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Photophysical Behavior of a New CO_2 Reduction Catalyst, $Re(CO)_2(bpy)\{P(OEt)_3\}_2^+$

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The photophysical and photochemical properties of the cation $Re(CO)_2(2,2'\text{-bipyridyl})\{P(OEt)_3\}_2^+$ (**P**$^+$), which is an effective photochemical reductant of CO_2, are examined by time-resolved infrared spectroscopy (TRIR) of the ν(CO) absorption bands, by UV/visible flash photolysis in both emission and absorption, and by spectroelectrochemistry in both infrared and UV/visible regions. It is shown that **P**$^+$ is first excited into a metal to ligand charge transfer state (MLCT) in which the charge is localized on the bpy ligand, resulting in an upward shift in the ν(CO) bands. This excited state is quenched by 1,4-diazabicyclo[2.2.2]octane to form the neutral species **P** with lowered ν(CO) infrared bands; there is a rapid back-reaction between **P** and DABCO. The kinetics of these processes are obtained. Preliminary experiments suggest that **P** must be further activated before the CO_2 reduction cycle starts.

Introduction

The photochemistry and electrochemistry of $XRe(CO)_3(L\text{-}L')$ complexes (X = Cl, Br, CH_3CN, etc.; L-L′ = either a bidentate polypyridyl such as 2,2′-bipyridyl or two monodentate ligands such as 4,4′-bipyridyl) have received a great deal of attention in the last 15–20 years. Virtually all the molecules of this type have low-lying metal to ligand charge transfer (MLCT) excited states, the other main state often being a π–π^*, intraligand transition.[1,2] There has been little or no evidence for the existence of an accessible ligand field state and this explains why almost all the complexes of this type are extremely photostable when excited into their low-energy states. However, these complexes do display interesting chemistry following MLCT excitation. As expected, $XRe(CO)_3(L\text{-}L')$ complexes are both better reductants and oxidants in their MLCT states than in the corresponding ground states.[3] For example, upon reductive quenching of the MLCT state, the reduced rhenium species can undergo substitution reactions and this has been used as a synthetic route to a range of Re(I) bipyridine compounds.[4]

One reason for the continuing interest in these complexes is the discovery[5a] that $ClRe(CO)_3(bpy)$ (bpy = 2,2′-bipyridyl) (**1**) and analogous complexes can act as both electro- and photocatalysts for the reduction of CO_2.[5–12] The major product of the reduction is CO along with small amounts of H_2 in solvents such as *N,N*-dimethylformamide (DMF) and acetonitrile. The remarkable feature of this system is that a single photocatalyst utilizes single electron transfers in the multielectron reduction of CO_2. It is believed that the anionic complex $[ClRe(CO)_3(bpy)]^-$, produced either photochemically or electrochemically, is the active precursor in the reduction process; hence the proposed first steps in the photochemical process can be summarized

$$ClRe(CO)_3(bpy) \xrightarrow[\text{DMF}]{h\nu} [ClRe(CO)_3(bpy)]^* \xrightarrow{\text{D}} [ClRe(CO)_3(bpy)]^- + D^+$$

where D is an electron donor, usually triethanolamine (TEOA) or triethylamine (TEA), present in ~20% concentration. However, the sequence of reactions following this photoinduced electron transfer reaction has not yet been established; for example, does it involve loss of CO, loss of Cl^-, or dechelation of the bpy ligand? It is also unclear, during photocatalytic reduction, whether substitution of CO_2 into the anionic complex and the second reduction process occur thermally or whether further photolytic energy is required. One of the difficulties in

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studying these reactions is that the usual spectroscopic techniques applied to investigating the photochemistry of the rhenium complexes do not provide enough information about the structures of the reacting complexes.

Recently, fast time-resolved infrared spectroscopy (TRIR) has been applied to investigating the excited states of the rhenium complexes. In particular, it has been shown that, in the MLCT excited states of $ClRe(CO)_3(L\text{-}L)$ (L-L = 2,2′-bpy (**1**) or $(4,4'\text{-bpy})_2$ (**2**)), the ν(CO) IR bands shift up in frequency since the metal is effectively oxidized.[13,14] TRIR should give us useful information about changes both of electronic structure of the carbonyl complexes and of the ligands.

Since **1** shows such promise as a CO_2 reduction catalyst, it is surprising that there are few reports using different rhenium complexes, although there is one study involving $ClRe(CO)_3$(ptpy) (ptpy = *p*-(2,6-di-2-pyridyl-4-pyridyl)phenyl) as both photo- and electrocatalyst.[15] However, we recently synthesised[11c] $[Re(CO)_2(bpy)\{P(OEt)_3\}_2]Br$ ($\mathbf{P^+Br^-}$) by the route

$$BrRe(CO)_3(bpy) \xrightarrow[\text{TEA, P(OEt)}_3]{h\nu} [Re(CO)_2(bpy)\{P(OEt)_3\}_2]Br$$

It has been shown[16] that $\mathbf{P^+}$ compounds can act as efficient photocatalysts for the reduction of CO_2 to CO with 1-benzyl-1,4-dihydronicotinamide (BNAH) as electron donor. $\mathbf{P^+}$ has some advantages for research using TRIR; for example, the lifetime of the excited state (~250 ns) is much longer than that of $ClRe(CO)_3bpy$ (~50 ns) and the C_{2v} symmetry of $\mathbf{P^+}$, with two equivalent CO groups,[11c] should simplify analysis of the structures (see below).

In this paper we describe investigations of both the photophysics and the redox chemistry of $\mathbf{P^+}$ using TRIR, UV/visible flash photolysis, and spectroelectrochemical techniques.

Experimental Section

Materials. Acetonitrile was distilled first over P_2O_5 and then over CaH_2. Tetrahydrofuran (THF) and CH_2Cl_2 were dried and distilled over CaH_2. *N,N*-Dimethylformamide (DMF) was dried over molecular sieve 4A and distilled at reduced pressure under Ar. The complexes $XRe(CO)_3(bpy)$ (bpy = 2,2′-bipyridyl; X = Cl, Br) were prepared according to the literature.[1] Other complexes were prepared as follows:

$\mathbf{[Re(CO)_2(bpy)\{P(OEt)_3\}_2]^+Br^-}$ ($\mathbf{P^+Br^-}$). The complex $BrRe(CO)_3(bpy)$ (0.7 g), triethylamine (30.0 mL), and triethyl phosphite (3.0 g) were dissolved in 300 mL of THF. The solution was introduced into a photolysis apparatus equipped with a condenser and a bubbler which were connected to a vacuum pump and to an argon supply, respectively. After three Ar filling−pump−Ar filling cycles, the solution was irradiated for 2 h with a 300-W Matushita tungsten−halogen lamp. During the irradiation, both the reaction vessel and the light source were cooled with ice-cold water and the Ar gas was circulated through the reaction solution with a pump. The photolysate was evaporated and chromatographed on 70 g of silica gel (35−70 mesh, Merck, 10181). After elution of the starting complex with 0−5% methanol in CH_2Cl_2 (1.7 L), $\mathbf{P^+}Br^-$ was eluted with 20% of methanol in CH_2Cl_2 (200 mL). Twenty-five percent of the starting complex was recovered, and the yield of $\mathbf{P^+}Br^-$ was 80% based on the starting complex consumed. Although further irradiation gave higher conversion of the starting complex, it caused photodecomposition of $\mathbf{P^+}Br^-$ to give mainly $Re(CO)_2(bpy)\{P(OEt)_3\}\{P(O)(OEt)_2\}$, which is more difficult to separate from the $\mathbf{P^+}Br^-$ by chromatography than the starting complex. $\mathbf{P^+}Br^-$ was purified by recrystallization from CH_2Cl_2−diethyl ether solvent mixtures and dried in vacuo to give a yellow powder.

$\mathbf{[Re(CO)_2(bpy)\{P(OEt)_3\}_2]^+Cl^-}$ ($\mathbf{P^+Cl^-}$). A chloride salt, $\mathbf{P^+}Cl^-$, was synthesized using a procedure analogous to that given for $\mathbf{P^+}Br^-$ except that $ClRe(CO)_3(bpy)$ was substituted for $BrRe(CO)_3(bpy)$ as starting material.

$\mathbf{[Re(CO)_2(bpy)\{P(OEt)_3\}_2]^+BPh_4^-}$ ($\mathbf{P^+BPh_4^-}$). The complex $\mathbf{P^+}Br^-$ (145 mg) was dissolved in 5 mL of methanol, and a concentrated methanol solution of $Na^+BPh_4^-$ was added dropwise to precipitate the yellow product, which was collected by filtration, washed with water, and then dried in vacuo. The yield was 95%.

Apparatus. IR spectra were recorded on JEOL JIR 6500, JIR 100, or Nicolet 205 spectrometer using ~2 cm^{-1} resolution. UV/vis absorption spectra were recorded on a Photal MCPD-1000 instrument, and luminescence spectra were measured with a Hitachi F-3000 spectrometer.

Electrochemistry. For cyclic voltammetry (CV) and column electrophoresis, a BAS100B electrochemical analyzer and a $Ag/AgNO_3$ (0.1 M) reference electrode were used. The supporting electrolytes were dried at 100 °C under vacuum before use. For CV a Pt electrode (BAS Model MF2005) was the working electrode and standard three-electrode methods were used. A flow-electrolytic method[17] was used for measuring IR and UV/vis absorption spectra of the reduced complexes. The working electrode was contained in a porous glass tube (1 mm i.d., 2 mm o.d., 30 mm length) and consisted of many strands of 0.1 mm diameter Pt wire or 7 μm carbon fiber. An acetonitrile solution containing $\mathbf{P^+}$ (0.5−0.8 mM) and R_4NClO_4 (0.1 M; R = *n*-Bu or Et) as electrolyte was purged with Ar for 20 min, and then flowed into a flow-through cell at a flow rate of 0.4 mL/min. Just after electrolysis, the solution was transferred to a CaF_2 cell (path length 3 mm) or a quartz cell (path length 5.1 mm) for spectral measurements.

Flash Photolysis: Fluorescence Lifetime and UV/Vis Transient Absorption Measurements. A Continuum YG680−10 Nd/YAG laser was employed as an excitation light source. A sample solution in a quartz flow cell (5 mm light path) was irradiated by the 355 nm light pulse (10 ns fwhm, 100 mJ/pulse). The fluorescence and monitoring light was detected using a Hamamatsu R666S photomultiplier tube or a Princeton Instruments IRY-700G/RB SMA detector (5 ns minimum gate width) through a Jobin Yvon HR-320 monochromator. Transient signals were stored on a Tektronix SCD1000 transient digitizer (1 GHz bandwidth). An Apple Macintosh IICX computer was used for controlling the instruments and for data analysis.

Time-Resolved Infrared (TRIR) Measurements. The Nottingham TRIR equipment has been described in detail elsewhere.[18] Briefly it consists of a XeCl excimer laser (308 nm, 20 ns pulse, Lumonics HyperEx 440) as the photolysis source and one of two tunable CW IR lasers to monitor the transient spectra. The work described here used either an Edinburgh Instruments PL3 CO laser tunable in 4 cm^{-1} steps over the range 2000−1600 cm^{-1} or a Mütek diode laser (Model MDS 1100, fitted with a MDS 1200 monochromator). The CO laser was monitored with a fast photovoltaic MCT detector (rise time ~125 ns, Laser Monitoring Systems S-025), and the diode laser systems were recorded with a MCT detector (rise time ~100 ns, Laser Monitoring Systems S-100). Signals were digitized with a Gould Model 4072 or 4084 digitizer. Spectra were built up "point-by-point" and show the IR absorbance **changes** following the laser pulse.

Results and Discussion

The Excited State. Figure 1 shows TRIR experiments designed to determine the IR spectrum, in the ν(CO) region, of the excited state of $\mathbf{P^+}Br^-$ in CH_2Cl_2. Two IR lasers (Figure 1a,b) are used for detection since, in our laboratory, the whole range cannot be covered by a single laser; in the region of overlap there is excellent consistency between the two experiments. Figure 2 shows the temporal behavior of the four IR

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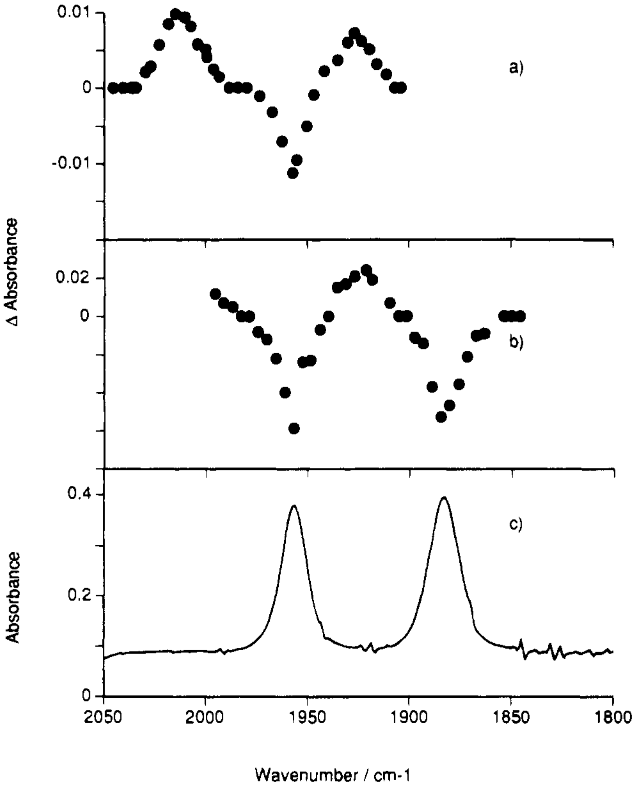

Figure 1. IR spectra in the ν(CO) region of $[Re(CO)_2(bpy)\{P(OEt)_3\}_2]^+Br^-$ ($\mathbf{P^+Br^-}$) in CH_2Cl_2 solution. (a) TRIR, using a diode laser, immediately after UV (308 nm, 20 ns) flash of $\mathbf{P^+Br^-}$ (5×10^{-4} M) in CH_2Cl_2 under 2 atm of Ar(g); path length 2 mm. Each point corresponds to a different IR laser wavelength. Points below zero correspond to a loss of parent ground state; points above zero correspond to generation of transients. (b) As above, except a CO laser replaced the diode laser. (c) Fourier transform IR of $\mathbf{P^+Br^-}$ (5×10^{-4} M) in CH_2Cl_2; path length 2 mm.

bands in Figure 1. Table 1 summarizes the frequency and kinetic data. It is clear that the ground state of $\mathbf{P^+}$ is depleted and produces a transient species with two ν(CO) IR bands. The transient cannot involve loss of CO because it has two CO modes. The most obvious interpretation is that flash photolysis generates the excited state of $\mathbf{P^+}$ ($\mathbf{P^{+*}}$); this is based on the fact that fluorescence and TRIR experiments give very similar lifetimes (Table 1). Further confirmation that the transient is the excited state comes from experiments in which the solvent was saturated with O_2, when the lifetime was reduced by an order of magnitude; experiments described in the next section also confirm this assignment. It should be noted that no photodecomposition occurs following flash photolysis at 308 nm. The two ν(CO) bands in the excited state are shifted up in frequency from the ground state by 56 and 45 cm^{-1}. This is comparable to what happens with $ClRe(CO)_3(2,2'\text{-bpy})$ (**1**)[14] and $ClRe(CO)_3(4,4'\text{-bpy})_2$ (**2**)[13] (see Table 2), where there is no doubt that the stable excited states are MLCT. Thus, as expected, the excited state $\mathbf{P^{+*}}$ is also MLCT, the increase in frequency of the ν(CO) modes being due to oxidation of the metal in the excited state. The UV/visible absorption spectrum of the excited species has maxima at 360 and 450 nm in acetonitrile solution (Figure 3), which are also similar[7,9] to those of the MLCT excited state of $ClRe(CO)_3bpy$ (λ_{max} = 370 and 475 nm).

Experiments have been also carried out with $\mathbf{P^+}BPh_4^-$ and various solvent systems. The results are summarized in Table 1. Flash photolysis generates the MLCT excited state of $\mathbf{P^+}$, which has a lifetime of ~250 ns, mostly independent of solvent and counteranion.

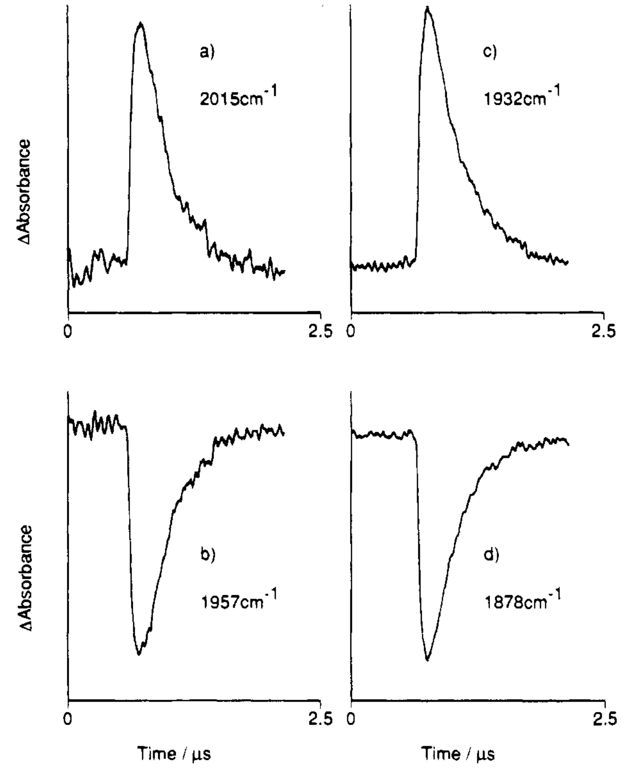

Figure 2. Decay traces for IR bands shown in Figure 1: (a, b) recorded using a diode laser; (c, d) recorded using a CO laser. Note that the decay curves are not obtained from the peak maxima. (a, c). The two ν(CO) bands are assigned to the excited state of $\mathbf{P^+}$ ($\mathbf{P^{+*}}$). (b, d). The two ν(CO) bands are assigned to the ground state of $\mathbf{P^+}$.

Table 1. Spectroscopic and Lifetime Data for $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^+X^-$ (X = Br, BPh_4)[a]

solvent	$\nu(CO)^{GS}$ (cm^{-1})[b]	$\nu(CO)^{ES}$ (cm^{-1})[c]	$\lambda_{max}{}^{GS}$ (nm)	$\lambda_{max}{}^{ES}$ (nm)	λ_{em} (nm)	τ_{em} (μs)	τ^d (μs)	τ^e (μs)
				X = Br				
CH_2Cl_2	1956	2012[f]	382	370	576	0.28	0.27	0.28
	1882	1927		470			0.27	0.29
CH_3CN	1956	*g*	372	360	573	0.25	0.29	0.28
	1881	1926		450			0.24	0.25
DMF	1953		369	365	570	0.27		
	1879			455				
				X = BPh_4				
CH_2Cl_2	1957	*g*	384	365	576	0.29	0.26	*g*
	1884	1925		460			0.24	0.31
CH_3CN	1955		372	360	573	0.25		
	1881			450				
DMF	1953	*h*	369	365	570	0.27	*h*	*h*
	1879	1922		455			0.26	0.24

[a] GS = ground state; ES = excited state; λ_{max} and λ_{em} refer to absorption and emission, respectively. τ_{em} is the excited state lifetime measured from luminescence decay. [b] FTIR spectra. [c] TRIR spectra. [d] From recovery of $\mathbf{P^+}$ TRIR bands. [e] From decay of excited state TRIR bands. [f] Monitored using IR diode laser. [g] Outside CO laser range. [h] Obscured by solvent absorption band.

The value of the energy-factored force field (EFFF), when applied to transition metal carbonyls, has been well demonstrated over many years.[19] The problem with complexes of Re such as **1**, which contain three CO groups, is that, with one axial and two equatorial CO groups, there are **four** force constants (the principal constants k_{ax} and k_{eq} and the two interaction constants k_{axeq} and k_{eqeq}) but only **three** frequencies. Thus a complete analysis of both ground and excited state force fields requires the use of either ^{13}CO isotopes or approximations.

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Table 2. ν(CO) Frequencies (cm^{-1}), EFFF Force Constants ($N\ m^{-1}$), and Bond Distance Changes (Å) for P^+, $Re(2,2'\text{-bpy})(CO)_3Cl$ (**1**), and $Re(4,4'\text{-bpy})_2(CO)_3Cl$ (**2**) in CH_2Cl_2 Solution

	ground state		excited state		differences			
complex	ν(CO)	k_{CO}[a]	ν(CO)	k_{CO}[a]	$\Delta\nu$(CO)	mean $\Delta\nu$(CO)	Δk_{CO}	Δr
P	1956	1488	2012	1568	+56	+51	+80	−0.010
	1882		1927		+45			
1[b]	2024	1502	2064	1580	+40		+78	−0.009
	1921	1550	1987	1642	+66	+55	+92	−0.011
	1899		1957		+58			
2[c]	2027	1486	2055	1566	+28		+80	−0.010
	1926	1552	1992	1644	+66	+53	+86	−0.010
	1891		1957		+66			

[a] Principal force constants. [b] Reference 14. [c] Reference 13.

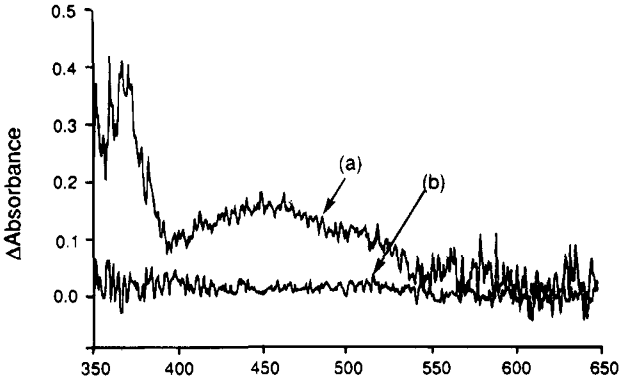

Figure 3. Difference transient UV/vis absorption spectra taken (a) 50 ns and (b) 2 μs after laser photoexcitation (355 nm, 10 ns) of an Ar-saturated acetonitrile solution containing P^+Br^- (3.0×10^{-4} M); path length 5 mm.

However, with P^+ and P^{+*} there are only two equivalent CO groups, and hence the force field involves only two force constants (the principal constant k_{CO} and the interaction constant $k_{CO,CO}$); with two observed frequencies, it can thus be solved exactly, and the details are given in Table 2. We recently showed[20] that the C−O bond length in metal carbonyls can be related with reasonable accuracy to the EFFF force constant by the relationship

$$r_{CO} = 1.647 - 0.184 \ln k_{CO} \quad (r \text{ in Å}; k \text{ in mdyn/Å})$$

Hence, the **change** in bond length can be estimated to an accuracy of ~0.001 Å from the change in force constant on promotion to the excited state. The calculated changes in bond length are given in Table 2 and compared with those of **1** and **2**. In principle, the changes in k_{CO} can be correlated with degree of charge transfer from ground to excited state. However there is no "calibrant" comparable with the vibrational shifts from bpy to bpy^- frequently seen with time-resolved resonance Raman spectroscopy. It is however striking that the changes in k_{CO} for the three complexes are so similar.

In principle, for a simple metal carbonyl with two CO groups, the bond angle between the CO groups is given by[19b]

$$\tan^2(\theta/2) = I(\text{antisym})/I(\text{sym})$$

where θ is the angle between the CO groups and I refers to the intensity of the appropriate modes. From the ground state spectrum (Figure 1c), a bond angle of ~91° is calculated, and from the excited state spectrum, we obtain a value of ~85°. Given the difficult of measuring intensities in the excited state, the implication is that there is no significant angular distortion from ground to excited state.

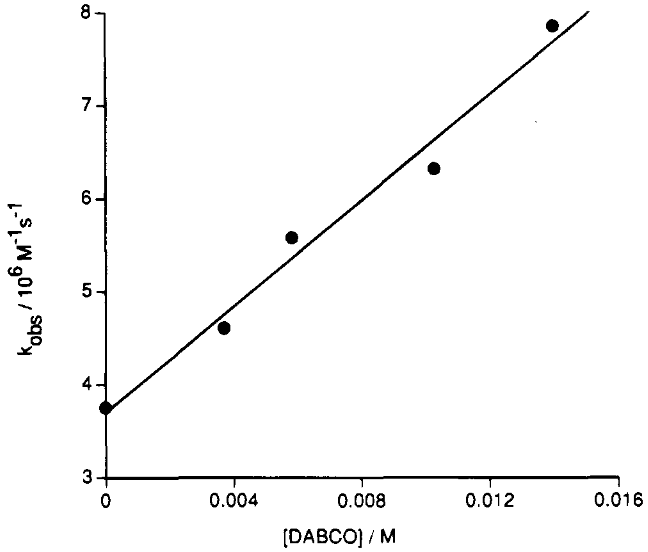

Figure 4. Observed rate constant of luminescence decay (k_{obs}) of P^{+*} as a function of DABCO concentration.

Redox Reactions of the Excited State. The next stage is to probe the reaction of the excited state with electron donors. In the presence of a substantial concentration of electron donor, the lifetime of the excited state is too short to monitor accurately by the available TRIR apparatus (see below). Thus, we first consider the results of UV/vis flash photolysis. The experiments were conducted with DABCO (1,4-diazabicyclo[2.2.2]octane) as the electron donor since, although the back electron transfer (see next section) is too fast to permit this molecule to be efficient in the CO_2 reduction cycle, it has more convenient spectroscopic properties than the usual molecule BNAH, which strongly absorbs at the wavelength of the photolysis light. The excited state P^{+*} is quenched by DABCO, the reaction obeying Stern−Volmer kinetics, as shown in Figure 4, with a rate constant of $k_q = 2.84 \times 10^8\ M^{-1}\ s^{-1}$. The product of this reaction has an absorption spectrum, shown in Figure 5a, displaying broad absorption features at λ_{max} ~400, ~485, and 511 nm.

Cyclic voltammetry of P^+ shows a reversible wave at −1.69 V and an irreversible wave at ~−2.45 V vs $Ag/AgNO_3$ in an acetonitrile solution containing 0.1 M Bu_4NClO_4 as electrolyte (Figure 6). UV/visible absorption spectra of a reduced rhenium complex were measured by spectroelectrochemical techniques. As shown in Figure 5b, new absorption maxima were observed at 349, 387, 484, and 511 nm. Both the intensity of the absorption and the measured current increased with more negative reduction potentials from −0.6 V up to ~−1.6 V but particularly reached saturation at ~2.0 V; Figure 7 shows the dependence of both the absorbance at 511 nm and the current

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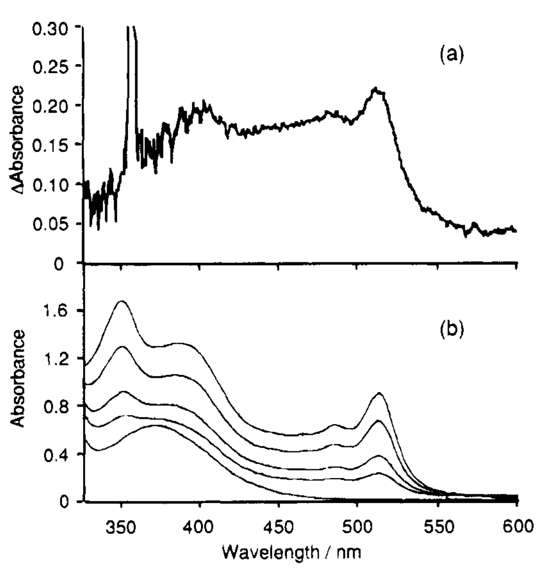

Figure 5. (a) Difference UV/vis absorption spectrum taken 50 ns after laser photoexcitation (355 nm, 10 ns) of an Ar-saturated acetonitrile soution containing P^+Br^- (3.0×10^{-4} M) and DABCO (0.11 M); path length 5 mm. (b) UV/vis absorption spectra recorded following column electrolysis of P^+Br^- (8.0×10^{-4} M) in an Ar-saturated acetonitrile solution containing 0.1 M Et_4NClO_4 at carbon fiber electrodes; path length 2.1 mm. The solution was reduced from 0 to −2.1 V at a constant flow rate of 0.4 mL min^{-1}. The spectrum in (a) is perturbed by the absorption band of $DABCO^+$, which occurs at ~460 nm; because the pump laser operates at 355 nm, it is not possible to detect the band which is seen at 349 nm in the electrochemistry experiment.

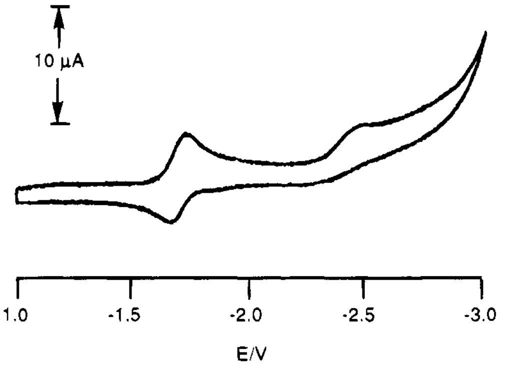

Figure 6. Cyclic voltammogram of $P^+BPh_4^-$ (6.0×10^{-4} M) in an Ar-saturated acetonitrile solution containing 0.1 M n-Bu_4NClO_4 taken by using a Pt working electrode and an $Ag/AgNO_3$ reference electrode. The scan rate was 200 mV/s.

for varying potentials. The spectrum remained unchanged for at least 30 min after the electrolysis, indicating that the reduced species is very stable under an Ar atmosphere. The number of electrons per P^+ molecule reduced (n) can be calculated using the equation

$$n = (i - i_b)/[P^+]_0 F v$$
$$= (6.5 \times 10^{-7} - 1.5 \times 10^{-7})/(8.0 \times 10^{-4}) \times 96480 \times (6.7 \times 10^{-6})$$
$$= 1.1$$

where i is the current (A) which is required for quantitative reduction of P^+, i_b (A) is the background current, $[P^+]_0$ (M) is the initial concentration of P^+, F (C) is the Faraday constant, and v (s^{-1}) is the flow rate of solution. The results clearly show that the reduced species observed by the electrolysis must be $Re(CO)_2bpy\{P(OEt)_3\}_2$ (**P**). Extinction coefficients (ϵ) at 349, 387, 484, and 512 nm were calculated to be 11 500, 9000, 4400, and 6200 M^{-1} cm^{-1}, respectively, by plotting absorbances against potentials as shown in Figure 7. The similarity of the absorption spectrum observed after laser flash photolysis of P^+ (Figure 5a) to that of **P** (Figure 5b) strongly suggests that the luminescence of P^+ is reductively quenched by DABCO to produce **P**, i.e.

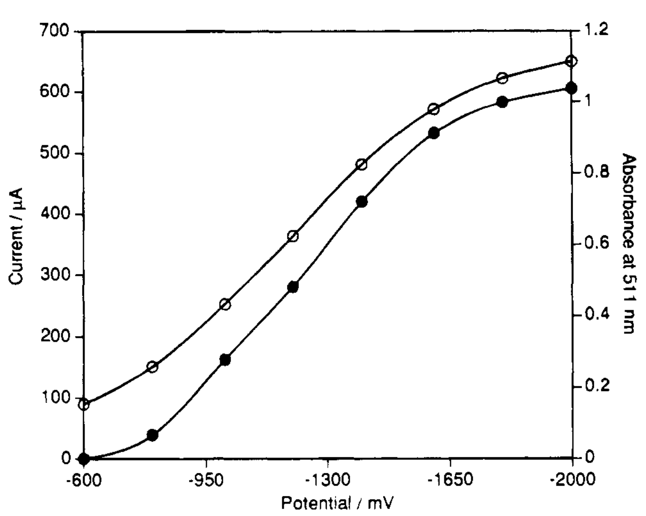

Figure 7. Current (●) and absorbance at 511 nm (○) as a function of electrolysis potential, observed in the same column electrolysis shown in Figure 5b.

$$P^+ \xrightarrow{h\nu} P^{+*} \xrightarrow{DABCO} P + DABCO^{\bullet+}$$

Further evidence for this comes from spectroelectrochemical experiments employing infrared spectroscopy in the ν(CO) region. Figure 8a shows the results of such an experiment; as electrochemical reduction proceeds, the IR bands of the parent compound, P^+, reduce in intensity and two new bands appear at 1928.5 and 1848.5 cm^{-1} (see Table 3). The shifts to low frequency (~27 and ~33 cm^{-1}) which occur on reduction arise because, although the extra electron is usually assumed to reside mostly in the bpy ligand (to give bpy^-), there is back-donation to the Re which in turn affects the back-donation to the CO groups, and hence the IR modes are lowered in frequency. Interestingly these shifts compare with the mean shift to low frequency (~31 cm^{-1}) of the ν(CO) bands in the CO_2 reductant **1**[10,14,22] but species which do not reduce CO_2, e.g. **2**, show[13b] a smaller mean shift of ~15 cm^{-1}. Note also that the intensities of the two new bands are approximately equal, implying that the angle between the two CO groups in the neutral species is also ~90°.

We are now in a position to examine TRIR experiments with DABCO. At ~100 ns, after flash photolysis of a solution of P^+Br^- in CH_3CN containing DABCO (50 mM), there is TRIR evidence for both the excited state (P^{+*}) and the reduced species (**P**). However, although the excited state has completely disappeared by 250 ns, the decay traces are not sufficiently accurate to measure the rates. Thus Figure 8b shows the TRIR spectrum at 250 ns; for comparison, Figure 8c shows an experiment in the absence of DABCO, i.e. generating the excited state. It is clear that after 250 ns the two ν(CO) bands of P^+ are depleted and two new ν(CO) bands appear at ~1932 and ~1847 cm^{-1}. From a comparison with the spectroelectrochemical data, this new species must be **P**.

Back Electron Transfer. In the flash photolysis experiments with DABCO, **P** is fairly short-lived. This is because of the back-reaction

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(22) Shu, C.-F.; Wrighton, M. S. *Inorg. Chem.* **1988**, *27*, 4326.

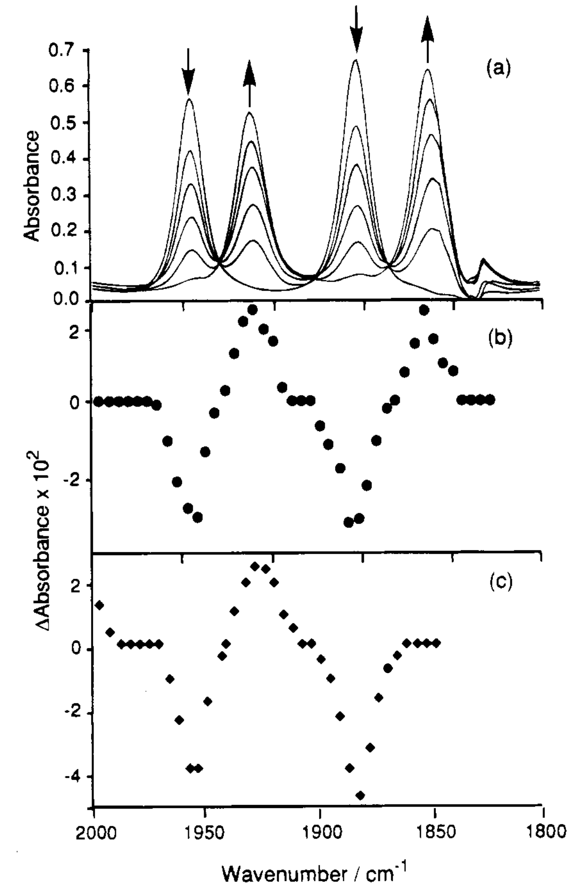


Figure 8. (a) ν(CO) IR spectra recorded following column electrolysis of P^+Cl^- (8.0×10^{-4} M) in an Ar-saturated acetonitrile solution containing 0.1 M n-Bu_4NClO_4 at the Pt wire electrode; path length 3 mm. The solution was reduced from 0 to −2.1 V at a constant flow rate of 0.2 mL min^{-1}. Downward arrows indicate loss of P^+; upward arrows show generation of **P**. (b) TRIR spectra in the ν(CO) region, of P^+Br^- (5×10^{-4} M) in an acetonitrile solution containing DABCO (50 mM), 250 ns after UV (308 nm, 20 ns) flash, under 2 atm Ar (g); path length 2 mm. (c) As for (b) except for the absence of DABCO.

Table 3. Spectroscopic Properties of $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^0$ (**P**) and Related Complexes in Acetonitrile Solution

	parent	reduced species			$\Delta\nu(CO)^h$	
	complex $\mathbf{P}^+$	$\mathbf{P}^b$	$\mathbf{P}^c$	$\mathbf{P}^{-\,b,d}$	$\mathbf{P}-\mathbf{P}^+$	$\mathbf{P}^--\mathbf{P}$
ν(CO) (cm^{-1})	1955.9^a	1928.5	1927.5	1900	~−27	~−28
	1881.3	1848.5	1852.0	1815	~−33	~−33
λ_{max} (nm)	372	349, 387	400			
		484	485	e		
		512	511			

[a] FTIR spectrum. [b] Spectroelectrochemistry results. [c] TRIR and UV/vis flash photolysis spectra. [d] The second reduction wave of $\mathbf{P}^+$ is irreversible, and therefore the exact identity of this species is unknown although the ν(CO) shifts do suggest that further reduction has occurred. [e] No bands were seen for the doubly reduced species.

$$\mathbf{P} + DABCO^{\bullet+} \xrightarrow{k_b} \mathbf{P}^+ + DABCO$$

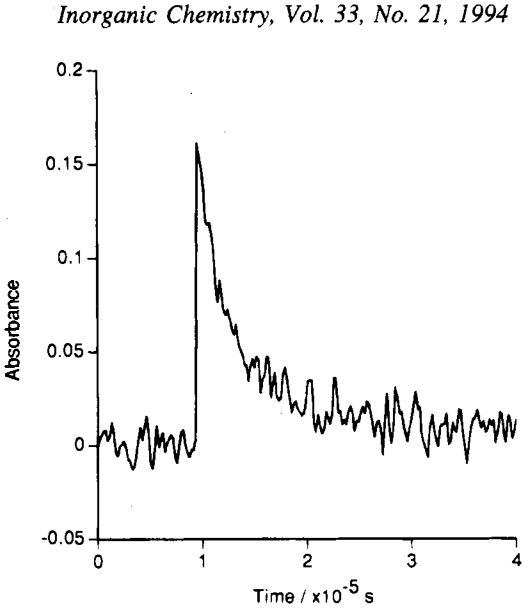
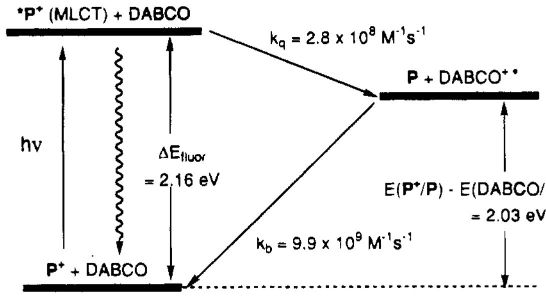


Figure 9. Kinetic trace showing the decay of **P** produced by reductive quenching of $\mathbf{P}^{+*}$ by DABCO (0.11 M) following laser excitation (355 nm, 10 ns) of $\mathbf{P}^+$ (3×10^{-4} M) in an Ar-saturated acetonitrile solution (path length 5 mm), monitored at 511 nm.

Scheme 1



Because **P** and $DABCO^{\bullet+}$ are generated in the same concentration, the rate constant for the second-order back-reaction can be obtained from a plot of 1/absorbance vs time. This should give a straight line of gradient $k_2/\epsilon l$, where ϵ is the extinction coefficient of the absorption band of **P** and l is the path length. Figure 9 shows the decay of the signal of **P** at 511 nm; the value of k_b obtained from this decay curve is $9.9 \times 10^9\ M^{-1}\ s^{-1}$, which is near to the diffusion controlled rate. In principle, the same data can be obtained from the decay of the IR bands in Figure 8b; the results, although less accurate, are consistent with the the UV/vis experiments. It should be noted that the rate constants for the photoinduced electron transfer between $\mathbf{P}^+$ and DABCO and for the back electron transfer are both reasonable values according to Marcus theory.[23] The overall photophysical processes can be summarized as shown in Scheme 1.

Conclusions

A combination of spectroscopic techniques has established that photolysis of the CO_2 reductant $Re(CO)_2$(2,2′-bipyridyl)-$(\{P(OEt)_3\}_2)^+$ ($\mathbf{P}^+$) promotes the complex into an excited state ($\mathbf{P}^{+*}$) with a lifetime of ~250 ns. The shifts from ground to excited state in the ν(CO) bands establish that, comparable to those other Re complexes, this state is an MLCT state with the charge localized on the bpy ligand. Reaction of the excited state with DABCO is monitored by both UV/visible and infrared spectroscopy; DABCO reduces $\mathbf{P}^{+*}$ to **P**, whose IR bands are shifted below those of $\mathbf{P}^+$. The back-reaction of **P** with $DABCO^+$ is fast. Preliminary experiments suggest that further activation of **P** is required before the reduction of CO_2 occurs.

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(23) Marcus, R. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1111.