Electrocatalytic Reduction of Carbon Dioxide by 2,2'-Bipyridine Complexes of Rhodium and Iridium

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Preparative studies on the complexes *cis*-[M(bpy)$_2$Cl$_2$]$^+$ have led to the isolation of *cis*-[M(bpy)$_2$(TFMS)$_2$]$^+$ (M is Rh^{III} or Ir^{III}; bpy is 2,2'-bipyridine; TFMS is the trifluoromethanesulfonate anion). The triflate complexes are reactive precursors that provide routes to new complexes such as *cis*-[Ir(bpy)$_2$H$_2$]$^+$ and are electrocatalysts for the reduction of CO$_2$. Electrocatalytic studies on *cis*-[Rh(bpy)$_2$X$_2$]$^+$ (X is Cl or TFMS) show that in the presence of CO$_2$ up to 80% of the current efficiency at an applied potential of −1.55 V (versus SSCE) in CH$_3$CN at a carbon-cloth electrode can be accounted for by the production of formate. The source of the formate proton is apparently the supporting electrolyte, [(*n*-Bu)$_4$N](PF$_6$), via the Hofmann degradation.

Although an attractive approach to the direct, noncatalyzed reduction of CO$_2$, electrochemical reduction at solid electrodes requires large negative potentials because of the formation of the high-energy one-electron-reduced intermediate CO$_2^-$.[1] The inherently large barrier arising from free CO$_2^-$ formation has been circumvented by the use of semiconductor electrodes, by using photoelectrochemical techniques, or by using transition-metal complexes as electrocatalysts.[2] Examples of transition-metal electrocatalysts for CO$_2$ reduction can be grouped into five classes; Co and Ni tetraaza macrocycles,[3] related phthalocyanine and porphyrin complexes,[4] metal clusters,[5] polypyridyl metal complexes such as *fac*-Re(bpy)(CO)$_3$Cl (bpy is 2,2'-bipyridine),[6] and the square-planar complex [Rh(diphos)$_2$]Cl (diphos is 1,2-bis(diphenylphosphino)ethane).[7] In most of these cases the catalyst precursor is capable of storing more than a single electron at potentials less negative than ca. −2.0 V and has the availability of at least one open coordination site after reduction. In several cases the metal complex undergoes reversible redox reactions that appear to be localized on one or more of the ligands.[6] In such cases subsequent reductive chemical transformations may well rely on the transfer of redox equivalents from the ligands to the metal, the ligands acting as an electron reservoir. The ability to store electrons in vacant π^* levels is one of the attractive features of polypyridyl complexes, and we have undertaken preparative and electrochemical studies in order to identify new polypyridyl-based electrocatalysts for CO$_2$ reduction.

Here we present the synthesis and redox chemistry of the complexes *cis*-[M(bpy)$_2$(OS(O)$_2$CF$_3$)$_2$]$^+$ (M is Rh(III) and Ir(III)) and the application of the Rh complex to the electrocatalyzed reduction of CO$_2$. Our results provide an example where the utilization of the electron reservoir[8] character of 2,2'-bipyridine

ligands promotes an apparently metal-centered reduction of CO$_2$.

Experimental Section

Measurements. Routine UV–vis spectra were recorded on a Bausch and Lomb Spectronic 2000 spectrophotometer. Infrared spectra were obtained on a Beckman IR 4250 spectrometer as mineral oil mulls or KBr pellets. A matched cell with neat solvent was placed in the reference beam for recording solution IR spectra. ^{1}H NMR spectral data were obtained on a Bruker WM-250 spectrometer, and ^{19}F spectral data were obtained with a Varian XL-100 instrument. In general, the gross coupling patterns are noted, although in some cases these are indistinct (in) and unresolved.

Electrochemical Measurements. Electrochemical measurements were made with a PAR Model 173 potentiostat/galvanostat equipped with a PAR 179 digital coulometer. Triangle wave forms for cyclic voltammetry were generated by using a home-built apparatus. Current–potential or current–time curves were recorded on a Hewlett-Packard Model 7015B X-Y recorder.

Cyclic voltammetry experiments were carried out in simple one-compartment cells with Pt-button or C-button working electrodes (Bioanalytical Systems), saturated calomel (SCE) or saturated sodium chloride calomel (SSCE) reference electrodes, and Pt-wire auxiliary electrodes. The electrodes were supported by a Teflon lid that was held in place by Parafilm while the interior was constantly flushed with argon.

Controlled-potential electrolysis (coulometry) experiments were performed by using a home-built three-compartment cell. The design incorporates the basic features necessary for accurate coulometry, namely a circular arrangement of the working electrode relative to the auxiliary electrode, separation of the working and auxiliary compartments with a fine-porosity glass frit, and isolation of the reference compartment with glass capillary tubing. The last feature is important, since it allows SCE electrodes to be used with negligible contamination of the working compartment by Cl$^-$ and H$_2$O. O-ring connectors (ACE Glass No. 5027-20) were found to be particularly convenient since they provided for the facile insertion of electrodes with minor variation in diameter. Also, analysis of gases above the solution showed negligible leakage of air, especially when the auxiliary solution was constantly sparged with Ar or CO$_2$. Working electrodes were either Pt gauze or carbon cloth,[12] while the reference and auxiliary electrodes were the same as those described above for cyclic voltammetry. Designs for this equipment can be obtained from the authors.

In a typical procedure, the reference, working, and auxiliary compartments were filled with 1.0, 10.0, and 4.0 mL of electrolyte solution, respectively. The working compartment was then purged with Ar for 10 min, a cyclic voltammogram was recorded, and constant-potential electrolysis was conducted at the same potential as the subsequent catalysis experiment. For potentials used in these experiments the current measured in this manner were less than 0.1 C if the electrolyte, solvent, and cell were acceptably clean and pure. The metal complex was then added to the working compartment and the system purged with Ar or CO$_2$ (99.8%) for at least 20 min. For long-term electrolysis experiments (greater than 20 C) in acetonitrile, it was found that the solution in the auxiliary compartment turned brown and malodorous and exhibited a tendency to flow into the working compartment. However, if 0.25 mL of H$_2$O was added to the auxiliary compartment, the solution stayed clear, bubbles of O$_2$ emanated from the auxiliary electrode, and there was much less tendency of the solutions in the two compartments to mix. The auxiliary solution was constantly purged during the long-term experi-

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ments with the same gas used in the working compartment.

The carbon-cloth electrode (Union Carbide Corp., VCA grade) was constructed by cementing a thin copper wire to the cloth with carbon paint (SPI Supplies). Under conditions similar to those used in catalysis experiments, oxidation of ferrocene solutions in acetonitrile gave *n* values of 0.9–1.1. In later experiments, it was found that a necessary condition for a successful carbon-cloth electrode is a resistance between the copper wire and the furthest extremity of the electrode of less than 10 Ω. However, samples of VCA grade carbon cloth from a different batch were observed to have very high resistance (several hundred ohms) and were unacceptable for use as coulometric electrodes. Other types of carbon cloth (i.e. graphite cloth, WCA grade) were also found to have the necessary low-resistance characteristics.

Coulometric experiments also were conducted inside a nitrogen-filled drybox with conventional H-cells. The reference electrode was conveniently made by opening a Ag/AgCl electrode (Bioanalytical Systems), removing the aqueous KCl solution, soaking the Vycor frit in acetonitrile for 24 h, refilling with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) in acetonitrile, and then replacing the Ag/AgCl wire. An electrode made in this fashion was robust, easy to manipulate in the drybox, and stable with less than 10-mV drift during the course of an experiment.

Gas Chromatographic Analyses. GC analyses were carried out with a Varian 1400 instrument equipped for $^1/_4$ in. o.d. glass columns and flame ionization detection (FID), a home-built low-temperature (−78 °C) gas chromatograph with an alumina column and thermal conductivity detection (TCD), or a Hewlett-Packard 5890A gas chromatograph equipped for $^1/_8$ in. o.d. stainless steel columns and either FID or TCD detection. Carbon monoxide was analyzed with the HP chromatograph on acid-washed 5A molecular sieves at 125 °C with the carrier gas at 35 psi inlet pressure. Hydrogen was analyzed on the low-temperature chromatograph with Ar carrier gas (40 psi). Tri-*n*-butylamine was analyzed with the HP chromatograph on 5% SE-30 over Chromosorb W-HP at 150 °C with nitrogen carrier gas (25 psi). Formate was converted to the methyl ester by taking a 1.0-mL aliquot of the catalysis solution and treating it with an excess (approximately 25 mg) of [Me$_3$O][SbCl$_6$]. This solution was then immediately analyzed with either the Varian or the HP chromatograph on 10% Carbowax 20m over Chromosorb W-HP at 60 °C (1 mm) to 140 °C (1 min) at 20 °C/min with nitrogen carrier gas (30 psi). The esterification reaction was continued, as described above, until the CH$_3$O$_2$CH peak reached a maximum, constant height. Carbonate (bicarbonate) was analyzed by evaporating the catalysis solution to dryness in a single-necked flask of known volume. The flask was fitted with a septum, and the gas within the flask was analyzed on Porapak Q at 75 °C with helium carrier gas (40 psi). Concentrated sulfuric acid (1.0 mL) was injected into the flask, and the gas was again sampled. This procedure was repeated until the carbon dioxide peak had reached a maximum and constant height.

Materials. Water was deionized and distilled from alkaline permanganate. Methanol (distilled over NaOCH$_3$), acetonitrile (distilled over CaH$_2$), and dichloromethane and 1,2-dichloroethane (distilled over P$_2$O$_5$) were all stored over activated molecular sieves after distillation. Acetone was distilled from anhydrous CaCO$_3$, and THF was distilled from sodium benzophenone ketyl prior to each use. Aromatic solvents were dried by azeotropic distillation prior to each use. All other solvents were reagent grade and were used without further purification. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) for electrochemical experiments was recrystallized twice from boiling 50/50 EtOH–H$_2$O, dried, recrystallized from CH$_2$Cl$_2$–Et$_2$O, and stored under vacuum. Several other purification procedures were tried, but as judged by the quality of solvent backgrounds in the electrochemical experiments, none were as good as the above method. 2,2′-Bipyridine, AgPF$_6$, and trifluoromethanesulfonic acid (TFMSH; the anion will be abbreviated TFMS) were obtained from Aldrich Chemical Co. All other materials were reagent grade and were used without further purification. 4,4′-Di-*tert*-butyl-2,2′-bipyridine (4,4′-(*t*-Bu)$_2$bpy) was a gift from Professor Joseph A. Connor of the University of Kent, Canterbury, England, and was used as received.

Preparations. The salts *cis*-[M(bpy)$_2$Cl$_2$]X·2H$_2$O (M = Rh, Ir; X = Cl, ClO$_4$, PF$_6$) were prepared and purified by literature procedures.[9,10]

***cis*-[Rh(bpy)$_2$(TFMS)$_2$]TFMS].** *cis*-[Rh(bpy)$_2$Cl$_2$]Cl·2H$_2$O (0.518 g, 0.930 mmol) was added to ca. 50 mL of *o*-dichlorobenzene under an inert atmosphere. After the addition of neat trifluoromethanesulfonic acid (0.50 mL, 5.6 mmol), the homogeneous solution was heated at reflux for 3 h. The solution was cooled to 0 °C and slowly poured into 100 mL of Et$_2$O at 0 °C. The mixture was stirred overnight and filtered to isolate the crude product. The solid so obtained was redissolved in acetonitrile, and the solution was filtered, evaporated to a small volume, and diluted with 25.0 mL of Et$_2$O. The off-white precipitate was collected by filtration and washed with acetone at −25 °C to remove a small amount

of a brown impurity. The yield of product was 0.372 g (46%).

Anal. Calcd: C, 32.03; H, 1.87; F, 19.83; N, 6.49; Cl, 0.00. Found: C, 32.21; H, 1.92; F, 19.69; N, 6.55; Cl, 0.83. ^{1}H NMR spectral data: (δ, relative to TMS): 9.33 (2 H, d), 8.68 (4 H, in), 8.50 (2 H, d), 8.22 (4 H, in), 7.52 (4 H, in). ^{19}F NMR: (relative to CFCl$_3$) −77.9 (s), −78.0 (s).

Spectroscopic (proton NMR data) and cyclic voltammetric evidence indicated the presence of trace amounts (<1%) of *cis*-[Rh(bpy)$_2$Cl-(TFMS)](TFMS) in the sample.

***cis*-[Rh(4,4′-(*t*-Bu)$_2$bpy)$_2$Cl$_2$]X (X = Cl, PF$_6$).** The synthetic procedure was very similar to that for the unsubstituted bipyridine complexes. The crude product was recrystallized from hot methanol–H$_2$O (1/1) to give essentially a quantitative yield of *cis*-[Rh(4,4′-(*t*-Bu)$_2$bpy)$_2$Cl$_2$]Cl. Methathesis with an excess of KPF$_6$ in boiling H$_2$O, followed by recrystallization from hot acetonitrile–H$_2$O, gave *cis*-[Rh(4,4′-(*t*-Bu)$_2$bpy)$_2$Cl$_2$](PF$_6$) in 60% yield (starting from 1.00 g of the chloride). Comparison of the cyclic voltammogram and the ^{1}H NMR spectrum of the product with that of *cis*-[Rh(bpy)$_2$Cl$_2$](PF$_6$) established the identity and purity of the product.

^{1}H NMR spectral data (δ, recorded in CH$_3$CN relative to TMS): 9.66 (2 H, d), 8.57 (2 H, d), 8.42 (2 H, in), 7.97 (2 H, dd), 7.42 (in).

***cis*-[Ir(bpy)$_2$Cl$_2$]TFMS].** To 200 mL of stirred CH$_3$CN was added 850 mg of *cis*-[Ir(bpy)$_2$Cl$_2$]Cl followed by ca. 30 drops of TFMSH (from a freshly opened ampule). After ca. 35 min the volume of the solution was reduced to ca. 150 mL by rotary evaporation and the resulting solution was filtered. The solid material left after this process was set aside and used in a separate synthesis. The filtrate was poured down a chromatography column (ca. 4 cm in diameter and 35 cm in length) that contained neutral alumina that had been packed in pure CH$_3$CN. Elution was begun with CH$_3$CN to give first a small orange band followed by a small lemon yellow band and finally a massive yellow band of the desired material. Continued elution resulted in a tiny amount of blue-green material that was discarded. Removing the solvent, isolating, and air-drying yielded 705 mg of product.

^{1}H NMR spectral data. (δ, recorded in CD$_3$CN with TMS as an internal standard): 9.77 (2 H, dd), 8.56 (2 H, d), 8.42 (4 H, overlapping multiplets), 8.08 (2 H, dd), 7.98 (2 H, m), 7.72 (2 H, dd), 7.39 (2 H, dt).

Anal. Calcd: C, 34.81; H, 2.21; N, 7.73. Found: C, 34.01; H, 2.43; N, 7.51.

***cis*-[Ir(bpy)$_2$(TFMS)$_2$]TFMS].** To ca. 60 mL of stirred *o*-dichlorobenzene was added 700 mg of *cis*-[Ir(bpy)$_2$Cl$_2$][TFMS] followed by 20 drops of TFMSH. The mixture was then put under a N$_2$ atmosphere and heated at reflux for 1 h. After this period, the reaction mixture was cooled to room temperature, another 20 drops of TFMSH were added, and this mixture was again brought to reflux for 2 h. When the mixture was cooled the second time, 300 mL of Et$_2$O was slowly added to the yellow-brown solution, which resulted in the precipitation of the finely divided pale yellow complex. The solid was washed copiously with Et$_2$O and dried with a vacuum pump at room temperature for 24 h; yield 890 mg (96%).

^{1}H NMR spectral data (δ, recorded in CD$_3$CN): 9.22 (2 H, d), 9.65 (2 H, d), 9.65 (4 H, overlapping multiplets), 9.13 (4 H, overlapping multiplets), 9.52 (2 H, dd), 9.42 (2 H, dt). Slight impurities that appear in the spectrum are *cis*-[Ir(bpy)$_2$Cl$_2$]$^+$ and an unknown complex that is assumed to be *cis*-[Ir(bpy)$_2$Cl(TFMS)]$^+$. Anal. Calcd: C, 28.48; H, 1.86; N, 5.78. Found (assuming one H$_2$O of hydration): C, 28.20; H, 1.79; N, 5.52.

[Ir(bpy)$_3$]PF$_6$]$_3$. To 10 mL of ethylene glycol was added 300 mg of bpy and 90 mg of *cis*-[Ir(bpy)$_2$(TFMS)$_2$][TFMS]. The solution was placed under an atmosphere of N$_2$ and then heated at reflux for 5 h. At the beginning of the heating period the solution turned orange but the orange color slowly faded to a pale yellow over the course of the reaction. After the solution was cooled to room temperature, 20 mL of aqueous NH$_4$PF$_6$ was added and this solution was cooled at 0 °C for 12 h. Filtration gave a pinkish white solid that was washed with ca. 10 mL of H$_2$O followed by CH$_2$Cl$_2$ and then Et$_2$O. The solid was dissolved in ca. 20 mL of 1/1 CH$_3$CN–H$_2$O to which 3 drops of 46% HPF$_6$ had been added. Slow removal of the CH$_3$CN gave 104 mg of an off-white powder that exhibited brilliant green emission under the short-wavelength irradiation of a hand-held mineral lamp.

^{1}H NMR spectral data (δ, recorded in CD$_3$CN): 8.67 (6 H, d), 8.40 (6 H, dt), 7.69 (12 H, overlapping multiplets). Anal. Calcd for a salt with three waters of hydration: C, 31.33; H, 2.61; N, 7.31. Found: C, 31.48; H, 2.24; N, 7.08.

***cis*-[Ir(bpy)$_2$H$_2$]PF$_6$].** To 20 mL of 4:1 H$_2$O/EtOH was added 150 mg of *cis*-[Ir(bpy)$_2$(TFMS)$_2$][TFMS] followed by 800 mg of KBH$_4$. The resulting mixture was placed under an atmosphere of N$_2$ and heated at reflux for 45 min. During the early stages of the reaction the solution turned deep green but slowly changed to orange-yellow. After the so-

Scheme I[a]

cis-[Ir(bpy)₂(TFMS)₂]⁺ →
- i → [Ir(bpy)₂(PPh₃)H]²⁺
- ii → [Ir(bpy)₂H₂]⁺
- iii → [Ir(bpy)₃]³⁺
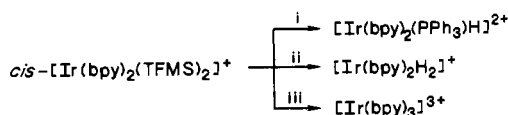
[a] Legend: (i) PPh₃, ethylene glycol, heat; (ii) KBH₄, ethanol–H₂O, heat; (iii) bpy, ethylene glycol, heat.

lution was cooled to room temperature, the addition of aqueous KPF₆ gave a bright orange-yellow product that was washed with H₂O and then air-dried. Column chromatography on neutral alumina using 2/1 followed by 1/1 toluene–CH₃CN resulted in the isolation of a yellow-orange, crystalline product in 65% yield (55 mg).

¹H NMR spectral data (δ, recorded in CD₃CN): 9.37 (2 H, d), 8.34 (4 H, dt), 8.06 (2 H, dt), 7.96 (2 H, dt), 7.76 (2 H, d), 7.45 (2 H, dt), 7.33 (2 H, dt) –17.90 (2 H, s). Anal. Calcd: C, 36.87; H, 2.76; N, 8.60. Found: C, 37.37; H, 2.93; N, 8.39.

cis-[Ir(bpy)₂(PPh₃)H][PF₆]₂. To 20 mL of ethylene glycol was added 150 mg of *cis*-[Ir(bpy)₂(TFMS)₂][TFMS] and 200 mg of PPh₃. The mixture was heated at reflux for 1 h, after which time the yellowish solution was cooled to room temperature, treated with 20 mL of aqueous KPF₆, and filtered. The yellowish filter cake was washed first with H₂O and then with Et₂O and air-dried. Column chromatography on neutral alumina using 2/1 followed by 1/1 toluene–CH₃CN as eluant gave a yellow band containing the pure complex. Slow removal of the solvent resulted in the microcrystalline product in 47% yield (77 mg).

¹H NMR spectral data (δ, recorded in CD₃CN): 8.55–8.02 (7 H, overlapping multiplets), 7.85 (1 H, dd), 7.54–7.40 (6 H, overlapping multiplets), 7.40–7.25 (15 H, overlapping multiplets), 7.19 (1 H, dt), 7.12 (1 H, dt), –17.84 (1 H, d). Anal. Calcd: C, 43.06; H, 3.02; N, 5.29. Found: C, 43.59; H, 3.08; N, 5.28.

Results and Discussion

Synthesis and Characterization of the Complexes *cis*-[M-(bpy)₂(TFMS)₂]⁺. The synthesis of the trifluoromethanesulfonato (triflato, TFMS) complexes was readily accomplished by the use of triflic acid in halogenated hydrocarbon solvents by using a procedure similar to that reported previously for the preparation of *cis*-Re(bpy)(CO)₃TFMS (eq 1).[13] For the Ir complex the

$$\text{cis-[M(bpy)}_2\text{Cl}_2\text{]}^+ + 2\text{TFMSH} \xrightarrow[\Delta]{o\text{-DCB}}$$
$$\text{cis-[M(bpy)}_2\text{(TFMS)}_2\text{]}^+ + 2\text{HCl} \quad (1)$$
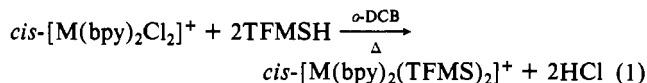
reaction shown in eq 1 was most efficiently carried out in a stepwise fashion, the first step involving metathesis of the outer-sphere counterion in *cis*-[Ir(bpy)₂Cl₂]Cl to give *cis*-[Ir(bpy)₂Cl₂][TFMS], followed by heating the complex with excess TFMSH to exchange for bound Cl⁻. Pure samples of [Rh(bpy)₂(TFMS)₂][TFMS] can be obtained in good yield by the direct reaction between *cis*-[Rh(bpy)₂Cl₂]Cl and an excess of neat triflic acid in refluxing 1,2-dichlorobenzene (DCB). However, the Ir reaction is best conducted by metathesis of *cis*-[Ir(bpy)₂Cl₂]Cl to *cis*-[Ir-(bpy)₂Cl₂][TFMS] followed by subsequent reaction of this salt with excess TFMSH in DCB at reflux. In both the Rh and Ir preparations small amounts of impurities (≲1%) appear in the isolated samples. They are most likely the salts *cis*-[M-(bpy)₂Cl(TFMS)][TFMS] as suggested by chlorine analyses and the presence of a small impurity wave in the cyclic voltammogram. While other halogenated solvents such as 1,2-dichloroethane can be used for the reactions, the complexes are more soluble in *o*-dichlorobenzene, where the reaction solution remains homogeneous, and the impurities resulting from incomplete reaction are minimized.

Distinctive Chemical Properties of *cis*-[Ir(bpy)₂(TFMS)₂]⁺. Iridium(III) complexes containing polypyridyl ligands are difficult to prepare and purify relative to the isoelectronic and isostructural analogues of Ru(II) or Os(II). The preparative chemistry of the [(bpy)₂Ir^III<] group is largely unexplored principally because of the kinetically sluggish rates for ligand substitution that necessitate rather forcing reaction conditions and lead to complicated product
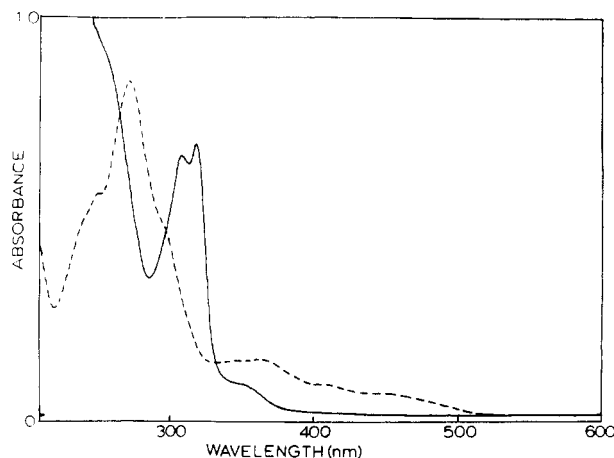
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Figure 1. Near-ultraviolet and visible spectrum of the two new hydrides [Ir(bpy)₂H₂][PF₆] (dashed line) and [Ir(bpy)₂(PPh₃)H][PF₆] (solid line), recorded in CH₃CN.
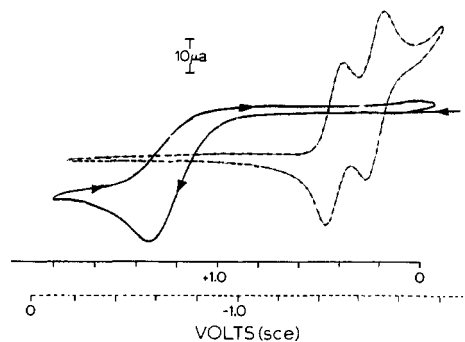

Figure 2. Cyclic voltammogram of [Ir(bpy)₂H₂][PF₆] recorded in 0.1 M TBAH–CH₃CN at a scan rate of 100 mV/s with a planar Pt working electrode.

distributions. The availability of the triflato complex provides a useful, general starting material to a family of Ir(III) complexes under relatively mild conditions.

Three characteristic reactions of *cis*-[Ir(bpy)₂(TFMS)₂]⁺ are shown in Scheme I. They include a new and improved synthesis of [Ir(bpy)₃]³⁺ [14] and the preparation of two new hydrido–bipyridine complexes.

The identification of the complexes was based on ¹H and ³¹P NMR spectroscopy, elemental analysis, UV–visible spectroscopy, and cyclic voltammetry (see Experimental Section). In Figure 1 are shown UV–visible spectra for *cis*-[Ir(bpy)₂H₂][PF₆] and *cis*-[Ir(bpy)₂(PPh₃)H][PF₆] in CH₃CN, and in Figure 2 is shown a cyclic voltammogram of *cis*-[Ir(bpy)₂(H₂)][PF₆] in 0.1 M TBAH–CH₃CN. Further exploitation of the preparative chemistry of *cis*-[Ir(bpy)₂(TFMS)₂]⁺ should yield a variety of complexes with interesting catalytic, photochemical, and structural properties.

Electrochemistry of the Rhodium and Iridium Complexes. Cyclic voltammetric data obtained for the Rh and Ir complexes in 0.1 M TBAH–CH₃CN at a Pt-button working electrode are summarized in Table I. For the complexes *cis*-[Ir(bpy)₂H₂]⁺ and *cis*-[Ir(bpy)₂(PPh₃)]⁺ and the well-studied[14] [Ir(bpy)₃]³⁺, chemically reversible reductions are observed at potentials expected for π*(bpy)-based reduction. Only one complex, *cis*-[Ir-(bpy)₂H₂]⁺, exhibits an oxidation wave more cathodic than +2.0 V, and that process is chemically irreversible.

Cyclic voltammograms for complexes of the type [Rh(bpy)₂X₂]⁺ (X = TFMS, Cl) in either CH₃CN or DMF with 0.1 M TBAH as supporting electrolyte show that an initial 2e reduction occurs at potentials that are similar for the triflato and chloro complexes (Table I, Figure 3). For either case, at a sweep rate of 200 mV/s, the coupled reoxidation wave is either completely absent or is very attenuated with a peak potential found at potentials more positive

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Table I. Cyclic Voltammetric Data for the Rh and Ir Bipyridine Complexes in 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)\text{-}CH_3CN$ vs the Sodium Chloride Calomel Electrode[a]

complex	$E_{p,a}$, V	$E_{p,c}$, V	$E_{1/2}$, V
$[Ir(bpy)_2(TFMS)_2][TFMS]$[b]	−0.94	−1.46	
	−1.16	−1.69	
	−1.34		
	−1.45		
$[Ir(bpy)_2H_2][PF_6]$[b]	+1.21[c]		
	−1.51	−1.44	−1.48
	−1.72	−1.64	−1.68
$[Ir(bpy)_2(PPh_3)H][PF_6]_2$[b]	−1.15	−1.09	−1.12
	−1.36	−1.29	−1.33
$[Ir(bpy)_3][PF_6]_3$[b]	−0.92	−0.86	−0.89
	−1.08	−0.97	−1.02
	−1.30	−1.18	−1.24
$[Rh(bpy)_2Cl_2][ClO_4]$[d]	−0.40	−0.92	
	−1.30	−1.39	−1.35
	−1.58	−1.72	−1.65
$[Rh(bpy)_2(TFMS)_2][TFMS]$[d,e]	−0.36	−0.84	
	−1.18	−1.26	−1.22
	−1.45	−1.55	−1.51
$[Rh(bpy)_2(TFMS)_2][TFMS]$[c]	−0.17	−0.36	
	−1.23[f]	−1.34	
	−1.52	−1.60[f]	
$[Rh(4,4'\text{-}(t\text{-}Bu)_2bpy)_2Cl_2][PF_6]$[c,e]	−0.29	−0.99	
	−1.35	−1.45	−1.40
	−1.64	−1.73	−1.68

[a] The sweep rate was 200 mV/s. For chemically reversible cases, $E_{1/2}$ values were calculated as the average of the anodic and cathodic peak potentials. [b] Pt-button working electrode. [c] Irreversible oxidation. [d] C-button working electrode. [e] DMF with 0.1 M TBAH as supporting electrolyte. [f] Partially obscured by an adsorption process.
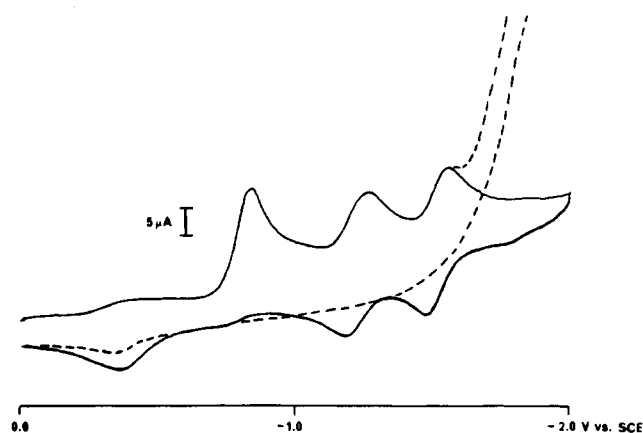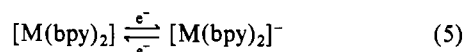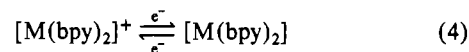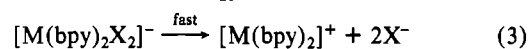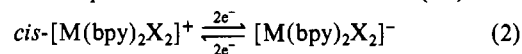

Figure 3. Cyclic voltammograms of cis-$[Rh(bpy)_2Cl_2][TFMS]$ in the absence (solid line) and presence (dashed line) of CO_2 recorded in DMF with 0.1 M TBAH at a carbon-button working electrode.

than $E_{p,c}$ by ~0.5 V for X = Cl. That the chemical process responsible for the irreversibility is loss of chloride ion during the reduction is supported by the observation that an oxidation wave appears at +1.0 V for the Cl_2/Cl^- couple. Our observations agree with those of Hanck, DeArmond, and co-workers on cis-[Rh(bpy)_2Cl_2]$^+$ under similar conditions.[15,16] At more negative potentials, two quasi-reversible, single-electron reductions appear at $E_{1/2}$ = −1.22 and −1.51 V. The cyclic voltammogram of $[Rh(4,4'\text{-}(t\text{-}Bu)_2bpy)_2Cl_2][PF_6]$ is very similar to that of the parent bipyridine complex except that the waves are shifted to more negative potentials by 0.16 V as expected for the greater σ electron donation of the tert-butyl groups attached to the bpy skeleton. The higher solubility of the complex made it useful for coulometry

(15) Kew, G.; DeArmond, K.; Hanck, K. W. *J. Phys. Chem.* **1974**, *78*, 727.
(16) Kahl, J. L.; Hanck, K. W.; DeArmond, K. *J. Phys. Chem.* **1978**, *82*, 540.

studies since the reduced complex remains soluble under the conditions of the experiment.

Preparative-scale reduction of $[Rh(4,4'\text{-}(t\text{-}Bu)_2bpy)_2Cl_2]^+$ in DMF at −1.00 V vs Ag/AgCl resulted in the passage of 2 e/Rh and the generation of an intense purple solution. Further reduction at −1.90 V occurred with n = 1.5 e/Rh rather than the expected 2 e/Rh. Sequential reoxidations were conducted first at −1.00 V, where n = 1.0 e/Rh and subsequently at 0.00 V, where n = 1.0 e/Rh. Cyclic voltammograms between each of the electrolysis steps were very similar to that of the initial solution. These results suggest that the reduced complex is not indefinitely stable under our conditions possibly because of trace oxygen or solvent impurities.

On the basis of our results, and those of Hanck, DeArmond, and co-workers,[15] the common pattern of reactions shown in eq 2–5 appears to take place for the reduction of the Rh(III) complexes.

$$cis\text{-}[M(bpy)_2X_2]^+ \underset{2e^-}{\overset{2e^-}{\rightleftharpoons}} [M(bpy)_2X_2]^- \qquad (2)$$

$$[M(bpy)_2X_2]^- \xrightarrow{fast} [M(bpy)_2]^+ + 2X^- \qquad (3)$$

$$[M(bpy)_2]^+ \underset{e^-}{\overset{e^-}{\rightleftharpoons}} [M(bpy)_2] \qquad (4)$$

$$[M(bpy)_2] \underset{e^-}{\overset{e^-}{\rightleftharpoons}} [M(bpy)_2]^- \qquad (5)$$

plexes. For several Ir complexes the "two-electron" step in reaction 2 can be resolved into sequential single-electron steps.[16]

The electrochemistry of the rhodium complexes was also examined in acetonitrile, since it was the solvent of choice for the CO_2 reduction studies. Here, the cyclic voltammogram of cis-$[Rh(bpy)_2Cl_2](ClO_4)$ agrees with that reported previously.[15] The first reduction occurs at $E_{p,c}$ = −0.92 V, compared to a reported value of −0.84 V. The second and third reductive waves occur at $E_{p,c}$ = −1.39 and −1.72 V, compared to earlier values of −1.46 and −1.67 V. The slight discrepancies probably arise from adsorption effects due to the higher concentrations used in our work which were close to saturation in metal complex.

There are significant differences in the initial 2e reduction of the triflato complex compared to that of the chloro complex. For example, the separation between the anodic and cathodic peak potentials is only 0.19 V compared to 0.52 V for the chloro complex. The shape and position of the reduction wave are affected by the electrode material, and the wave appears more reversible at a carbon electrode than at a platinum electrode. That the triflate complex does not solvolyze in CH_3CN was demonstrated by ^{19}F NMR spectral studies that show two resonances in a 2/1 ratio; this pattern is consistent with two coordinated triflates and a single triflate counterion.

Current enhancement is observed in cyclic voltammograms of solutions saturated in CO_2, but only for the second of the two reversible, bpy-based reductions of $[Rh(bpy)_2]^+$ (Figure 3). The electronic structure of the first reduction product, $[Rh(bpy)_2]^0$, has been investigated by EPR spectroscopy. The results of that study led to the conclusion that the added electron occupies an orbital which is a mixture of metal $d\pi$ and bipyridine π^* orbitals.[15,16] In a related study of $[Rh(bpy)(diene)]^n$ (n = 0, 1−; diene = cyclooctadiene, norbornadiene) it also appears that the redox orbitals are extensively mixed.[17] The conclusions reached are based on the similarity of the EPR signals to that for bpy$^-$ and on the absence of Rh hyperfine coupling. Thus, even though there is some metallic character in the acceptor orbitals, they remain largely π^*(bpy) in character and therefore point toward the role of the polypyridyl ligands as "electron reservoirs".

Electrocatalytic Reduction of CO_2. Current enhancements in CO_2-saturated CH_3CN, which are indicative of the electrocatalyzed reduction of CO_2, are observed for all of the complexes except $Ir(bpy)_3^{3+}$ and cis-$[Ir(bpy)_2H_2]^+$ in the region −1.2 to −1.6 V (see Table II). The latter two complexes were not investigated as CO_2 reduction catalysts. We describe here, in a detailed way,

(17) Fordyce, W. A.; Pool, K. H.; Crosby, G. A. *Inorg. Chem.* **1982**, *21*, 1027.

Table II. Electrocatalytic Reduction of CO_2 with the Catalyst *cis*-[Rh(bpy)$_2$(TFMS)$_2$][TFMS] in CH_3CN^a

expt no.	electrode	amt of current, C				turnovers^d
		total^b	H$_2$	HCO$_2^{-c}$	NBu$_3$	
1	C	66.8	e	82.6	e	6.8
2	C	77.0	12.6	64.3	e	8.0
3	C	111.0	16.9	51.8	e	10.5
4	Pt	142.0	28.5	38.7	59.2	12.3
5	C (2% H$_2$O)	156.2	8.5	36.0	0.8	10.9

^{a}Experiments were conducted in CH_3CN saturated with CO_2 by using 0.1 M TBAH as the supporting electrolyte with 2–3 mM added $[Rh(bpy)_2Cl_2]^+$. ^{b}Total coulombs passed by the electrode. ^{c}Determined as methyl formate (see text). ^{d}Total turnovers for all products. ^{e}Not determined.

only the electrocatalytic properties of the Rh complexes.

The cyclic voltammogram of $[Rh(bpy)_2(TFMS)_2]^+$ in the presence of CO_2 clearly shows a catalytic current enhancement that begins at the first bipyridine reduction wave but is predominately associated with the second reduction. Upon the return oxidation sweep the cathodic peaks appear at $E_{p,c} = -1.62$ V and $E_{p,c} = -1.77$ V in the presence of CO_2. The catalytic nature of the current enhancement is also shown by the attenuation of the bpy-based reoxidation processes

$$Rh(bpy)_2^- \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} Rh(bpy)_2^0$$
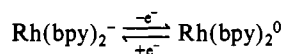
and even the Rh-based return wave is reduced in amplitude under these conditions. Greater current enhancements are observed in dimethylformamide, but due to considerable interference during product analysis from DMF hydrolysis products, CH_3CN was used in the electrocatalytic experiments. This choice is an unfortunate compromise since the solubility characteristics of the complexes in CH_3CN are not optimal.

Controlled-potential electrolyses were performed in a cylindrical gastight cell by using electrolyte solutions that were 0.1 M in tetra-*n*-butylammonium hexafluorophosphate in acetonitrile. They were purged with CO_2 for a minimum of 15 min prior to the electrolysis. With the solutions saturated in CO_2, $[CO_2] = 0.14$ M, the concentration of CO_2 is considerably in excess of the catalyst (2.0–3.0 mM in $[Rh(bpy)_2X_2]^+$ (X = Cl$^-$, CF$_3$SO$_3^-$)). The electrolysis experiments were normally conducted for 40–100 min, and after the initial high current levels for reduction the electrocatalytic current level remained fairly constant (±20%) throughout the remainder of the experiment.

Product analyses (Table II) showed that formate, H_2, tri-*n*-butylamine, and butene were the predominate reduction products. Under no conditions was CO observed as a product. Gas chromatography was used to determine the composition of the gases above the solution and the concentration of tri-*n*-butylamine in the solution. Formate was analyzed by treating an aliquot of the solution with an excess of $[O(CH_3)_3](SbCl_6)$ followed by GC analysis for methyl formate. Control experiments were performed to demonstrate that the products were, in fact, derived from CO_2 and that the reduction of CO_2 was catalyzed by the metal complex. The control experiments consisted of identical electrolyses in the presence of the metal complex under Ar and electrolyses without the metal complex but with added CO_2.

Experiment 2 in Table II is a representative CO_2 electrocatalysis experiment. Electrolysis of a solution 2.5 mM in $[Rh(bpy)_2Cl_2]^+$ (3.75 × 10^{-2} mmol) at –1.55 V with a carbon-cloth electrode under CO_2 resulted in a transient, intense purple solution characteristic of $[Rh(bpy)_2]^+$ followed by formation of a pale green solution containing a small amount of colloidal black precipitate. The solid material never amounted to more than 10% by weight of the starting catalyst; the bulk of the reduced starting material remained in solution. After the catalytic run, a CV of the solution revealed a broad featureless increase in current beginning at ca. –1.2 V. In 1 h, 77 C was passed and product analysis gave hydrogen (4.6 × 10^{-2} mmol) and formate (2.3 × 10^{-1} mmol as methyl formate). When we corrected for the equivalents needed for the initial two-electron reduction of the complex and noted
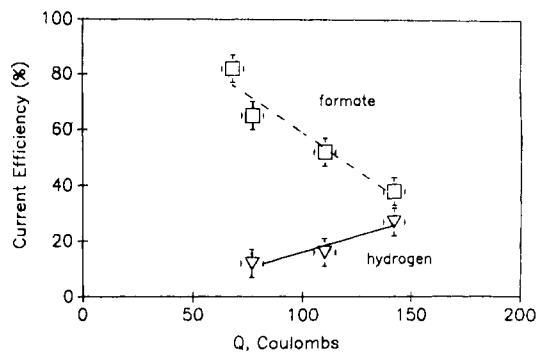
Figure 4. Variations in current efficiencies for formate and hydrogen production as a function of coulombs passed.

that two electrons were required for the production of both HCO_2^- and H_2, the current efficiencies were 64% and 12%, respectively, for HCO_2^- and H_2.

Results obtained in experiments 1 and 4 in Table II show that the protons required for the reduction products are derived from the tetra-*n*-butylammonium ions of the supporting electrolyte. The ability of quaternary ammonium salts to act as acids in strongly basic solutions via the Hofmann degradation

$$N[(CH_2)_3CH_3]_4^+ + B \rightarrow$$
$$N[(CH_2)_3CH_3]_3 + BH^+ + H_2C=CHCH_2CH_3 \quad (6)$$
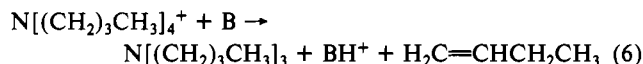
is well-known.[18] In experiment 4 the protons appear in the reduction products as either H_2 (0.21 mmol) or formate (0.27 mmol). This value is in good agreement with the amount of NBu_3 produced, 0.61 mmol, especially when it is considered that trace H_2O or other protic impurities would necessarily decrease the yield of ammine. Note that, in experiment 5 in Table II, addition of H_2O to the electrolysis solution results in almost no amine but a significant amount of formate is still produced. Apparently, H_2O acts as the proton source for this case, as expected.
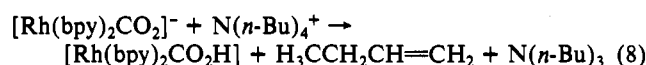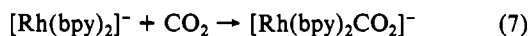
From the data presented in Table II and shown graphically in Figure 4, the product studies have led to some interesting observations. In all cases the major reduction product is formate and the minor product hydrogen. However, as shown in Figure 4, the current efficiency for formate production decreases as the number of coulombs passed increases, at the expense of an enhanced current efficiency for hydrogen. The latter observation is particularly surprising since the solution necessarily becomes more basic as the electrolysis proceeds. Although the total current efficiency for the appearance of the reduction products never approaches 100%, a possible reason for this is the formation of undetected reduction products such as formaldehyde and methanol. A reasonable alternative is that the bpy ligands of the rhodium complex are reduced by hydrogenation; this would explain the absence of bipyridine-based π^* reductions in cyclic voltammograms after the catalytic runs. Such an irrecoverable chemical change in the catalyst could explain why the system gradually moves from the reduction of CO_2 toward H_2 production. However, it is especially noteworthy that the electrocatalyzed production of H_2 only appears as a pathway in the presence of added CO_2. Coulometric experiments under Ar are relatively uncomplicated, there is no sign of electrocatalytic behavior, and H_2 is not produced as a product.

The apparent deactivation of the catalytic capabilities of the system may be tied to the appearance of a black, insoluble material that appears as a suspension during catalytic reduction. By IR analysis, the material, which is completely insoluble in common organic solvents, contains both bipyridine modes and bands attributable to $\nu(C=O)$ modes. Wet chemical tests, i.e., complete dissolution in aqua regia, show that the material is not rhodium metal. This material may be responsible for ~20% of the reducing equivalents that are not accounted for as H_2 or HCO_2^-.

(18) Cope, A. C.; Trumbull, E. R. In *Organic Reactions*; Wiley: New York, 1960; Vol. 11, p 317. Although precautions were taken to exclude H_2O from the system, hydroxide ion could promote the same reaction.

Possible Reduction Mechanisms. The low solubility and high oxygen sensitivity of the reduced complexes $[Rh(bpy)_2]^0$ and $[Rh(bpy)_2]^-$ in acetonitrile and other organic solvents makes further mechanistic experiments very difficult. We can, by analogy to the known stoichiometric chemistry of rhodium and iridium phosphines with CO_2, propose reasonable mechanistic possibilities for the catalytic chemistry.

The electrochemical results show that the initial CO_2 reduction chemistry originates in the two-electron-reduction product $[Rh(bpy)_2]^-$ and that the proton requirement in the reduction products is derived from the supporting electrolyte. Since $[Rh(bpy)_2]^+$ *must* be reduced by 2e before catalysis occurs, and the reduction takes place at the bpy ligands, the bpy(π^*) levels act as "electron reservoirs" for the net two-electron reduction of CO_2. An interaction between CO_2 and the reduced complex is required to explain the appearance of H_2 as a product and the use of the quaternary ammonium electrolyte as a proton source, whether for the production of formate or of H_2. An appealing set of reactions that may play a role are shown in eq 7 and 8. The first

$$[Rh(bpy)_2]^- + CO_2 \rightarrow [Rh(bpy)_2CO_2]^- \quad (7)$$

$$[Rh(bpy)_2CO_2]^- + N(n\text{-}Bu)_4^+ \rightarrow$$
$$[Rh(bpy)_2CO_2H] + H_3CCH_2CH{=}CH_2 + N(n\text{-}Bu)_3 \quad (8)$$

step involves binding to the highly reduced, electron-rich, anionic complex. Although the nature of the presumed complex between $[Rh(bpy)_2]^-$ and CO_2 and the mode of CO_2 binding are not known, it is tempting to speculate that CO_2 is carbon-bound. With such binding and extensive electronic donation from the electron-rich metal to CO_2 the oxygen atoms could become sufficiently basic to attack the tetraalkylammonium atoms of the supporting electrolyte. Precedents for oxygen basicity in metal–CO_2 complexes is provided by the examples of $Rh(das)_2(\eta^1\text{-}CO_2)Cl^{19}$ and

$[Co(salen)(CO_2)K(THF)]_n.^{20}$ Following protonation, a bound formate anion in $[Rh(bpy)_2CO_2H]$ should behave chemically in a fashion analogous to that of bound Cl^- in $[Rh(bpy)_2Cl]$, i.e., rapid dissociation to give $[Rh(bpy)_2]^+$ for reentry into the reduction cycle via eq 9.

$$[Rh(bpy)_2CO_2H] \xrightarrow{CH_3CN} [Rh^I(bpy)_2]^+ + H-\overset{\overset{\textstyle O}{\|}}{C}-O^- \quad (9)$$
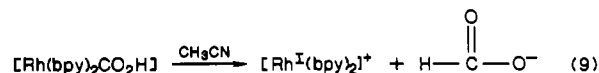
Although such reaction sequences may play a role, especially early in the catalysis, it is clear that the underlying chemistry is far more complex as shown by (1) the appearance of H_2 as a competitive product, (2) the change in the HCO_2^-/H_2 ratio with electrolysis time, (3) the appearance of the black solid during the electrolysis period, and (4) the loss of the well-defined bpy-(π^*)-based electrochemistry as the electrolysis proceeds. Nonetheless, when the tetra-*n*-butylammonium ion is used as the source of protons, the catalysts are able to achieve initial formate production rates of ca. 0.2 turnover/min at −1.55 V at a carbon-cloth electrode with a current efficiency of up to 80%.

Registry No. cis-$[Rh(bpy)_2(TFMS)_2](TFMS)$, 116971-15-4; cis-$[Rh(bpy)_2Cl_2]Cl\cdot2H_2O$, 22710-42-5; cis-$[Rh(bpy)_2Cl(TFMS)](TFMS)$, 116971-17-6; cis-$[Rh(4,4'-(t\text{-}Bu)_2bpy)_2Cl_2]Cl$, 116996-77-1; cis-$[Rh(4,4'-(t\text{-}Bu)_2bpy)_2Cl_2](PF_6)$, 116996-79-3; cis-$[Ir(bpy)_2Cl_2][TFMS]$, 116971-18-7; cis-$[Ir(bpy)_2Cl_2]Cl$, 22710-60-7; cis-$[Ir(bpy)_2(TFMS)_2]$-$[TFMS]$, 91030-49-8; $[Ir(bpy)_3][PF_6]_3$, 91042-30-7; cis-$[Ir(bpy)_2H_2]$-$[PF_6]$, 91172-41-7; cis-$[Ir(bpy)_2(PPh_3)H][PF_6]_2$, 91042-32-9; cis-$[Rh(bpy)_2Cl_2][ClO_4]$, 49727-33-5; CO_2, 124-38-9.

(19) Herskowitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615.

(20) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405.

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Synthetic Routes to New Polypyridyl Complexes of Osmium(II)

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New luminescent complexes of Os(II) that contain either 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) as the chromophoric acceptor ligand have been prepared by a combination of established and new synthetic methods. Extensive use of Os(IV) and Os(III) precursors, e.g., $Os^{IV}(bpy)Cl_4$ and *mer*-$Os^{III}(PMe_2Ph)_3Cl_3$, has led to the preparation of materials with ancillary ligands such as tertiary phosphines as preparative intermediates, including $Os^{III}(bpy)(PMe_2Ph)Cl_3$ and cis-$Os^{II}(phen)(diphosphine)Cl_2$. Further substitution of chloro ligands into complexes such as these results in the formation of emissive complexes of Os(II). Another new synthetic route utilizes the versatile Os(II) precursor $Os(bpy)_2CO_3$, which allows the facile preparation of dicationic, di-substituted species such as $[Os(bpy)_2(norbornadiene)]^{2+}$. Another general procedure, based on the control of solvent and temperature in the substitution chemistry of cis-$Os(bpy)_2Cl_2$, has been further developed to produce a variety of new complexes of the types cis-$[Os(bpy)_2(L)Cl]^+$ and cis-$[Os(bpy)_2(L)_2]^{2+}$, where L is a phosphine, arsine, nitrogen, or olefin donor ligand. In a few cases, phosphine entering groups cause the cis geometry to be unfavorable and new *trans*-$[Os(bpy)_2(L)_2]^{2+}$ complexes have also been isolated. The resultant complexes comprise the largest family of transition-metal-based excited-state reagents with "tunable" photophysical and redox properties available. When possible, the new complexes have been characterized by UV–visible spectroscopy, emission spectroscopy, cyclic voltammetry, and ^{31}P and/or ^1H NMR spectroscopy.

Introduction

Since the discovery of $[Ru(bpy)_3]^{2+}$ as an efficient photosensitizer, an enormous effort has been expended on the synthesis and chemistry of related polypyridine complexes of Ru, particularly those with the ligands 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen). Such complexes have proven to be of value in the development of redox catalysts[1] and in the study of ground-

and excited-state electron-transfer processes.[2] The excited states of $[Ru(bpy)_3]^{2+}$ and similar complexes have been utilized in energy

(1) (a) Vining, W. J.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2023. (b) Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221C. (c) Vining, W. J.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2023. (d) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310.