *J. Chem. Soc. B* **1967**, 106.

(38) Whittle, C. P. *J. Heterocycl. Chem.* **1977**, *14*, 191.

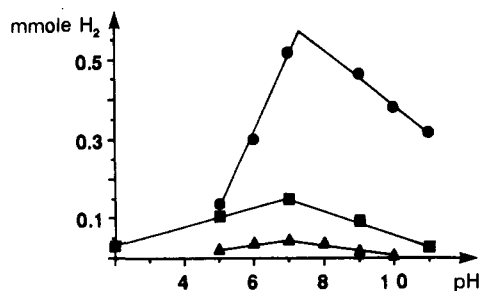


Figure 1. Effect of pH on the photochemical generation of H_2 : (●) complex **3a**, (■) complex **6**, and (▲) complex **2a**, 1 atm CO , 20 °C, 2-h irradiation.

monothioglycerol (thio-) matrix unless otherwise specified. UV-vis spectra: Shimadzu UV-260 spectrophotometer in MeCN; molar extinction coefficients from absorbance measurements on at least two different concentrations of complex. FT-IR spectra: Bruker IFS 66 spectrometer in D_2O solution with a CaF_2 Perkin-Elmer cell and Bruker IFS 25 spectrometer in KBr pellets. The pH value of the reaction mixture was measured with a Metrohm 632 apparatus equipped with a 7-mm glass electrode. Elemental analyses were performed by the Institut de Chimie, Strasbourg analytical service. For quantum yield determinations a 1000-W Xe-Hg lamp in combination with a Schoffel, Model GM 250, monochromator was used as a monochromatic light source at 370, 410, 440, and 550 nm with 5–15 nm open slits. Incident light intensity was determined with an aqueous solution of recrystallized $NH_4Cr(NH_3)_2(NCS)_4$ (Reinecke's salt) as a chemical actinometer⁴² and was typically 3.06×10^{-6} einstein $min^{-1} cm^{-2}$ at 410 ± 10 nm.

Results and Discussion

In order to study the parameters affecting the catalysis as well as to investigate the mechanism of the catalytic cycle the reaction has been performed under many varying conditions with several different complexes. Below, the independent effects of pH, concentration of various components, temperature, light intensity, reaction time, and ligand structure including ligand substituent are discussed.

(a) Catalytic Conditions. The results obtained for some typical experiments, using complexes 1–8 are given in Table I. Dimer 1,³⁰ the precursor to all of the complexes described in this paper, was inactive when irradiated under CO .

No system produced significant amounts of H_2 ($< 1 \mu L$) in the dark or in the absence of CO . The truly photochemical nature of this process was verified in two separate experiments with complexes **2a** and **3a**. When they were irradiated for only 0.25 h (instead of 2 h, experimental 3 and 8, respectively, in Table I) and then stirred for 1.75 h in the dark, only small amounts of H_2 (0.14 mL and 1.54 mL, respectively) were formed, showing that irradiation is essential for catalytic activity. All of the complexes show some catalytic activity, analyzed as the amount of H_2 and CO_2 produced, with varying efficiencies, when irradiated in the presence of CO .

pH Effects. The catalytic activity of all complexes was strongly dependent on pH (from 2 to 11) with an optimum activity lying between pH 5–7 (Figure 1). Catalytic activity was not affected by buffer concentration (0.001–1 M); however, at low concentration (< 0.001 M) the buffer is no longer effective and a decrease of activity with time, due to an increase in pH, was observed during the photolysis.

Catalyst Concentration Effects. In order to determine which parameters limit the efficiency of the system, its activity has been studied as a function of the concentration of complex **3a**. The experimental data obtained are collected in Table II. The rate of H_2 formation increases with increasing catalyst concentration. Between 0.045 and 0.2 mM concentration, the reaction showed a first-order rate dependence on catalyst concentration with a calculated rate constant of $0.34 h^{-1}$. Above 0.2 mM a saturation effect was observed, due to a photofiltering effect of the complex on the photoactivation process (Figure 2). The limiting catalyst concentration before saturation was dependent on light intensity

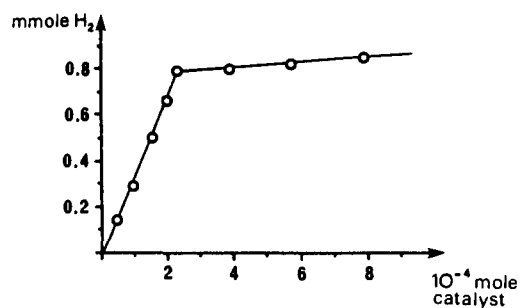


Figure 2. Effect of catalyst concentration (complex **3a**) on the photochemical generation of H_2 : 20 °C, 1 atm CO , pH 7.0, 2-h irradiation.

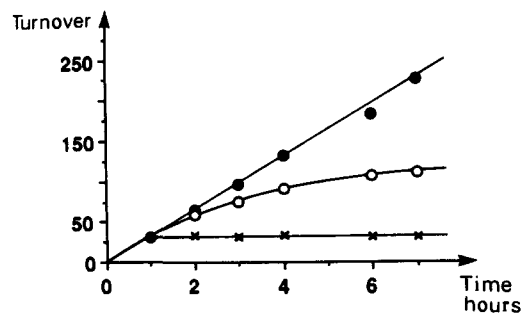


Figure 3. Turnover of complex **3a** as a function of irradiation time. Each value corresponds to one experiment: (O) the Schlenk flask was saturated with CO at the beginning of the experiment and photolyzed over the desired time (constant volume of CO); (●) the Schlenk flask was saturated with CO every hour and photolyzed over the desired time (constant pressure of CO); (X) turnover frequency calculated, in this last case, by dividing the number of moles of H_2 obtained every hour by the number of moles of the starting complex. All experiments were carried out at 20 °C and pH 7.0.

(when irradiated with monochromatic light at 410 nm; conditions are described in Table V). In this case, a saturation effect due to CO dissolution in water (low solubility⁴³) was not observed but has previously been found for a thermal WGS, in the presence of higher catalyst concentration (above 10^{-3} M).^{23b} The fact that the overall turnover does not increase with catalyst concentration suggests the mononuclear nature of the chemical catalyst, as opposed to a cluster type species. Catalytic systems involving clusters have been well documented in the literature.⁴⁴

Reaction Time. The photochemical WGS has also been studied as a function of time using complex **3a**, and the results are given in Table III. Kinetic studies showed H_2 generation to be nonlinear with respect to time when CO pressure was not adjusted every hour. In this case the Schlenk flask was saturated with CO at the beginning of the experiment, and its pressure decreased continuously as the photocatalysis proceeds. However, a linear H_2 formation was observed when the solution was degassed each hour and the initial quantity of CO redissolved in the medium. A rate constant of $0.25 mmol H_2 h^{-1}$ was calculated in this last case, showing a good photochemical stability of the WGS over a 7-h irradiation period (Figure 3). The activity of the system decreased slowly with longer irradiation times (days), due to the slow formation of deep-green unidentified insoluble material (possibly clusters) obtained by labilization of the ligands (excess bipyridine in the system leads to some increase in catalytic activity, which has been already discussed in the literature^{45,45} for other related systems).

(b) Ligand and Substituent Effect. In order to investigate any ligand and/or ligand substitution effects on the reaction, different

(41) Ziessel, R.; Lehn, J.-M. *J. Organomet. Chem.* **1990**, *382*, 157.

(42) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.

(43) Linke, W. F. In *Solubilities of Inorganic and Metal-Organic Compounds*; McGregor and Werner, Inc.: Washington, D.C., 1958; Vol. I, p 453.

(44) Laine, R. M. *J. Mol. Catal.* **1982**, *14*, 137.

(45) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990.

(46) Ziessel, R. In *Enzymatic and Model Carboxylation and Reduction Reactions for Carbon Dioxide Utilization*; Aresta, M., Schloss, J. V., Eds.; Reidel: Dordrecht, 1990; Series C, Vol. 314, pp 79–100.

Table I. Photochemical WGSR Catalyzed by Iridium Complexes 1–8^a

expt no.	complex, conditions	pH ^b	V _{H₂} (mL)	V _{CO₂} ^c (mL)	overall turnover ^d
1	1	7.0			
2	2a, 2c, 3a, dark ^e	7.0			
3	2a	5.0	0.6	0.6	3
		6.0	0.9	0.3	5
		7.0	1.1	0.2 (1.1)	6
		8.0	0.9	traces	5
		9.0	0.6	traces	3
		10.0	0.2		1
4	2a, 25 equiv bpy ^f	7.0	1.4	0.3 (1.4)	8
		8.0	1.2	traces	6
		10.0	0.3		1
5	2b	7.0	1.1	0.2	6
6	2c ^g	7.0	0.4	0.1	3
7	2d	7.0	1.1	0.2	6
8	3a	5.0	3.3	3.2	6
		6.0	7.2	2.0 (7.1)	38
		7.0	12.3	2.5 (12.2)	58
		9.0	11.0	traces	52
		10.0	9.1		43
		11.0	7.6		36
9	3b	2.0	1.5	1.5	8
		5.0	4.2	1.5 (4.1)	22
		7.0			
10	3c	2.6	0.3	0.2	1
		5.0	1.2	1.1	6
		7.0	0.6	0.1	3
11	3d ^h	5.0–9.0	traces		
12	3e	5.0			
		7.0	0.5	0.1	2
		9.0	1.2	traces	6
13	4a	5.0	3.9	3.8	19
		7.0	10.1	2.0 (9.8)	48
		9.0	12.9	traces	61
14	4b	5.0	4.3	4.2	20
		7.0	11.1	2.2 (10.6)	52
		9.0	11.3	traces	53
15	5a ⁱ	7.0	1.7	0.3 (1.6)	10
	5a, 15 equiv phen ^j	7.0	2.2	0.4 (2.1)	13
16	5b ^k	7.0	0.5	0.1	4
17	6	2.0	0.8	0.8	6
		5.0	2.5	2.4	20
		7.0	3.6	0.7 (3.4)	29
		9.0	2.2	traces	15
		11.0	0.7		5
18	7	2.0–7.0	traces		
19	8	7.0	7.9	1.6 (7.8)	37

^aAt room temperature and various pH. 2-h irradiation with white light ($\lambda > 400$ nm) of 15-mL solution containing $5\text{--}5.5 \times 10^{-4}$ M of complex. Each experiment has been performed twice and showed good reproducibility with an error of $\pm 5\%$. ^bAdjusted using a 0.01 M phosphate buffer. ^cBecause of the $\text{CO}_2\text{H}_2\text{O}/\text{HCO}_3^-$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$ equilibrium the stoichiometric amount of CO_2 was only obtained with a pH value lower or equal to 3. The values given in brackets were obtained by prior acidification of the solution with HCl (1 M). ^dCalculated by dividing the number of mol of H_2 obtained by the number of mol of the starting complex. ^eDark reaction with a 15 h contact time. ^fCompared to the starting Ir^{III} complex and added as a CH_3CN (0.5 mL) solution. ^g7.5 mL of 0.01 M phosphate buffer and 7.5 mL of CH_3CN . ^hDecoloration of the solution after a few minutes irradiation. ⁱA yellow product deposited on the wall of the flask during the irradiation.

Ir(III) complexes were studied. The effects of changing, (i) the monodentate ligand (active catalytic site), (ii) the chelate ligand (photosensitive part), (iii) the nature of substituent groups of the bidentate ligand (electronic effect), (iv) the substitution position of the electron withdrawing groups on the 2,2'-bipyridine ligand, were studied and are discussed below. In each of the complexes studied the Cp* unity remained unchanged.

(i) In order to investigate any effect of changing the chloro anion, the unsubstituted 2,2'-bipyridine complexes (2a–d) were studied. Replacement of the chloro anion by a more labile triflate (2b) (expt no. 3 and 5, Table I) or hydroxo (2d) (expt no. 7) ligand had no effect on the rate of reaction and the same efficiencies as for the chloro complex were observed. The thermal displacement

Table II. Photochemical WGSR Catalyzed by Complex 3a^a

expt no.	cata. concn (mM)	V _{H₂} (mL)	V _{CO₂} ^b (mL)	overall turnover ^c
20	0.045	3.5	0.7	62
21	0.093	7.0	1.4	209
22	0.156	12.0	2.4 (11.7)	214
23	0.200	15.9	3.9	221
24	0.233	18.9	3.8 (18.7)	225
25	0.389	19.0	3.8	136
26	0.576	19.6	3.9 (19.4)	95
27	0.794	20.1	4.0	70

^aAt room temperature and various catalyst concentrations. 3 h irradiation time with white light ($\lambda > 400$ nm) of 15 mL phosphate buffer (0.01 M) solution at pH = 7.0. ^bValues given in parentheses were obtained by prior acidification of the solution with HCl (1 M). ^cCalculated by dividing the number of mol of H_2 obtained by the number of mol of the starting complex.

Table III. Photochemical WGSR Catalyzed by Complex 3a as a Function of Time^a

expt no.	time (h)	pressure of CO ^b (atm)	V _{H₂} (mL)	V _{CO₂} (mL)	overall turnover ^c	turnover freq ^d
28	1	<1	6.0	1.2	32	32
29	2	<1	10.8	2.2	58	29
30	3	<1	14.0	2.8	75	25
31	4	<1	16.8	3.3	90	23
32	6	<1	19.8	3.9	106	18
33	7	<1	20.5	4.1	110	16
34	1	1	6.0	1.2	32	32
35	2	1	12.1	2.4	65	33
36	3	1	17.9	3.5	96	32
37	4	1	24.3	4.8	130	33
38	6	1	35.9	7.1	182	32
39	7	1	41.8	8.3	224	32

^aAt room temperature. White light ($\lambda < 400$) irradiation of 15 mL phosphate buffer (0.1 M) solution containing 6.4×10^{-4} M of complex, at pH = 7.0. ^bExpt 27–32, the internal pressure of CO continually decreased during the catalysis, whereas in expt 33–38 P_{CO} was maintained constant and adjusted to 1 atm every hour. ^cCalculated by dividing the number of mol of H_2 obtained by the number of mol of the starting complex. ^dCalculated by dividing the number of mol of H_2 obtained per hour by the number of mol of the starting complex.

of Cl⁻ by CO (formation of the first intermediate of the catalytic cycle) appears therefore not to limit the efficiency of the process. The hydride complex 2c showed some loss of activity with respect to the chloro complex (expt no. 6); however, this can be explained by its low solubility in water requiring the addition of CH_3CN (50%) which probably strongly perturbed the catalysis by competitive coordination of CH_3CN to the Ir(III) center.

(ii) The use of various polypyridine chelates showed that 1,10-phenanthroline ligands increase the efficiency compared to the 2,2'-bipyridine analogues (expt no. 3 and 15 in Table I). It should, however, be noted that because of the low solubility of complex 5a in the presence of a CO atmosphere, this system is kinetically unstable, as has been previously observed.³¹ Introduction of a water soluble sulfonate group into the phen ligand (6) gave a much more active and stable catalyst (expt no. 17 in Table I). Coordination studies of the 2,2':6',2''-terpyridine ligand with $\text{Ir}_2\text{Cp}^*_2\text{Cl}_4$ showed the complex 7 to be monocharged (electrospray mass spectrometry, see expt no. part), the ligand being bidentate with one uncoordinated pyridine. No catalytic activity of this complex was observed suggesting that the catalytic site could be blocked by a uncoordinated pyridine. Hence the single vacant site created by anion loss plays an important mechanistic role (vide supra) also observed by the total inhibition of the WGSR in the presence of 25 equiv of either pyridine or triphenylphosphine with $[\text{Cp}^*\text{Ir}(\text{bpy})\text{Cl}]^+ 2a$ photolyzed under standard conditions.

(iii) A remarkable increase in catalytic activity (by one order of magnitude) was observed when the nonsubstituted 2,2'-bipyridine ligand in complex 2a was substituted with electron withdrawing groups such as $-\text{COOH}$ (complexes 3a and 4a), $-\text{COO}i\text{Pr}$ (complex 3b), or $-\text{SO}_3\text{H}$ (complex 4b). Conversely, a decrease in activity was observed when an electron donating substituent such as $-\text{NMe}_2$ (complex 3e) was used (see Table I).

This clearly demonstrates that the substituents on the bipyridine strongly affect the rate limiting step of the process, via an electronic effect. Indeed, the activation energy of the overall process is decreased by a factor 2 in the presence of two carboxylate substituents (e.g., for complex **3a**, vide supra). The presence of electron withdrawing groups on the bipyridine chelate decreases the electron density on the iridium center. As a consequence the metal only weakly coordinates CO, compared to the unsubstituted parent compound, as indeed observed by FT-IR. An increase of the stretching frequency by 26 cm^{-1} was determined for the carbonyl intermediate **A** starting from the carboxylate substituted complex **3a**. This effect clearly affects all the subsequent steps of the catalytic cycle. This straightforwardly demonstrates the role of thermal processes coupled to the photochemical ones. To our knowledge these points have only received very limited attention in the literature and for the first time are clearly shown here. It has, however, previously been demonstrated that the excited states properties of luminescent ruthenium⁴⁷ or osmium⁴⁸ metal complexes could be controlled by substitution of 2,2'-bipyridine chelates with electron withdrawing or donating groups. Analogous substituent effects on the 2,2'-bipyridine ligand in related rhodium complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}^{\text{III}}(\text{bpyRR}')(\text{H}_2\text{O})]\text{Cl}_2$ have recently been studied. Their effects on electrochemical behavior and their effectiveness as redox catalysts toward the reduction of NAD(P)^+ to NAD(P)H was also recently investigated.⁴⁹

(iv) It is worth noting that the substitution position of the carboxylate on the bpy had some influence on catalytic activity (compare expt no. 8, 4,4'-position) and expt no. 13 (5,5'-position) in Table I). The absence of catalytic activity of the NO_2 substituted bpy (complex **3d**) was due to a light assisted hydrolysis of the NO_2 group, followed by loss of the ligand (this was monitored by the disappearance of the metal-ligand charge transfer absorption band at $\lambda_{\text{max}} = 486 \text{ nm}$).

Thus, the order of catalytic activity of the various complexes with respect to CO oxidation is $\text{bpy-4,4'-(COOH)}_2 \sim \text{bpy-5-SO}_3\text{H} > \text{bpy-5,5'-(COOH)}_2 \gg \text{bpy-4,4'-(COO}i\text{Pr)}_2 > \text{phen-C}_6\text{H}_4\text{-(SO}_3\text{Na)}_2 > \text{phen} > \text{bpy} \gg \text{bpy-4,4'-(NMe}_2)_2 \sim \text{bpy-4,4'-(Br)}_2$. This order does not seem to vary with pH as demonstrated for complexes **2a**, **3a**, and **6** over a large range of pH values (see Figure 1). The order of catalytic activity largely reflects the basicity of the nitrogen-containing ligand, which in turn influences the electron density at the cationic iridium center. Lower electron density on the iridium facilitates nucleophilic attack of water on the carbonyl intermediate (formed by CO displacement of the Cl^-) and thus to a faster formation of the iridium(I) and iridium(III)-hydrido intermediates (see mechanistic section).

(c) **Activation Energies.** In order to gain more insight into the mechanism of this reaction we have studied the effect of temperature on the rate of H_2 formation. The results obtained are collected in Table IV, for three complexes (**2a**, **3a**, and **3b**). The rate of the WGSR (r in $\mu\text{mole H}_2\text{-h}^{-1}$) was studied between 15 and 45 $^\circ\text{C}$; the exothermic nature of the reaction does not favor it at higher temperatures. Activation energies (E_a) of 29.6, 22.2, and of 14.6 kJ mol^{-1} were found for complexes **2a**, **3b**, and **3a**, respectively. Assuming that the photochemical step has a very low activation energy,^{50,51} the values measured in Figure 4 indicate, by comparison with similar values obtained in *thermal WGS* processes described in the literature,^{5,20b} that decarboxylation of intermediate **B** (Scheme II) is clearly the rate limiting step. Other

(47) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Skarda, V.; Thomson, A. J. *J. Chem. Soc., Perkin Trans. II* 1984, 1293.

(48) Ciana, L. D.; Dressick, W. J.; Sandrini, D.; Maestri, M.; Ciano, M. *Inorg. Chem.* 1990, 29, 2792.

(49) Steckhan, E.; Herrmann, S.; Ruppert, R.; Dietz, E.; Frede, M.; Spika, E. *Organometallics* 1990, 10, 1568.

(50) In general, photochemical processes are fast and therefore their activation energy cannot be high (see for instance ref 51). If the activation energy of the photochemical step is large, the photochemical reaction would be slow and the radiationless decay would prevail, so that the quantum yield would be low. A high quantum yield (12.7%) has been measured for this system, so the hypothesis that the activation energy of the photochemical step is negligible compared to that of the thermal step seems therefore reasonable.

(51) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: New York, 1970.

Table IV. Photochemical WGSR Catalyzed by Complexes **2a**, **3a**, **3b**, as a Function of Temperature^a

expt no.	complex, conditions	T (K)	V _{H₂} (mL)	V _{CO₂} ^b (mL)	turnover freq ^c
40	2a , pH = 7.0	313	0.63	0.12 (0.61)	8
41	2a , pH = 7.0	308	0.47	0.09 (0.45)	6
42	2a , pH = 7.0	303	0.39	0.07 (0.36)	5
43	2a , pH = 7.0	298	0.31	0.06 (0.29)	4
44	2a , pH = 7.0	291	0.24	0.05 (0.21)	3
45	2a , pH = 7.0	289	0.24	0.05 (0.22)	3
46	3a , pH = 7.0	313	3.29	0.65 (3.25)	42
47	3a , pH = 7.0	308	2.90	0.58 (2.86)	37
48	3a , pH = 7.0	303	2.59	0.52 (2.58)	33
49	3a , pH = 7.0	298	2.35	0.57 (2.31)	30
50	3a , pH = 7.0	293	2.20	0.44 (2.12)	28
51	3a , pH = 7.0	289	2.04	0.40 (2.01)	26
52	3b , pH = 5.0	313	1.57	1.50	20
53	3b , pH = 5.0	308	1.33	1.28	17
54	3b , pH = 5.0	303	1.18	1.13	15
55	3b , pH = 5.0	298	1.02	0.98	13
56	3b , pH = 5.0	293	0.86	0.83	11
57	3b , pH = 5.0	289	0.78	0.75	10

^a 1-h irradiation time with white light ($\lambda > 400 \text{ nm}$) of 10 mL phosphate buffer (0.01 M) solution containing $3.2 \times 10^{-4} \text{ M}$ of complex. The solution was kept in the dark during 20 min for thermal equilibrium. ^b Values given in parentheses were obtained by prior acidification of the solution with HCl (1 M). ^c Calculated by dividing the number of mol of H_2 obtained per hour by the number of mol of the starting complex.

Table V. Quantum Yields of H_2 and CO_2 Formed in the WGSR Catalyzed by Complex **3a**^a

expt no.	irradiation wavelength (slits) nm	pH	V _{H₂} (mL)	Φ_{H_2} ^b (%)	V _{CO₂} ^c (mL)	Φ_{CO_2} ^d (%)
58	370 ± 10	7.0	1.15	7.0	0.23 (1.13)	6.9
59	390 ± 10	7.0	0.73	9.8	0.15 (0.68)	9.1
60	410 ± 10 ^e	7.0	1.88	12.7	0.34 (1.86)	12.6
61	420 ± 10	7.0	1.73	12.6	0.35 (1.71)	12.5
62	442 ± 10	7.0	2.08	11.6	0.42 (2.06)	11.5
63	500 ± 10	7.0	0.58	8.5	0.12 (0.54)	7.9
64	550 ± 10	7.0	1.41	5.7	0.28 (1.39)	5.6
65	410 ± 5 ^e	5.0	0.46	3.4	0.44	3.3
66	410 ± 5 ^e	7.0	1.69	12.5	0.34 (1.67)	12.4
67	410 ± 5 ^e	9.0	1.51	11.2	(1.49)	11.1

^a 2-h irradiation with monochromatic light of 5 mL phosphate buffer (0.01 M) containing $1.8 \times 10^{-3} \text{ M}$ of complex **3a**, at room temperature. ^b Calculated by dividing the number of mol of H_2 by the number of photons determined by chemical actinometry. ^c Values given in parentheses were obtained by prior acidification of the solution with HCl (1 M). ^d Calculated by dividing the number of mol of CO_2 by the number of photons determined by chemical actinometry. ^e Light intensity determined by chemical actinometry⁴² was $3.06 \times 10^{-6} \text{ einstein min}^{-1} \text{ cm}^{-2}$ for expt 60 and $5.41 \times 10^{-7} \text{ einstein min}^{-1} \text{ cm}^{-2}$ for expt 65–67.

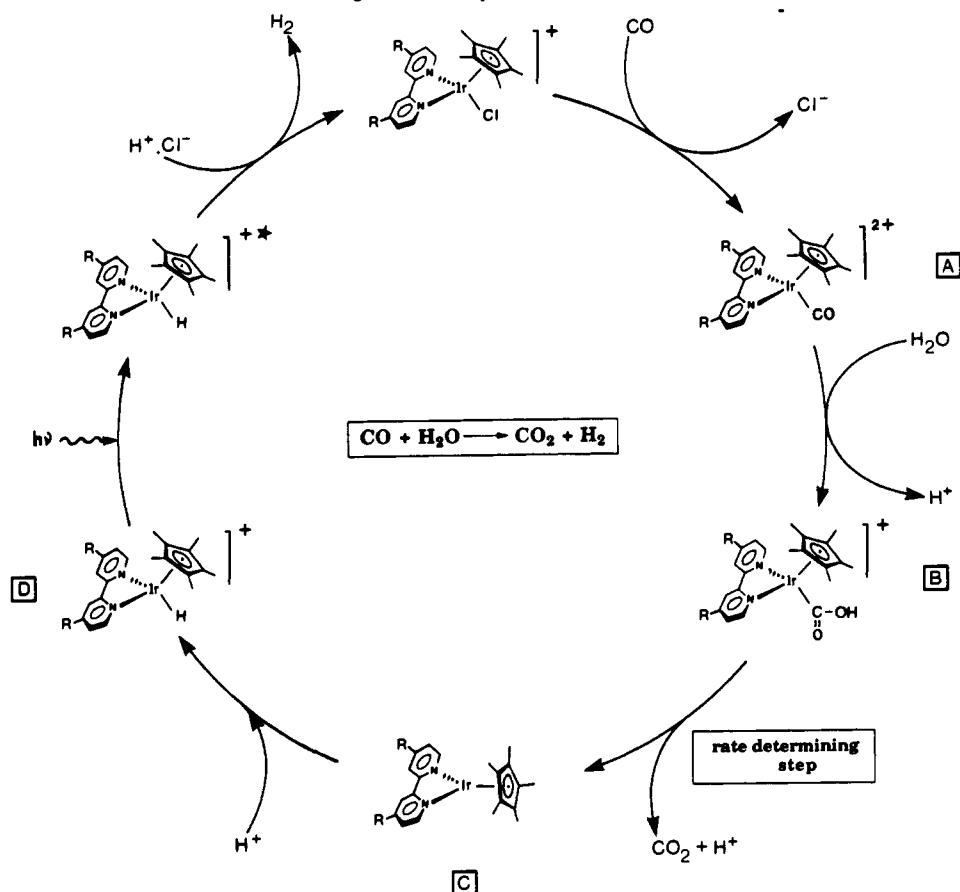
studies on systems having higher activation energies (96–100 kJ mol^{-1}) show that the rate limiting step is no longer decarboxylation but the reductive elimination of H_2 .^{3b,23b} The presence of an electron withdrawing group on the 2,2'-bipyridine chelate clearly decreases the activation energy of the WGSR and thus favors the decarboxylation of the intermediate. This is in good agreement with the previous observation that classical organic acids are much easier to decarboxylate when an additional electron withdrawing group is present in the molecule.^{52,53}

(d) **Isolation and Reactivity of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{I}}(\text{bpy-4,4'-(COOH)}_2)]$, **8**, Intermediate C.** When a solution of complex **3a** (in phosphate buffer and CD_3CN 4:1) under CO was kept in the dark, an intensification of the yellow color ($\lambda_{\text{max}} = 410 \text{ nm}$) rapidly takes place and the solution ultimately turns orange. Complex **8** was isolated as orange monocrystals by low-temperature crystallization from the catalytic mother solution, in the dark, and

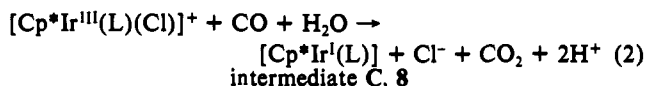
(52) Oae, S.; Tagaki, W.; Uneyama, K.; Minomido, I. *Tetrahedron* 1968, 24, 5283.

(53) Buncel, E.; Venkatachalam, T. K.; Menon, B. C. *J. Org. Chem.* 1984, 49, 413.

Scheme II. Proposed Reaction Mechanism for the Homogeneous Catalysis of the Photochemical WGSR



characterized by (NMR, FAB⁺ and UV-vis absorption spectroscopies) ($\lambda_{\text{max}} = 410 \text{ nm}$, $\epsilon = 1300 \text{ mol}^{-1} \text{ l cm}^{-1}$). The single crystal structure of complex **8** was recently determined and confirms (Figure 5) the absence of any coordinated anion as well as the absence of any counter anion, attesting that the oxidation state of the metal center is +1.⁵⁴ In addition, two Ir-C(Cp*) bond lengths appear to be significantly longer than the three other Ir-C(Cp*) bonds. This may be indicative of a (η^3 -allyl, ene) ring bonding mode of the Cp* ligand rather than a η^5 -Me₅C₅ ligand, a situation which has previously been found in [Cp*Rh(CO)₂].⁵⁵ This dissymmetry is also consistent with the observation that the bipyridine plane deviates (14.5°) from orthogonality with respect to the Cp* mean plane leading to a flattened basket shaped molecule (Figure 5b). During photocatalysis the color of the solution also deepened; however, it never turned deep orange, indicating that the stationary concentration of the intermediate is small during the optimal catalytic conditions. The same observations have been made for most of the complexes active in the photoinduced WGSR; however, isolation and characterization of the intermediate has only been achieved with the starting complex **3c**. The two electrons needed for the Ir(III) to Ir(I) reduction come from the CO, which is oxidized to CO₂ (global reaction in eq 2).



Complex **8** is an excellent catalyst for the WGSR (expt no. 19 in Table I) with a catalytic activity only 1.5 times lower than the corresponding $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{III}}(\text{bpy-4,4}'\text{-(COOH)}_2)\text{Cl}]^+$, **3a**, starting species. The absence of chloride anion in the solution might explain the small decrease of catalytic activity. The role of the chloride anion in the catalytic cycle has been discussed

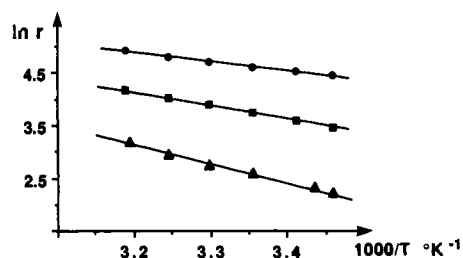


Figure 4. Effect of temperature on the rate r [$\mu\text{mol H}_2 \text{ min}^{-1}$] of the photochemical WGSR: $2.3 \times 10^{-4} \text{ M}$ of catalyst, complex **3a** (●), complex **3b** (■), and complex **2a** (▲), 1 atm CO, pH 7.0, 1-h irradiation.

elsewhere.³¹ $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{I}}(\text{bpy-4,4}'\text{-(COOH)}_2)]$, **8**, was proved to be one of the possible active intermediate of the WGSR-cycle by studying its thermal and photochemical reactivity toward protons, in the absence of CO. When complex **8** was allowed to react with H⁺,⁵⁶ in the dark, the formation of the characteristic hydride was observed ($\delta = -11.45 \text{ ppm}$, Figure 6 and eq 3).



One can assume that complex **8** reacts rapidly in these conditions as its proton spectrum (e.g., 6,6' proton resonance at 9.29 and Cp* proton resonance at 1.80 ppm, see expt part) cannot be observed simultaneously with that of the hydride (Figure 6a). Under these conditions⁵⁶ only 5% H₂ with respect to the starting Ir(I) complex **8**, were detected by GC (at even lower pH the yield of H₂ production was still very low). This yield increases to 84% after visible light irradiation. At the same time, the hydride signal rapidly decreases (Figure 6b after only 0.5-min photolysis) and finally disappears (Figure 6c after 2-min irradiation), which proves the high reactivity of $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{III}}(\text{L})(\text{H})]^+$ upon irradiation.

(54) Ziessel, R.; Matt, D.; Deronzier, A.; Chardon-Noblat, S.; Toupet, L.; Balgroune, F.; Granjean, D. *Acta Crystallogr. C*, in press.

(55) Lichtenberger, D. L.; Blewins, C. H.; Ortega, R. B. *Organometallics* 1984, 3, 1614.

(56) At pH ca. 5.0 [0.01 M phosphate buffer and CD₃CN (4:1 v/v)] in a vacuum sealed NMR tube, in the dark, with 15-min ultrasound (monocrystals dissolution).

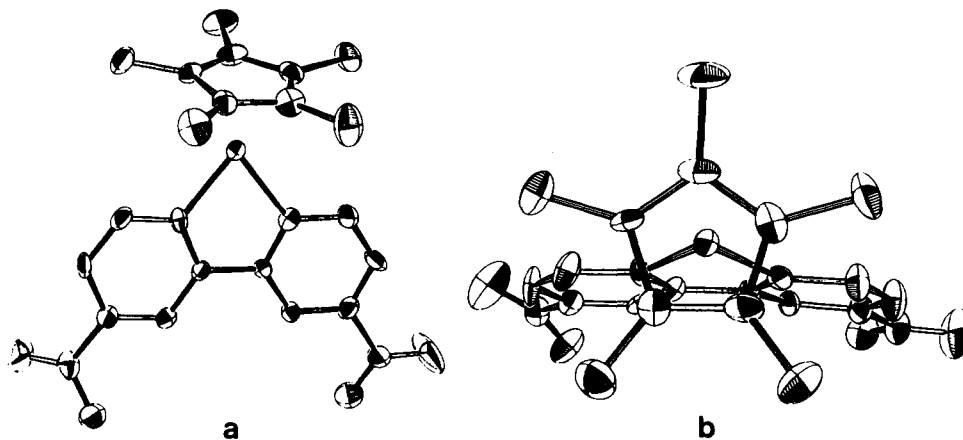


Figure 5. (a) Molecular geometry for $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{I}}(\text{bpy-4,4}'\text{-(COOH)}_2)]^+$, **8**. The ellipsoids are scaled to represent the 50% probability surface. Hydrogen atoms are omitted for clarity (from ref 54). (b) Molecular geometry for $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{I}}(\text{bpy-4,4}'\text{-(COOH)}_2)]^+$, **8**, viewed through the Cp* (centroid) and the iridium axis (from ref 54).

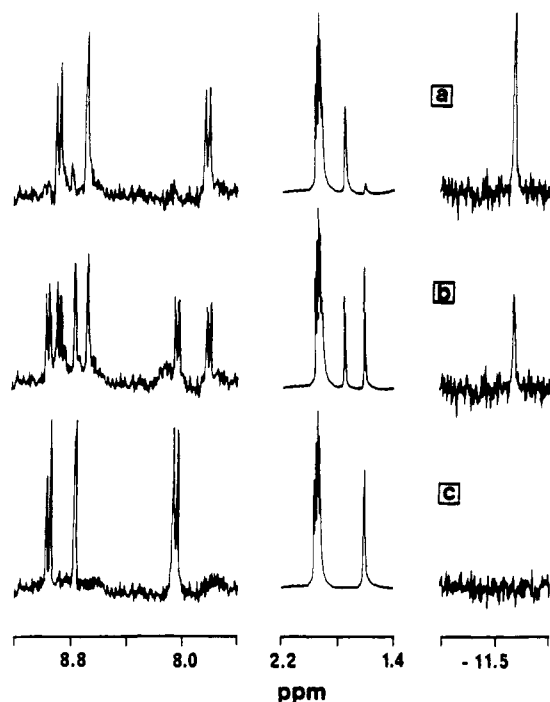


Figure 6. ^1H NMR spectra of a solution⁵³ containing $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{I}}(\text{bpy-4,4}'\text{-(COOH)}_2)]^+$, **8**, after 1 h in the dark (a), after 0.5 min photolysis (b), and after 2 min photolysis (c).

This could also indicate that there was some light contamination in the previous dark reaction. Based on its reactivity with protons, both in the dark and under irradiation, complex **8** is considered to be one of the intermediates of the WGSR. However, simultaneous direct decarboxylation from **B** to **D**, during the catalysis cannot be excluded.

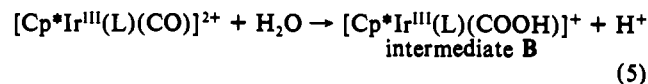
(e) ^1H , ^{13}C NMR, and FT-IR Studies. The photochemical conversion of ^{13}CO to $^{13}\text{CO}_2$ (and/or $\text{H}^{13}\text{CO}_3^-$) was also monitored by ^{13}C NMR spectroscopy, which showed the decrease in intensity of the ^{13}CO signal (182.0 ppm) along with the simultaneous increase of the $^{13}\text{CO}_2$ (123.0 ppm) and $\text{H}^{13}\text{CO}_3^-$ (157.8 ppm) resonances (Figure 7). ^{13}C NMR spectroscopy also showed the appearance, *in the dark*, of new resonances in the carbonyl, bpy, and Cp* region of the spectrum (Figure 7a). These signals are due to the formation of an iridium(III)-carbonyl compound (intermediate **A** in Scheme II) formed by thermal displacement of Cl^- (eq 4).



The $\text{Ir}^{\text{III}}\text{-CO}$ species, although not isolated, were characterized by ^{13}C NMR ($\delta = 178.2$ ppm for complex precursor **2a** and 180.1 ppm for complex precursor **3a**, using CD_3CN as internal standard),

FT-IR ($\nu_{\text{CO}} = 2069$ cm^{-1} for precursor **2a** and 2095 cm^{-1} for precursor **3a** in D_2O), and UV-vis absorption spectroscopy (broad bands centered at 402 nm for precursor **2a** and 410 nm for precursor **3a**). As previously observed the formation of this intermediate could be hindered by the presence, in solution, of competitor ligands such as triphenylphosphine or free pyridine, or by the presence of a pendant pyridine group (terpyridine complex **7**) in the coordination sphere of the iridium(III) metal center.

(f) Mechanistic Considerations. The catalytic cycle (Scheme II) involves the nucleophilic attack of water on intermediate **A** with formation of the hydroxy carbonyl intermediate **B** (eq 5), whose formation might also be strongly favored by the presence of an electron withdrawing group on the bpy ligand.



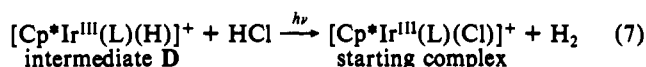
Related carboxylato- Ir^{III} -bpy derivatives⁵⁷ and exchange reactions of water oxygen with cationic carbonyl oxygen⁵⁸ have previously been described. An analogous ruthenium(II) complex $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CO})(\text{COOH})]^+$ obtained by nucleophilic attack of OH^- on $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CO})_2]^{2+}$ has been isolated and characterized by spectrophotometry and demonstrated to be one of the intermediates of a thermal WGSR.^{21b}

Decarboxylation of intermediate **B** (the rate limiting step, see activation energies section) gives the Ir(I) complex (intermediate **C**) (eq 6) which, after protonation, gives the photoactive hydrido- Ir^{III} complex^{31,32} (intermediate **D**) (eq 3).



Decarboxylation reactions of this kind are often involved in WGSR. For instance, $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CO})(\text{COOH})]^+$ gives CO_2 and $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CO})(\text{H})]^+$ has been extensively studied in the literature.^{21b}

Finally, molecular hydrogen and the starting complex were formed by a photochemical protonation of the hydrido complex (intermediate **D** in eq 7).



The photochemical nature of this last step was established as follows: (i) No H_2 was produced in the dark. (ii) When complexes **2a**, **3a**, and **3b** were kept in the dark under 1 atm of CO in a sealed NMR tube the ^1H NMR spectrum of the solution shows peaks at $\delta = -11.40$, -11.80 , and -12.09 ppm, respectively, for the appropriate hydride intermediates **D** in Scheme II. Formation of intermediate **D**, probably proceeds through the formation of an Ir(I) complex, as demonstrated in the case of complex **3a**.

(57) Albano, V.; Bellon, P. L.; Sansoni, M. *Inorg. Chem.* 1969, 8, 298.
 (58) Darensbourg, O. K. *Isr. J. Chem.* 1977, 15, 247.

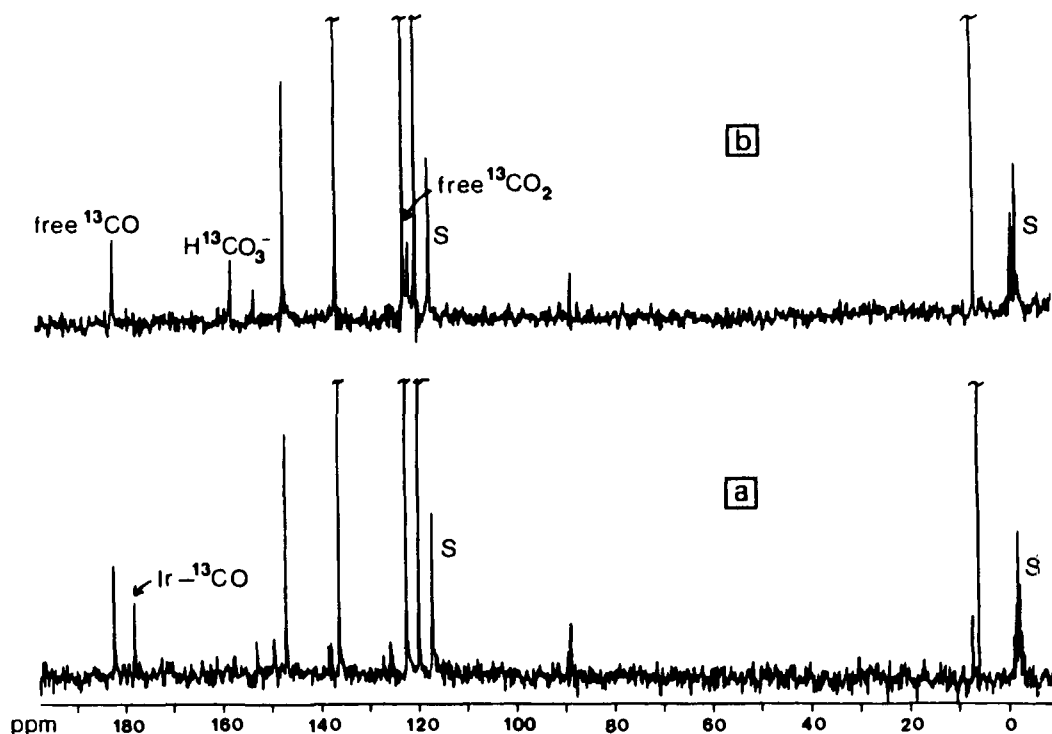
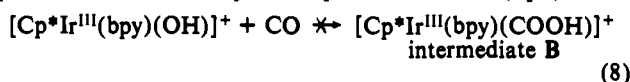


Figure 7. ^{13}C NMR spectra of a solution containing complex **2a** at pH ca. 5.0 [0.01 M phosphate buffer and CD_3CN (4:1 v/v)] in a sealed tube under a reduced pressure of ^{13}CO : (a) in the dark and (b) after 30 min photolysis.

Qualitatively, the hydride signal evolved somewhat faster when the chelate ligand was bpy-4,4'-(COOH)_2 than $\text{bpy-4,4'-(COO}i\text{Pr)}_2$, while both were faster than unsubstituted bpy . Unfortunately, due to experimental difficulties (e.g., beam quality, no temperature control, or stirring of the sample) these results could not be precisely quantified. The qualitative order of appearance of the hydride signals seems to follow the order of catalytic activity previously discussed, as well as the sequence of withdrawing power illustrated as the Hammett constants $\sigma_{\text{bpy COOH}} > \sigma_{\text{bpy COO}i\text{Pr}} > \sigma_{\text{bpy}}$.⁵⁹ All of the hydride signals disappeared after short photolysis times as observed in Figure 6.

(iii) Dissolution of isolated $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{III}}(\text{bpy})(\text{H})]^+$ ^{31,32} in a water/acetonitrile (1:1) solution, under vacuum in the dark resulted in no H_2 formation. However, upon irradiation near stoichiometric amounts of H_2 were generated. This also confirmed our observations for the reactivity of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{III}}(\text{bpy})(\text{H})]^+$ generated from $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{I}}(\text{L})]$ (section d and Figure 6).

We also found that only the hydrido complexes **2c** and **5b** exhibit a strong metal-to-ligand charge-transfer excited state, luminescent in CH_3CN solution at room temperature (λ_{em} 665 nm, excited-state lifetime τ° 80 ns for **2c** and λ_{em} 665 nm, τ° 190 ns for **5b** in CH_3CN solution at 293 K).⁶⁰ The corresponding chloro complexes **2a** and **5a** showed no interesting photophysical properties. Based on all these observations the photoassisted transformation of the hydride to H_2 is much faster than the other photochemical processes of the present system (e.g., photoinduced extrusion of Cl^- , photoassisted nucleophilic attack of H_2O on $\text{Ir}^{\text{III}}\text{-CO}$ or photoinduced reduction of intermediate B to C). The possibility that intermediate B could be formed by insertion of CO into an $\text{Ir}^{\text{III}}\text{-OH}$ (formed in basic media by displacement of the Cl^- anion) was ruled out by the absence of any thermal or photochemical reactivity of complex **2d** with CO (eq 8).



(g) **Catalysis of the WGSR Rather than Formate Decomposition.** Other systems¹⁹ have clearly shown that H_2 and CO_2 formation proceeds via decomposition of HCOO^- which was formed by reaction of CO with alkaline solution (under pressure and at high

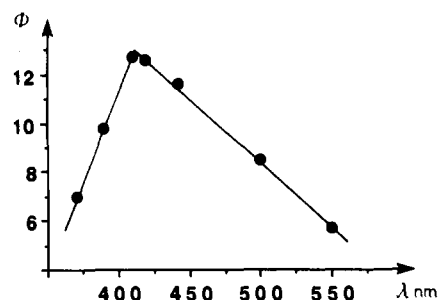


Figure 8. Quantum yield of the photochemical WGSR catalyzed by complex **3a**, as a function of the excitation wavelength (pH 7.0, 20 °C, 2-h irradiation).

temperature) and that the contribution of the true WGSR was only marginal. This has been proved to be the case for $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$), and other catalysts may function, at least in part, as formate decomposition catalysts. $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}^{\text{III}}(\text{L})\text{-Cl}]^+$, **3a**, is a modest catalyst for the photoconversion of HCOO^- into CO_2 and H_2 the observed turnover frequency being 2 h^{-1} at room temperature under visible light irradiation.⁶¹ Under the mild temperature, pressure and light conditions used, it is very unlikely that HCOOH could be formed in a system that is highly efficient for generating H_2 in the presence of CO. ^{13}C NMR spectroscopy (Figure 7), showed no $\text{H}^{13}\text{COO}^-$ ⁶² formation under ^{13}CO during the WGSR. In addition, typical activation energies for formate decomposition (ca. 146 kJ mol^{-1})^{19,20b} are much higher than the one measured in the present system.

(h) **Quantum yields (Φ).** Table V contains a compilation of quantum yield data obtained under a variety of experimental conditions. The key findings can be summarized as follows: (i) photoinduced WGSR in the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{bpy-4,4'-(COOH)}_2)\text{Cl}]^+$, **3a**, system occurs with a quantum efficiency that reaches 12.7% upon $410 \pm 5 \text{ nm}$ irradiation; (ii) H_2 and CO_2 production reaches a maximum value between 410 and 420 nm (Figure 8); (iii) Φ_{H_2} diminishes by increasing (to pH 9) or decreasing (to pH 5) the pH of the solution. This confirms earlier results obtained with white light;²⁸ (iv) Φ_{H_2} is independent of light

(59) Ritchie, C. D.; Sager, W. F. *Prog. Org. Chem.* 1967, 2, 323.

(60) Sandrini, D.; Maestri, M.; Ziessel, R. *Inorg. Chim. Acta* 1989, 163, 177.

(61) Watson, K. J.; Ziessel, R. *Inorg. Chim. Acta* 1992, 187, 125.

(62) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* 1985, 56.

intensity as observed in expt no. 60 and 66 (light intensity 3.06×10^{-6} and 5.41×10^{-7} einstein $\text{min}^{-1} \text{cm}^{-2}$, respectively). The WGSR of the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{III}}(\text{bpy-4,4'-(COOH)}_2)\text{Cl}]^+$ system is surprisingly efficient given the many steps involved in the process (Scheme II) and the requirement that the metal complex functions as both CO oxidation and H_2O reduction catalyst as well as photosensitizer. Its efficiency compares well with the highly specific photoinduced reduction of CO_2 to CO mediated by fac- $\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3\text{Cl}$.^{63,64} In this case also the quantum yield for CO formation reaches values as high as 15% despite the multielectron nature of the process.

Summary

The results of the present study lead to several conclusions regarding the mechanism of the photochemical WGSR catalyzed by the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{III}}(\text{L})\text{Cl}]^+$ complexes. (1) The process is both specific and efficient for the photoinduced oxidation of CO and reduction of H_2O . Quantum yields reach 12.7% with 410-nm irradiation and may prove to be higher in the presence of even more electron withdrawing groups (like $-\text{SO}_2\text{CH}_3$ or $-\text{CF}_3$) on the 2,2'-bipyridine chelate. (2) The initial thermal step in the overall reaction sequence involves the coordination of carbon

monoxide by displacement of the chloride anion. (3) A two electron reduction of the Ir(III) metal center generates the neutral $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{I}}(\text{L})]$ complex **8** which has been isolated and fully characterized. (4) Reactivity studies have proved that **8** is the key intermediate of the overall WGSR process. Oxidative addition of the proton on **8** gives the hydride complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{III}}(\text{L})(\text{H})]^+$ which has also been characterized. (5) The photochemical step of the catalytic cycle is the protonation of this hydride to give H_2 and the starting complex. (6) Activation energies show that decarboxylation of intermediate **B** is the rate limiting step. Moreover, the presence of an electron withdrawing group on the bpy chelate halves the activation energy and thus favors the decarboxylation of **B**. Finally, this new family of iridium(III) complexes provides excellent catalysts for the photoassisted WGSR.

Acknowledgment. We thank Professor V. Balzani, Dr. D. Matt, and Dr. K. J. Watson for helpful and stimulating discussions, Dr. C. de Bellefon for measuring FT-IR spectra, E. Piedmont for assistance in the determination of the quantum yields, M. Y. Guibert for performing the GC/MS analyses, P. Malt e for determining 400 MHz NMR spectra, S. Lips for technical assistance with the carbon dioxide GC analysis, A. Geyer for the glass blowing of the thermostated Schlenk cell, and D. Blitz for help with the preparation of the manuscript. Financial support for this work was provided by the Centre National de la Recherche Scientifique.

(63) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* 1986, 69, 1990 and references cited therein.

(64) Kutal, C.; Weber, M. A.; Ferrandi, G.; Geiger, D. *Organometallics* 1985, 4, 2161.

Metathetical Reactions of Re(VII) Alkylidene-Alkylidyne Complexes of the Type $\text{Re}(\text{CR}')(\text{CHR}')[\text{OCMe}(\text{CF}_3)_2]_2$ ($\text{R}' = \text{CMe}_3$ or CMe_2Ph) with Terminal and Internal Olefins

Robert Toreki, G. Alan Vaughan, Richard R. Schrock,* and William M. Davis

Contribution from the Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received June 25, 1992.

Revised Manuscript Received September 24, 1992

Abstract: 1-Decene and methyl 9-decenoate react with *syn*- and *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ to give *syn*- and *anti*- $\text{Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{Me}](\text{OR}_{\text{F}_6})_2$ and *syn*- and *anti*- $\text{Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Me}](\text{OR}_{\text{F}_6})_2$, respectively ($\text{OR}_{\text{F}_6} = \text{OCMe}(\text{CF}_3)_2$). The new alkylidene complexes are unstable in the presence of excess terminal olefin and decompose upon attempted isolation. However, vinylferrocene reacts relatively smoothly and reversibly with *syn*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ in a noncoordinating solvent to yield *tert*-butylethylene and primarily *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHFc})(\text{OR}_{\text{F}_6})_2$ (Fc = ferrocenyl). *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHFc})(\text{OR}_{\text{F}_6})_2$ ($a = 9.769$ (2) Å, $b = 30.746$ (7) Å, $c = 10.140$ (2) Å, $\beta = 116.78$ (1)°, $V = 2719$ (2) Å³, space group = $P2_1/a$, $Z = 4$, $\text{FW} = 815.50$, $\rho(\text{calcd}) = 1.992 \text{ g/cm}^3$, $R = 0.052$, $R_w = 0.050$) was shown to be a pseudotetrahedral species with an unusually acute $\text{Re}=\text{C}_\alpha-\text{C}_\beta$ angle (114.8 (7)°) and short $\text{Re}=\text{C}$ bond (1.70 (1) Å). In the presence of THF or dimethoxyethane, complexes of the type *syn*- or *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHR})(\text{OR}_{\text{F}_6})_2\text{S}_2$ ($\text{R} = \text{Me, Et, Ph}$; $\text{S} = \text{THF}$ or 0.5DME) could be prepared in high yield from $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ and $\text{CH}_2=\text{CHR}$. Heteroatom-substituted (O, S, or N) terminal olefins react more rapidly than ordinary olefins with $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ in the presence of THF to yield complexes of the type *syn*- or *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHX})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ ($\text{X} = \text{OR, SR, NR}_2$, or *p*-dimethylaminophenyl). The X-ray structure of *syn*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ ($a = 10.318$ (1) Å, $b = 18.303$ (2) Å, $c = 16.181$ (2) Å, $\beta = 96.98$ (2)°, $V = 3033$ (1) Å³, space group = $P2_1/c$, $Z = 4$, $\text{FW} = 819.74$, $\rho(\text{calcd}) = 1.795 \text{ g/cm}^3$, $R = 0.052$, $R_w = 0.050$) showed it to be a pseudooctahedral complex containing *cis* alkylidyne and alkylidene ligands and a THF ligand *trans* to each. The $\text{Re}-\text{O}$ bond to the THF *trans* to the neopentylidyne ligand is significantly longer than that *trans* to the ethoxymethylene ligand; presumably it is the THF ligand *trans* to the neopentylidyne ligand that exchanges more rapidly with free THF in solution. 2-Pentene or methyl oleate is metathesized in the presence of $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$, and intermediate alkylidene complexes can be observed in each case. Addition of 3-hexene to $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ followed by TMEDA yields $\text{Re}(\text{C-}t\text{-Bu})(\text{CHEt})(\text{OR}_{\text{F}_6})_2(\text{TMEDA})$. Internal olefins are metathesized only very slowly by $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ in the presence of several equivalents of THF or DME or especially in neat THF or DME.

Introduction

It is now well-established that many d^0 alkylidene complexes of Ti, Nb, Ta, Mo, or W will react with olefins¹⁻⁷ and that practical

olefin metathesis or ring-opening metathesis polymerization (ROMP) catalysts can be designed rationally by ligand variation.^{2,8}

(1) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986.

(2) Schrock, R. R. *J. Organomet. Chem.* 1986, 300, 249.

(3) Kress, J.; Aguero, A.; Osborn, J. A. *J. Molec. Catal.* 1986, 36, 1.

(4) Kress, J.; Osborn, J. A.; Amir-Ebrahimi, V.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* 1988, 1164.

(5) Grubbs, R. H.; Tumas, W. *Science* 1989, 243, 907.