Ion-Pair Charge Transfer Photochemistry in Rhenium(I) Borate Salts

Bruce H. McCosar and Kirk S. Schanze*,[†]

Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, Florida 32611-7200

Received May 9, 1996[⊗]

The photophysics and photochemistry of the salt [(bpy)Re(CO)$_3$(py)$^+$][BzBPh$_3$$^-$] (**ReBo**, where bpy = 2,2′-bipyridine, py = pyridine, Bz = $C_6H_5CH_2$ and Ph = C_6H_5) has been investigated in THF and CH_3CN solutions. UV−visible absorption and steady-state emission spectroscopy indicates that in THF **ReBo** exists primairly as an ion-pair. A weak absorption band is observed for the salt in THF solution that is assigned to an optical ion-pair charge transfer transition. Stern−Volmer emission quenching studies indicate that $BzBPh_3^-$ quenches the luminescent dπ (Re) → π* (bpy) metal-to-ligand charge transfer excited state of the (bpy)Re(CO)$_3$(py)$^+$ chromophore. The quenching is attributed to electron transfer from the benzylborate anion to the photoexcited Re(I) complex, $(bpy^{-\bullet})Re^{II}(CO)_3(py)^{+*} + BzBPh_3^- \rightarrow (bpy^{-\bullet})Re^{I}(CO)_3(py) + BzBPh_3^{\bullet}$. Laser flash photolysis studies reveal that electron transfer quenching leads to irreversible reduction of the Re(I) cation to $(bpy^{-\bullet})Re^{I}(CO)_3(py)$. Photoinduced electron transfer is irreversible owing to rapid C−B bond fragmentation in the benzylboranyl radical, $PhCH_2BPh_3^{\bullet} \rightarrow PhCH_2^{\bullet} + BPh_3^{\bullet}$. Quantitative laser flash photolysis experiments show that the quantum efficiency for production of the reduced complex $(bpy^{-\bullet})Re^{I}(CO)_3(py)$ is unity, suggesting that C−B bond fragmentation in the benzylboranyl radical occurs more rapidly than return electron transfer within the geminate radical pair that is formed by photoinduced electron transfer.

Introduction

Photoinduced charge transfer processes in transition metal complexes have been extensively investigated.[1−4] Research in this area is motivated by a number of factors. First, a significant amount of information concerning the electronic structure of inorganic and metal−organic complexes has been provided by studies of charge transfer spectroscopy;[5−8] furthermore, studies of the spectroscopy and dynamics of charge transfer excited states have provided a wealth of experimental data that has guided theoretical work on electron transfer processes.[2c,5−7,9−11] Second, metal complexes that exhibit charge transfer absorption bands in the visible region have provided the paradigm for chemical systems that convert light to chemical energy.[12] Finally, there has been recent interest in the application of metal complexes that feature charge transfer absorption and luminescence to the development of molecular probes for biology and chemical sensing.[13,14]

While a substantial body of the experimental work concerning charge transfer processes in metal−organic systems has centered on inner-sphere transitions such as metal-to-ligand charge transfer (MLCT),[2] ligand-to-metal charge transfer (LMCT),[3] and ligand-to-ligand charge transfer (LLCT),[15,16] there have been a number of investigations that have focused on the properties of "outer-sphere" transitions that involve charge transfer to or from a species that is not directly coordinated to the metal center.[16−18] In general, such outer-sphere charge transfer transitions involve an ion-pair comprising an anionic electron donor and a cationic electron acceptor and are termed ion-pair charge transfer (IPCT) transitions.[16]

Our group has been developing (photo)chemical probes that can be applied to study electronic structure and dynamics of charge transfer excited states in metal complexes.[19] Toward this objective, we have applied a number of "reactive" organic donors that undergo rapid, irreversible chemical processes triggered by single electron oxidation. To date, these reactive donors have been used mainly to probe ligand-to-ligand charge transfer states in transition metal complexes.[19]

The study presented herein describes the application of "reactive electron donors" to probe ion-pair charge transfer in salts comprising a cationic metal complex acceptor and an anionic organic "reactive donor". The objective of this study

---

[†] E-mail: kschanze@chem.ufl.edu.

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1996.

(1) Gafney, H.; Adamson, A. W. *J. Am. Chem. Soc.* **1972**, *94*, 8238.

(2) (a) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710. (b) Bock, C. R.; Connor, J. A.; Guitierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815. (c) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, *30*, 389.

(3) Endicott, J. F. In *Concepts of Inorganic Chemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; p 81.

(4) Balzani, V.; Scandola, F. In *Photoinduced Electron Transfer*, Part D; Fox, M. A., Chanon, M. D., Eds.; Elsevier: Amsterdam, 1988; p 148.

(5) (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086. (b) Tom, G. M.; Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 7827. (c) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

(6) (a) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 4393. (b) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289.

(7) (a) Doorn, S. K.; Hupp, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 4704. (b) Lu, H.; Petrov, V.; Hupp, J. T. *Chem. Phys. Lett.* **1995**, *235*, 521.

(8) Zink, J. I.; Shin, K.-S. *Adv. Photochem.* **1991**, *16*, 119.

(9) Walker, G. C.; Barbara, P. F.; Doorn, S. K.; Hupp, J. T. *J. Phys. Chem.* **1991**, *95*, 5712.

(10) Spears, K. G.; Wen, X.; Arrivo, S. M. *J. Phys. Chem.* **1994**, *98*, 9693.

(11) (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (b) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437.

(12) (a) *Energy Resources Through Photochemisry and Catalysis*; Grätzel, M., Ed.; Academic Press: New York, 1983. (b) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49.

(13) Pyle, A. M.; Barton, J. K. *Prog. Inorg. Chem.* **1990**, *38*, 412.

(14) Demas, J. N.; DeGraff, B. A. *Anal. Chem.* **1991**, *63*, 829A.

(15) Vogler, A.; Kunkeley, H. *Commun. Inorg. Chem.* **1990**, *9*, 201.

(16) For reviews of work in the area of ion-pair charge transfer see: (a) Vogler, A.; Kunkely, H. In *Photoinduced Electron Transfer II*; Mattay, J., Ed.; Topics in Current Chemistry 158; Springer-Verlag: Berlin, 1990; p 1. (b) Billing, R.; Rehorek, D.; Hennig, H., *Ibid.* p 151.

(17) (a) Kochi, J. K.; Bockman, T. M. *Adv. Organomet. Chem.* **1991**, *33*, 51. (b) Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 4669.

(18) (a) Wang, Z.; Kutal, C. *Inorg. Chim. Acta* **1994**, *226*, 285. (b) Sugimoto, H.; Hataoka, H.; Mori, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1301. (c) Sabbatini, N.; Bonazzi, A.; Ciano, M.; Balzani, V. *J. Am. Chem. Soc.* **1984**, *106*, 4055.

(19) (a) Wang, Y.; Hauser, B. T.; Rooney, M. M.; Schanze, K. S. *J. Am. Chem. Soc.* **1993**, *115*, 5675. (b) Wang, Y.; Lucia, L. A.; Schanze, K. S. *J. Phys. Chem.* **1995**, *99*, 1961. (c) Wang, Y.; Schanze, K. S. *J. Phys. Chem.* **1996**, *100*, 5408.

S0020-1669(96)00507-1 CCC: $12.00

was to design a system in which photoexcitation of an ion-pair could be coupled to an exceedingly fast, irreversible chemical process. We rationalized that by monitoring the efficiency of the overall photochemistry it would be possible to gain information concerning the electronic structure and dynamics of the IPCT state produced by photoexcitation.

In order to design an effective system, an anionic electron donor is required which undergoes a rapid chemical process triggered by single electron oxidation. Our studies were guided by Schuster and co-workers' recent work which indicates that alkyltriphenylborates ($R{-}BPh_3^-$) undergo an exceedingly rapid C−B bond fragmentation upon single electron oxidation, i.e.,[20]

$$R{-}BPh_3^- \xrightarrow{-e^-} R{-}BPh_3^\bullet \xrightarrow{\text{fast}} R^\bullet + BPh_3 \qquad (1)$$

Thus, in the present study we have focused attention on salts which pair the cationic metal complex acceptor $(bpy)Re^I(CO)_3(py)^+$ (bpy = 2,2′-bipyridine and py = pyridine) with the anionic "reactive" donor benzyltriphenylborate, $BzBPh_3^-$ (Bz = C_6H_5-CH_2- and Ph = C_6H_5-). This system is of interest for several reasons. First, the $(bpy)Re^I(CO)_3(py)^+$ cation exhibits a comparatively long-lived $d\pi$ (Re) → π^* (bpy) MLCT excited state which is strongly luminescent. This excited state is a relatively strong oxidant and has been well characterized with respect to its photoredox reactions with a variety of neutral electron donors.[21] Second, in nonpolar solvents at relatively low concentration $[(bpy)Re^I(CO)_3(py)^+][BzBPh_3^-]$ exists predominantly as an ion-pair. In contrast, in polar solvents at relatively low concentration, this salt exists primarily as solvent-separated or free ions. Therefore, comparison of the overall efficiency of the photochemistry observed for the salts in nonpolar and polar solvents allows evaluation of the effect on ion-pairing on the rates of the charge transfer processes.

Experimental Section

General Synthetic Methods. Anhydrous THF was prepared by distilling over NaK/benzophenone prior to use. Triphenylboron was prepared by acidifying an aqueous solution of the NaOH adduct with CO_2, filtering out the solid, drying it *in vacuo*, and purifying it by vacuum sublimation. All other solvents and chemicals were of reagent grade and used without purification. NMR spectra were taken on a GE QE 300-MHz instrument.

***fac*-(2,2′-Bipyridyl)tricarbonylpyridylrhenium(I) Hexafluorophosphate ($RePF_6$).** This compound was prepared and purified by using a literature method[19a,22] and was isolated as a bright yellow powder in 88% yield. Anal. Calcd for $C_{18}H_{13}F_6N_3O_3PRe$: C, 33.24; H, 2.01; N, 6.46. Found: C, 32.85; H, 1.73; N, 6.08. ^1H NMR (300 MHz, CD_3CN): δ 7.28 (t, 2H, 2 × *m*-pyridyl), 7.78 (t, 2H, 2 × 5-bpy), 7.84 (t, 1H, *p*-pyridyl), 8.25 (t, 2H, 2 × 4-bpy), 8.29 (d, 2H, 2 × *o*-pyridyl), 8.38 (d, 2H, 2 × 6-bpy), and 9.22 (d, 2H, 2 × 3-bpy). ^{13}C NMR (75 MHz, CD_3CN): δ 124.5, 126.4, 128.6 (*m*-, *p*-, and *o*- pyridyl, respectively), 139.7, 140.9, 151.7, and 153.6 (5-, 4-, 6-, and 3-bpy, respectively).

Tetramethylammonium Benzyltriphenylborate (TBo).[20a] Triphenylboron (788 mg, 3.25 mmol) was dissolved in 20 mL of anhydrous THF in a 250-mL Schlenk flask. After degassing with argon, 10 mL of 1.0 M benzylmagnesium chloride in diethyl ether (10 mmol) was added to the flask via a syringe. Purged a final time with argon, the mixture was allowed to stir and react for 1 h at 0 °C and 2 h more at room temperature. The Schlenk flask was then maintained under vacuum until all the THF solvent had evaporated. Following this, 10 mL of argon-degassed water was added via a cannula. Under a mild flow of argon, the flask was shaken and stirred to dissolve the $MgCl^+$ salt of the product. Another Schlenk flask containing an argon-degassed solution of 1.5 g of tetramethylammonium chloride (13.6 mmol) in 30 mL of water was prepared, and the aqueous borate solution was transferred into this Schlenk flask by filter cannula, whereupon a cloudy-white precipitate formed immediately. After thorough mixing of the solution, the precipitate was allowed to settle and crystallize further before being collected on a Büchner funnel in air. The product was recrystallized twice by dissolving the solid in a minimum amount of dry acetonitrile and dropping the solution into a rapidly stirring beaker of diethyl ether (typically 6- to 10-fold of the amount of the acetonitrile). The product was obtained as a white powdery solid, yield 1.06 g (80%). Anal. Calcd for $C_{29}H_{34}BN$: C, 85.50; H, 8.41; N, 3.44. Found: C, 85.64; H, 8.70; N, 3.46. ^1H NMR (300 MHz, CD_3CN): δ 2.48 (q, 2H, benzyl CH_2 split by spin $+^3/_2$ boron nucleus), 3.08 (s, 12H, 4 × methyls), 6.56 (d, 2H), 6.65−6.85 (m, 6H), 6.94 (t, 6H), and 7.21 (m, 6H). ^{13}C NMR (75 MHz, CD_3CN): δ 54.90 (methyls), 121.41, 125.19, 125.22, 125.25, 125.68, 129.23, and 134.75

***fac*-(2,2′-Bipyridyl)tricarbonylpyridylrhenium(I) Benzyltriphenylborate (ReBo).** The following procedure was performed under red light. In a Schlenk tube, 306 mg of **$RePF_6$** (470 μmol) and 193 mg of **TBo** (473 μmol) were dissolved in 25 mL of argon-degassed acetonitrile. Degassed water was added to the acetonitrile solution via cannula until the stirred solution became cloudy; at this point, a minimum amount of degassed acetonitrile was added to clear it again. The acetonitrile was then evaporated under reduced pressure, leaving a brownish oil in water. This oil was extracted by cannula addition of degassed methylene chloride (triple or greater the volume of the remaining water). After vigorous mixing, no trace of the oil remained and the methylene chloride layer was yellow. The methylene chloride solution was carefully transferred via a cannula to a dry Schlenk flask containing anhydrous $MgSO_4$. On the following day, the methylene chloride solution was decanted from the $MgSO_4$ and transferred by cannula to another dry, argon-degassed Schlenk flask, whereupon the solution was concentrated to 10 mL volume under reduced pressure. The methylene chloride solution was then transferred directly into a 500 mL flask containing 300 mL of air-saturated diethyl ether that was being stirred. At this point the yellow ReBo product began to precipitate slowly. The powdered precipitate became less sticky by allowing it to stir in the diethyl ether for 20−30 min. The product was obtained as an air-stable yellow powder, yield 315 mg (80%). Solid **ReBo** was air-stable; however, in solution the salt decomposes on exposure to light or air. Anal. Calcd for $C_{43}H_{35}BN_3O_3Re$: C, 61.57; H, 4.21; N, 5.01. Found: C, 61.19; H, 4.04; N, 4.82. ^1H NMR (300 MHz, CD_3CN): δ 2.48 (q, 2H, **Bo** benzyl CH_2 split by spin $+^3/_2$ boron nucleus), 6.54 (d, 2H, **Bo** aromatics), 6.61−6.84 (m, 6H, **Bo** aromatics), 6.92 (t, 6H, **Bo** aromatics), 7.16−7.30 (m, 8H, Bo aromatics overlapping with Re 2 × *m*-pyridyl), 7.74 (t, 2H, Re 2 × 5-bpy), 7.82 (t, 1H, Re *p*-pyridyl), 8.20 (t, 2H, Re 2 × 4-bpy), 8.28 (d, 2H, Re 2 × *o*-pyridyl), 8.31 (d, 2H, Re 2 × 6-bpy), and 9.20 (d, 2H, Re 2 × 3-bpy).

Photophysical and Photochemical Experiments. Except for UV−visible absorbance measurements, all photochemical experiments were carried out in solvents that were thoroughly degassed with argon. UV−visible spectra were recorded using an HP 8452A diode array spectrophotometer; spectra shown in this work are composites of many measurements, taken over a wide range of dilutions, with absorbances discarded if greater than 1 or less than 0.01. Luminescence lifetimes and steady-state emission data were determined using methods and equipment described in previous publications.[21,22] Luminescence quantum yields were determined relative to $Ru(bpy)_3^{2+}$ in degassed water (Φ_{em} = 0.057) and were corrected for differences in solvent refractive index. Transient absorption experiments were performed using a nanosecond flash photolysis system also described previously,[22b] exciting the samples with the third harmonic of a Nd:YAG laser (355 nm, 6 ns fwhm).

Relative actinometry transient absorption experiments were carried out by using a modified version of the technique described by Carmichael and Hug[23] and by us in a previous publication.[21b] Briefly,

---

(20) (a) Chatterjee, S.; Davis, P. D.; Gottschalk, P.; Kurz, M. E.; Sauerwein, B.; Yang, X.; Schuster, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 6329. (b) Murphy, S. T.; Zou, C.; Miers, J. B.; Ballew, R. M.; Dlott, D. D.; Schuster, G. B. *J. Phys. Chem.* **1993**, *97*, 13152.

(21) (a) Schanze, K. S.; MacQueen, D. B.; Perkins, T. A.; Cabana, L. A. *Coord. Chem. Rev.* **1993**, *122*, 63. (b) Lucia, L. A.; Schanze, K. S. *Inorg. Chim. Acta* **1994**, *225*, 41.

(22) (a) MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 7470. (b) Wang, Y.; Schanze, K. S. *Chem. Phys.* **1993**, *176*, 305.

(23) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

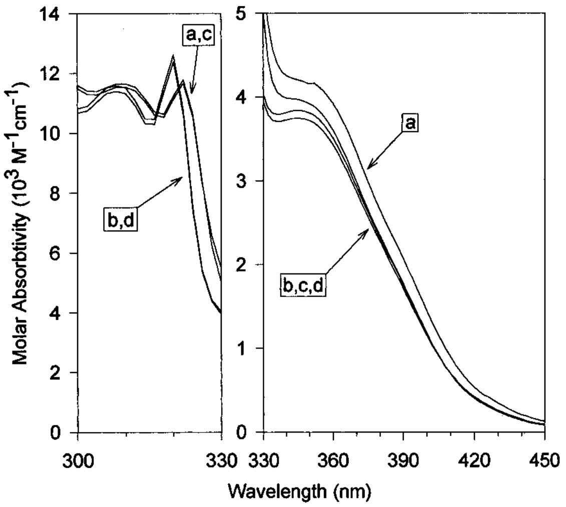


Figure 1. UV−visible absorption spectra of **RePF$_6$** and **ReBo**. (a) **ReBo**/THF; (b) **ReBo**/CH$_3$CN; (c) **RePF$_6$**/THF; (d) **RePF$_6$**/CH$_3$CN. Spectra were obtained on solutions with 1.0^{-4} M concentrations.

a solution of **RePF$_6$** (c = 120 μM) in THF served as an actinometer. The transient absorption of the Re → bpy MLCT excited state (Re$_{\text{MLCT}}$) was monitored at 370 nm and the concentration produced by the laser pulse was determined by using the value of $\Delta\epsilon_{370}^{\text{MLCT}}$ for Re$_{\text{MLCT}}$ at 370 nm (11 300 M^{-1} cm^{-1})[21b]

$$\text{concentration of Re}_{\text{MLCT}} = \frac{\Delta A_{370\text{ nm}}^{t=0}}{\Delta\epsilon_{370}^{\text{MLCT}}} \tag{2}$$

where $\Delta A_{370\text{ nm}}^{t=0}$ is the transient absorption signal extrapolated to zero time. Sample solutions contained **RePF$_6$** (c = 120 μM) along with **TBo** added in a concentration sufficient to quench 90% of the Re−bpy MLCT emission. The transient absorption of the neutral Re complex (bpy$^{-\bullet}$)Re$^{\text{I}}$(CO)$_3$(py) (**Re-0**) produced in the sample solutions by 355 laser excitation was monitored at 350 nm and its concentration was determined by using the value of $\Delta\epsilon_{350}^{\textbf{Re-0}}$ at 350 nm (5800 M^{-1} cm^{-1})[21b]

$$\text{concentration of } \textbf{Re-0} = \frac{\Delta A_{350\text{ nm}}}{\Delta\epsilon_{350}^{\text{Re}-0}} \tag{3}$$

where $\Delta A_{350\text{ nm}}$ is the transient absorption signal at 350 nm for the sample solution. Actinometer and sample solutions were run consecutively and repeatedly at laser powers ranging from 0.1 to 2.0 mJ/pulse (exposure area ca. 0.25 cm^2). The **RePF$_6$** actinometer solutions were contained in a 3.0 mL quartz cuvette and were stirred vigorously during data acquisition. **ReBo** sample solutions were contained an a recirculating cell with a total volume of 50 mL to minimize the effects of irreversible photochemistry upon the yield determinations.

Results

Salts and Solvents. The focus of this study is on the properties of the ion-pair [(bpy)Re$^{\text{I}}$(CO)$_3$(py)$^+$,BzBPh$_3$$^-$] (**ReBo**), which contains the photoactive Re(I) cation paired with the benzylborate electron donor. The properties of [(bpy)Re$^{\text{I}}$(CO)$_3$(py)$^+$,PF$_6$$^-$] (**RePF$_6$**) were examined in parallel to allow assessment of the photophysics of the Re(I) cation in the absence of the benzylborate donor. Both salts were examined in THF and CH$_3$CN, which were selected as examples of nonpolar and moderately polar solvents, respectively. As outlined below, under the conditions of the experiments carried out herein, **ReBo** and **RePF$_6$** exist primarily as ion-pairs in THF and as free ions in CH$_3$CN.

Absorption Spectroscopy. The absorption spectra of **ReBo** and **RePF$_6$** in the near-UV and visible regions as dilute solutions in THF and CH$_3$CN are presented for comparison in Figure 1. For convenience these spectra are separated into two spectral regions, with the first extending from 300 to 330 nm in the UV and the second from 330 nm in the UV to 450 nm in the visible. In the first region, both **ReBo** and **RePF$_6$** exhibit two comparatively strong transitions ($\epsilon \geq$ 10 000 M^{-1} cm^{-1}) which are ascribed primarily to ligand localized (bpy and py) π,π^* transitions.[19c] Although for each salt these ligand localized π,π^* transitions are blue-shifted slightly in CH$_3$CN compared to THF, the significant feature is that the spectra of **ReBo** and **RePF$_6$** in the same solvent are superimposable in this region. Thus, we conclude that the benzylborate anion has no effect on the absorption of the complex in the 300−330 nm region in THF where ion-pairing is expected to be significant.

In the second region, both **ReBo** and **RePF$_6$** exhibit a broad, featureless absorption with $\epsilon \approx 4 \times 10^3$ M^{-1} cm^{-1}. This absorption is due primarily to the dπ (Re) → π^* (bpy) MLCT transition. However, close inspection of the 330−450 nm region reveals an interesting feature: the spectra of **RePF$_6$**/THF, **RePF$_6$**/CH$_3$CN, and **ReBo**/CH$_3$CN are closely similar, while **ReBo**/THF shows slightly greater absorptivity between 330 and 450 nm. It is important that the enhanced absorptivity of **ReBo** in THF is reproducible and quite clearly is a property unique to **ReBo** in the nonpolar solvent. A difference spectrum of **ReBo** relative to **RePF$_6$** in THF indicates that the enhanced absorptivity is due to a broad, featureless transition with $\lambda_{\max} \approx$ 350 nm and $\epsilon_{\max} \approx$ 300 M^{-1} cm^{-1}. We attribute this broad absorption band observed for **ReBo** in THF to an ion-pair charge transfer (IPCT) transition from the benzylborate anion to the Re(I) cation.

Emission Spectroscopy of RePF$_6$ and ReBo. As noted above, the (bpy)Re$^{\text{I}}$(CO)$_3$(py)$^+$ chromophore displays a moderately intense luminescence that emanates from the dπ (Re) → π^* (bpy) MLCT excited state manifold.[21a] In order to probe the effect of the benzylborate anion and ion-pairing on the MLCT state, steady state and time resolved luminescence experiments were carried out on **RePF$_6$** and **ReBo** in CH$_3$CN and THF solutions.

Both complexes display a broad, featureless MLCT luminescence in CH$_3$CN and THF solution; emission band maxima (λ_{em}) and luminescence quantum efficiencies (Φ_{em}) are listed in Table 1. First, Φ_{em} for **ReBo** is lower compared to **RePF$_6$** in the same solvent. The extent of quenching of the steady-state luminescence by the benzylborate is quantified by the parameter, $\Phi^{\textbf{ReBo}}/\Phi^{\textbf{RePF}_6}$ (Table 1) which indicates that luminescence from **ReBo** is suppressed (compared to **RePF$_6$**) by approximately a factor of 2 in CH$_3$CN and a factor of 10 in THF. Emission lifetimes (τ_{em}) were also determined for the two complexes in CH$_3$CN and THF (Table 1). Consistent with the steady-state luminescence data, τ_{em} is suppressed for **ReBo** compared to **RePF$_6$** and the extent of lifetime quenching in each solvent is quantified by the parameter $\tau^{\textbf{ReBo}}/\tau^{\textbf{RePF}_6}$ (Table 1). In CH$_3$CN solution, τ_{em} and Φ_{em} are quenched to the same extent by the benzylborate anion; however, in THF solution Φ_{em} is quenched to a much greater extent than τ_{em} by the borate.

Several conclusions can be drawn from the luminescence data presented thus far. First, it is clear that the benzylborate quenches the MLCT excited state. Given that the singlet (and triplet) states of the borate are at significantly higher energies relative to the Re → bpy MLCT state, it is unlikely that quenching is due to energy transfer.[18a,20] Rather, we believe that the quenching is due to electron transfer from the benzylborate anion to the photoexcited Re(I) complex, i.e.

$$(\text{bpy}^{-\bullet})\text{Re}^{\text{II}}(\text{CO})_3(\text{py})^{+*} + \text{BzBPh}_3^{\,-} \rightarrow (\text{bpy}^{-\bullet})\text{Re}^{\text{I}}(\text{CO})_3(\text{py}) + \text{BzBPh}_3^{\bullet} \tag{4}$$

Table 1. Luminescence Properties of Re(I) Salts[a]

salt	solvent	λ_{max}^{em}/nm	Φ_{em}	τ_{em}/ns	$\Phi^{ReBo}/\Phi^{RePF_6}$	$\tau^{ReBo}/\tau^{RePF_6}$	$10^{10}\ k_q^{SS}$/M^{-1} s^{-1}	$10^{10}\ k_q^{LT}$/M^{-1} s^{-1}
RePF$_6$	CH$_3$CN	588	0.055	234			1.9	1.8
RePF$_6$	THF	586	0.067	238			13	3.4
ReBo	CH$_3$CN	588	0.035	160	0.64	0.68		
ReBo	THF	584	0.0081	102	0.12	0.43		

[a] λ_{max}^{em} is emission maximum; Φ_{em} is emission quantum yield; τ_{em} is emission lifetime; k_q^{SS} and k_q^{LT} are apparent Stern−Volmer quenching constants for **TBo** computed from steady-state and emission decay data, respectively.

Electron transfer quenching is supported by the fact that the free energy change for eq 4 is estimated to be −0.1 eV in CH$_3$CN based on the oxidation potential of BzBPh$_3^-$ ($E_{ox} \approx +1.09$ V)[20a] and the excited state reduction potential of (bpy)Re^I(CO)$_3$(py)$^+$ ($E_{red} \approx +1.22$ V).[21a]

Second, the consistency of the steady-state and lifetime quenching in CH$_3$CN implies that electron transfer quenching occurs only by a dynamic (i.e. diffusional) pathway in this solvent. However, the disparity between the steady-state and lifetime quenching in THF solution strongly implies that in this solvent quenching occurs by both static and dynamic pathways.[24−26] These qualitative results provide evidence that under the conditions of the emission studies ($c \approx 120\ \mu$M), in CH$_3$CN the Re(I) cation and benzylborate anion exist predominantly, if not exclusively, as free ions, while in THF solution at 120 μM the salts exist predominantly as ion-pairs wherein electron transfer quenching is very rapid, i.e.

$$[(\text{bpy}^{-\bullet})\text{Re}^{\text{II}}(\text{CO})_3(\text{py})^{+}*,\text{BzBPh}_3^{-}] \xrightarrow{\text{fast}} [(\text{bpy}^{-\bullet})\text{Re}^{\text{I}}(\text{CO})_3(\text{py}),\text{BzBPh}_3^{\bullet}] \quad (5)$$

Stern−Volmer Luminescence Quenching. In order to carefully probe the effect of ion-pairing on the MLCT emission Stern−Volmer luminescence quenching studies were carried out. The concentration of the (bpy)Re^I(CO)$_3$(py)$^+$ lumiphore was fixed at 120 μM by addition of **RePF$_6$** and the concentration of the BzBPh$_3^-$ quencher was varied by addition of [NMe$_4^+$][BzBPh$_3^-$] (**TBo**). Total luminescence quenching (i.e., static and dynamic) was assessed by analysis of steady state intensity quenching according to eq 6 while the contribution of dynamic quenching only was evaluated by analysis of lifetime quenching data according to eq 7. In eqs 6 and 7, $I°_{em}$ and $\tau°_{em}$ refer to

$$\frac{I°_{em}}{I_{em}} = 1 + k_q^{SS}\tau°_{em}[\text{BzBPh}_3^-] \quad (6)$$

$$\frac{\tau°_{em}}{\tau_{em}} = 1 + k_q^{LT}\tau°_{em}[\text{BzBPh}_3^-] \quad (7)$$

the steady-state emission intensity and lifetime, respectively, of **RePF$_6$** in the solvent of interest and k_q represents the second-order rate constant for quenching as determined from the slope of the Stern−Volmer plots, with the superscripts SS and LT referring to steady-state and lifetime, respectively.

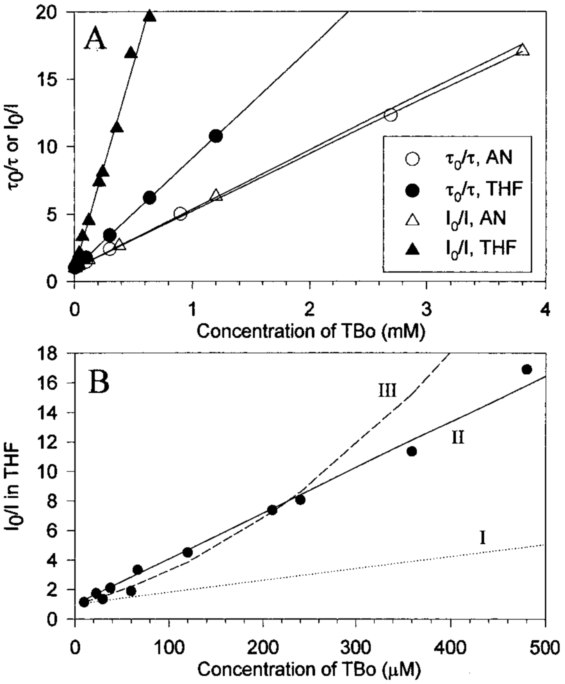


Figure 2. (A) Stern−Volmer plots for quenching of **RePF$_6$** by **TBo**. Polygons represent experimental data and solid lines are linear least squares fits of the data. (B) Comparison of experimental I_0/I data points in THF to various theoretical fits: *I* (dotted line), linear least-squares fit of τ_0/τ data; II (solid line), linear least-squares fit of I_0/I data; III (dashed line), "best" fit of experimental data to eq 9 (see text).

Figure 2A illustrates the intensity and lifetime Stern−Volmer plots for THF and CH$_3$CN solutions. First, the plots of $I°/I$ and $\tau°/\tau$ for CH$_3$CN solutions are exactly co-linear. This clearly indicates that in CH$_3$CN dynamic quenching occurs exclusively and **ReBo** exists as free ions. The Stern−Volmer data for solutions in THF contrasts with that in CH$_3$CN. Plots of both $I°/I$ and $\tau°/\tau$ are more steeply sloped for THF compared to those for CH$_3$CN, which qualitatively indicates that quenching is more efficient in the less polar solvent. Another distinguishing feature of the THF data is that the slope of the $I°/I$ plot is significantly greater than that of the $\tau°/\tau$ plot. The latter feature is a clear indication that static quenching occurs in THF and further indicates that **ReBo** exists predominantly as ion-pairs in this solvent.[24−26]

Before discussing the quantitative analysis of the Stern−Volmer quenching data, it is useful to note that the rate of dynamic quenching cannot exceed the diffusion limit. The Debye−Stokes equation can be used to estimate the rate constant for a diffusion-limited process[27]

$$k_q^{\text{diff}} = \frac{2N_Ak_BT}{3\eta}\left(\frac{(r_A + r_D)^2}{r_Ar_D}\right)\left(\frac{b}{e^b - 1}\right) \quad (8)$$

where $b = (Z_DZ_Ae^2)/(4\pi\epsilon_o\epsilon r_{DA}k_BT)$, N_A is Avogadro's number, η is the solvent viscosity, e is the electron charge, ϵ_o is the permittivity of free space, ϵ is the static dielectric constant of the solvent, r_{DA} is the reaction encounter distance, Z_D and Z_A are the charges on the donor (D) and acceptor (A) ions, respectively, and r_D and r_A are the radii of D and A, respectively. By using $Z_A = +1$ and $r_A = 4.2$ Å for the (bpy)Re(CO)$_3$(py)$^+$ acceptor and $Z_D = -1$ and $r_D = 4.7$ Å for the BzBPh$_3$ donor

---

(24) Bolletta, F.; Maestri, M.; Moggi, L.; Balzani, V. *J. Phys. Chem.* **1974**, *78*, 1374.

(25) Rybak, W.; Haim, A.; Netzel, T. L.; Sutin, N. *J. Phys. Chem.* **1981**, *85*, 2856.

(26) Frank, R.; Rau, H. *J. Phys. Chem.* **1983**, *87*, 5181.

(27) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper and Row: New York, 1987; pp 212−220.

and $r_{DA} = r_D + r_A$, eq 8 predicts that for CH_3CN and THF, respectively, k_q^{diff} is 4.0×10^{10} M^{-1} s^{-1} and 1.0×10^{11} M^{-1} s^{-1}.

The $I°/I$ and $\tau°/\tau$ data for both CH_3CN and THF solutions were subjected to linear-least squares analysis according to eqs 6 and 7, and the k_q values are listed in Table 1.[28] As expected, for CH_3CN solutions the k_q^{SS} and k_q^{LT} values are the same within experimental error and are close to the diffusion limit calculated by the Debye–Stokes equation. This is reasonable, given that electron transfer from $BzBPh_3^-$ to $(bpy^{-\bullet})Re^{II}(CO)_3(py)^{+*}$ is exothermic by ≈ 0.1 eV.[1c,20] The k_q^{LT} value determined from the THF lifetime data is also in accord with an electron transfer reaction that occurs at slightly less than the diffusion controlled limit.[1c,20] However, a linear fit of the $I°/I$ data for THF solution provides an apparent quenching rate constant that is substantially greater than that obtained by lifetime quenching and slightly greater that the diffusion limit estimated by Debye–Stokes equation. This observation clearly indicates that static quenching occurs in this solvent.

Under conditions where static quenching occurs, the steady-state emission intensity of the $(bpy)Re(CO)_3(py)^+$ chromophore is expected to follow a dependence of the form,[24,26]

$$\frac{I°_{em}}{I_{em}} = (1 + k_q\tau°[Q])(1 + \beta K_{IP}[Q]) \qquad (9)$$

where k_q is the rate constant for diffusional quenching, β is the ratio of the extinction coefficients for the $(bpy)Re(CO)_3(py)^+$ chromophore as a free ion and in the ion-pair ($\epsilon_{ion-pair}$ / $\epsilon_{free\ ion}$), K_{IP} is the assocation constant for the $[(bpy)Re(CO)_3(py)^+, BzBPh_3^-]$ ion pair, and [Q] is the concentration of the benzylborate quencher. This equation predicts that the plot of $I°/I$ will display upward curvature. Inspection of Figure 2A reveals that over the concentration range of **TBo** that was examined, curvature in the $I°/I$ plot is not readily apparent. However, the Stern–Volmer experiments in THF were limited because **TBo** was not soluble above 1 mM. Furthermore, the experiments were not carried out at constant ionic strength, and previous studies demonstrate that under these conditions linear plots of $I°/I$ are observed for systems in which ion-pairing is important.[25] Nonetheless, in an effort to provide an estimate for K_{IP}, eq 9 was used to fit the plot of $I°/I$ for the THF solution data. The dashed line in Figure 2B was calculated by using eq 9 with $k_q = 3.4 \times 10^{10}$ M^{-1} s^{-1}, $\beta = 1.0$, and $K_{IP} = 8 \times 10^3$ M^{-1}. While the value of K_{IP} arrived at in this manner is clearly only an approximation, it is in accord with values determined by Kochi and Bockman for ion-pairs comprised of monovalent organic cations paired with monovalent organometallic anions in THF solution.[17]

In summary, the Stern–Volmer luminescence quenching experiments lead to the following conclusions. (1) In CH_3CN solution for concentrations ≤5 mM quenching of the Re → bpy MLCT state occurs exclusively by dynamic quenching. No ion-pairing is apparent within this concentration range. (2) In THF solution MLCT quenching occurs by static and dynamic pathways. In this solvent ion-pairing is significant even at concentrations ≤0.1 mM. (3) The luminescence data is consistent with an association constant $K_{IP} = 8 \times 10^3$ M^{-1} for **ReBo** in THF.

Transient Absorption Spectroscopy. Nanosecond laser flash photolysis experiments were carried out in order to identify the following: (1) the primary products of excited state electron transfer between the Re(I) cation and the benzylborate anion; (2) the quantum efficiency for formation of the electron transfer products. These studies were carried out in THF and CH_3CN with the objective of determining whether ion-pairing has an effect on the nature and/or yields of the electron transfer products. All experiments were carried out with the concentration of $(bpy)Re(CO)_3(py)^+$ held at 120 μM and the concentration of $BzBPh_3^-$ was adjusted by addition of **TBo**. The optical density of solutions at the laser excitation wavelength (355 nm) was matched in all samples.

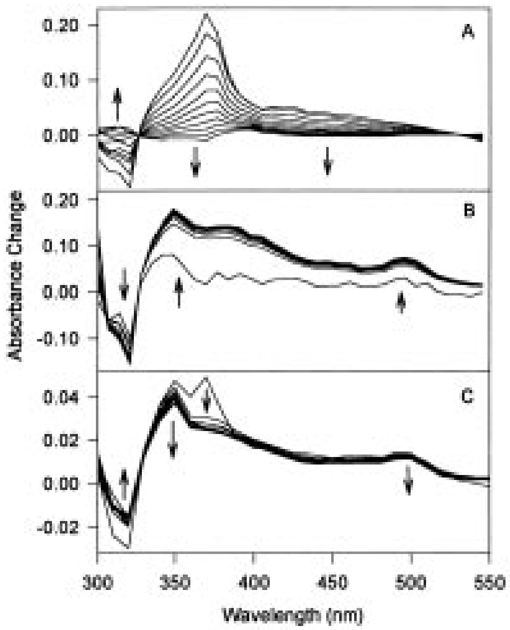


Figure 3. Transient absorption-difference spectra: (A) 120 mM **RePF₆** in THF solution, delay times ranging from 0 to 400 ns after laser pulse; (B) 58 mM **RePF₆** and 100 mM triethylamine in THF solution, delay times ranging from 0 to 40 μs after laser pulse; (C) 120 mM **RePF₆** and 360 mM **TBo** in THF solution, delay times ranging from 0 to 3.2 μs after laser pulse.

Figure 3A illustrates transient absorption difference spectra for a solution of **RePF₆** in THF at delay times ranging from 0 to 400 ns following laser excitation. The strong absorption at 370 nm and moderate bleaching at 320 nm are characteristic of the Re → bpy MLCT excited state. In accord with this assignment the transient decays with $\tau = 240$ ns, in good agreement with the emission lifetime. The difference molar absorptivity for the MLCT state of **RePF₆** in THF at 370 nm ($\Delta\epsilon_{370}$) was determined to be 11 300 M^{-1} cm^{-1} by the relative actinometry method relative to the MLCT state of $(bpy)Re(CO)_3(4\text{-benzylpyridine})^+$ in CH_3CN ($\Delta\epsilon_{370} = 11\,600$ M^{-1} cm^{-1}).[21b]

Figure 3B illustrates transient absorption spectra for a solution of **RePF₆** in THF with 100 mM of triethylamine electron donor at delay times ranging from 0 to 40 μs following laser excitation. The difference absorption spectra are assigned to the neutral complex, $(bpy^{-\bullet})Re^I(CO)_3(py)$, that is produced by electron transfer quenching of the MLCT excited state by triethylamine, i.e.,[21b]

$$(bpy^{-\bullet})Re^{II}(CO)_3(py)^{+*} + NEt_3 \rightarrow (bpy^{-\bullet})Re^{I}(CO)_3(py) + NEt_3^{+\bullet} \qquad (10)$$

The $(bpy^{-\bullet})Re^I(CO)_3(py)$ chromophore displays a moderate (difference) absorption at 350 nm and a weak band at 490 nm in the visible. The neutral complex persists for long times following laser excitation because $NEt_3^{+\bullet}$ irreversibly decomposes and therefore cannot undergo return electron transfer with

---

(28) *A priori* the $I°/I$ data for THF solutions should not be linear. This point is discussed more thoroughly below.

the reduced complex.[29] In previous work we have determined that the molar absorptivity of the (bpy$^{-\bullet}$)Re^{I}(CO)$_3$(py) chromophore at 350 nm is $\Delta\epsilon_{350} = 5800$ M^{-1} cm^{-1}.[21b]

Figure 3C illustrates transient absorption spectra for a THF solution of **RePF$_6$** in the presence of 360 μM **TBo** for delay times ranging from 0 to 3.2 μs following laser excitation. The spectrum at the earliest delay time features a band at 370 nm which is characteristic of the Re → bpy MLCT state; however, the spectra at later delay times are clearly due to the neutral complex (bpy$^{-\bullet}$)Re^{I}(CO)$_3$(py). The transient absorption attributed to (bpy$^{-\bullet}$)Re^{I}(CO)$_3$(py) does not decay substantially within the timescale accessible by the nanosecond flash system (200 μs), indicating that return electron transfer to the oxidized benzylborate donor is infeasible. The luminescence quenching studies indicate that under the conditions used for the data shown in Figure 3c, >90% of the Re → bpy MLCT state is quenched and approximately (75%) of the Re(I) is present in ion-pairs with the benzylborate anion. Thus, the data in Figure 3c are consistent with the prompt formation of (bpy$^{-\bullet}$)Re^{I}(CO)$_3$(py) via photoinduced electron transfer from the benzylborate anion (eqs 4 and 5) followed by rapid decomposition of the benzylboranyl radical via C−B bond fragmentation

$$\mathrm{PhCH_2BPh_3^{\bullet}} \rightarrow \mathrm{PhCH_2^{\bullet}} + \mathrm{BPh_3} \qquad (11)$$

The C−B bond fragmentation is expected to produce the benzyl radical which absorbs moderately at 318 nm ($\Delta\epsilon \approx 8000$ M^{-1} cm^{-1});[30] however, the absorption of this transient is is not apparent in Figure 3C. This may be due to strong ground state bleaching which is observed between 300 and 330 nm due to depletion of the ground state Re(I) chromophore.

A transient absorption experiment carried out on a CH$_3$CN solution of **RePF$_6$** that contained **TBo** at a concentration of 1.6 mM produced time resolved spectra that are virtually the same as those shown for the THF solution in Figure 3c. Thus, the quenching of the Re → bpy MLCT state by BzBPh$_3^-$ in the more polar solvent environment also produces the neutral complex (bpy$^{-\bullet}$)Re^{I}(CO)$_3$(py).

A series of quantitative transient absorption studies were effected to determine the absolute quantum yield of (bpy$^{-\bullet}$)-Re^{I}(CO)$_3$(py) that is produced by photoinduced electron transfer. The objective of these experiments was to compare the efficiency for formation of the neutral complex: (1) in THF solution where (bpy)Re^{I}(CO)$_3$(py)$^+$ is present largely as ion-pairs with BzBPh$_3^-$ and static quenching predominates; (2) in CH$_3$CN solution where (bpy)Re^{I}(CO)$_3$(py)$^+$ is present predominatly as the free ion and only diffusional quenching occurs. In order to allow direct comparision of the yields in the two solvents, the experiments were carried out with the same concentration of (bpy)Re^{I}(CO)$_3$(py)$^+$ (to insure that the samples had the same optical density); however, the **TBo** quencher concentration was adjusted such that 90% MLCT quenching was achieved in both solvents (CH$_3$CN, [**RePF$_6$**] = 120 μM, [**TBo**] = 1.6 mM; THF, [**RePF$_6$**] = 120 μM, [**TBo**] = 300 μM). In both cases the yields of (bpy$^{-\bullet}$)Re^{I}(CO)$_3$(py) were determined relative to the yield of the Re → bpy MLCT excited state produced in a THF solution of **RePF$_6$** for laser powers ranging from 0.1 to 2.0 mJ/pulse (see Experimental Section for details).

Figure 4 illustrates a compilation of the quantitative transient absorption data for THF and CH$_3$CN solutions presented as a plot of the concentration of (bpy$^{-\bullet}$)Re^{I}(CO)$_3$(py) produced in the sample solution vs the concentration of the Re → bpy MLCT state produced in the actinometer at corresponding laser powers. Several features are of interest with respect to this data. First, the slope of the correlation in this figure is equal to the ratio of the concentration of (bpy$^{-\bullet}$)Re^{I}(CO)$_3$(py) produced in the sample to the concentration of the MLCT state produced in the actinometer, averaged over the range of laser powers used for the experiment. Assuming that the quantum efficiency for formation of the MLCT state is unity, this ratio provides the quantum yield for formation of the (bpy$^{-\bullet}$)Re^{I}(CO)$_3$(py) by photoinduced electron transfer. The interesting feature is that, for the experiments in THF and CH$_3$CN, the data follow the same correlation and the slope is approximately 0.92. In view of the fact that in both solvents the transient absorption experiments were performed under conditions where the MLCT state was quenched with 90% efficiency (i.e., $\phi = 0.90$), this result indicates that in both CH$_3$CN and in THF (bpy$^{-\bullet}$)-Re^{I}(CO)$_3$(py) is produced with *unit efficiency* following BzBPh$_3^-$ quenching of the Re → bpy MLCT state.

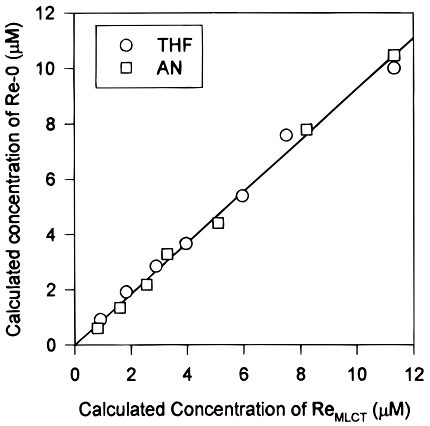


Figure 4. Plot of concentration of (bpy$^{-\bullet}$)Re(CO)$_3$(py) vs concentration of MLCT excited state, (bpy$^{-\bullet}$)Re(CO)$_3$(py)$^{+*}$, produced at laser powers ranging from 0.1 to 2.0 mJ/pulse. Circles and squares represent data for THF and CH$_3$CN solutions, respectively. The solid line represents the linear regression fit to the two data sets. The slope of the line is 0.92.

Steady State Photochemical Products. Although the work presented herein is primarily concerned with the initial products produced by photoinduced electron transfer in **ReBo** (i.e., products present within 50 μs of excitation), several qualitative experiments were carried out to determine the identity of the ultimate product(s) produced by continuous photolysis. Before presenting these results, however, it is useful to note that several groups have studied the reactivity of 19 e$^-$ complexes of type (bpy$^{-\bullet}$)Re(CO)$_3$(L), where L is either a neutral ligand such as pyridine or R−CN or an anion such as halide or triflate.[31,32] These studies suggest that the 19 e$^-$ complexes are unstable and dissociate into a 17 e$^-$ radical via loss of L (eq 12).

$$(\mathrm{bpy}^{-\bullet})\mathrm{Re(CO)_3(L)} \rightarrow (\mathrm{bpy})\mathrm{Re(CO)_3^{\bullet}} + \mathrm{L} \qquad (12)$$

Electrochemical studies suggest that this process takes place on timescales ranging from milliseconds to seconds after reduction.[31] Thus, the 19 e$^-$ species (bpy$^{-\bullet}$)Re(CO)$_3$(py) is anticipated to be stable on the time scale of the transient absorption experiments presented above, while permanent photochemistry observed for **ReBo** is expected to derive from

---

(29) Monserrat, K.; Foreman, T. K.; Grätzel, M.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 6667.

(30) Chatgilialoglu, C. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, p 1.

(31) O'Toole, T. R.; Younathan, J. N.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 3923.

(32) Stor, G. J.; Hartl, F.; van Outersterp, J. W. M.; Stufkens, D. J. *Organometallics* **1995**, *14*, 1115.

secondary reactions of the 17 e$^-$ radical, (bpy)Re(CO)$_3^{\bullet}$ which forms by dissociation of (bpy$^{-\bullet}$)Re(CO)$_3$(py).[31,32] In view of these facts, the photoproducts of continuous photolysis of **ReBo** are expected to arise either by dimerization of (bpy)Re(CO)$_3^{\bullet}$ or coupling of the metal and benzyl radicals (eqs 13 and 14).

$$2(\mathrm{bpy})\mathrm{Re(CO)}_3^{\bullet} \rightarrow (\mathrm{bpy})(\mathrm{CO})_3\mathrm{Re\text{-}Re(CO)}_3(\mathrm{bpy}) \quad (13)$$

$$(\mathrm{bpy})\mathrm{Re(CO)}_3^{\bullet} + \mathrm{PhCH}_2^{\bullet} \rightarrow (\mathrm{bpy})\ (\mathrm{CO})_3\mathrm{Re\text{-}CH}_2\mathrm{Ph} \quad (14)$$

Our first experimental investigations examined the changes in the UV−visible absorption spectrum induced by photolysis of a degassed CH$_3$CN solution of **ReBo** (c = 1.2 mM) at 436 nm. Irradiation induces the appearance of a broad visible absorption band with $\lambda_{\max} \approx 450$ nm and a concomitant decrease in the near-UV absorption of **ReBo**. An isosbestic point at $\lambda \approx 400$ nm is maintained during the early stages of photolysis (to ca. 25% conversion). Next, FTIR studies were carried out to monitor changes in the carbonyl stretching bands (ν_{CO}) induced by photolysis. In CH$_2$Cl$_2$ solution **ReBo** exhibits characteristic ν_{CO} bands at 1936 cm^{-1} (broad) and 2037 cm^{-1}. The FTIR spectrum of the photoproduct(s) in CH$_2$Cl$_2$ (produced by irradiation of **ReBo** at 436 nm in degassed CH$_3$CN solution) is characterized by ν_{CO} bands at 1897 cm^{-1} (broad) and 2023 cm^{-1}. Finally, the mass spectrum of the photoproduct mixture (low resolution, positive ion FAB) shows prominent ions at m/e 517 and m/e 427.

The product studies are consistent with the overall photochemistry occurring as suggested by eq 14, with (bpy)Re(CO)$_3$−CH$_2$Ph being the major photoproduct. The UV−visible absorption data indicate that the major photoproduct has a single visible absorption band which is at a lower energy compared to the MLCT absorption of (bpy)Re(CO)$_3$(py)$^+$. This is inconsistent with the visible absorption of the dimer (bpy)(CO)$_3$Re−Re(CO)$_3$(bpy), which displays three visible absorption bands ($\lambda_{\max}$ = 470, 600, and 805 nm).[32] On the other hand, the absorption data is consistent with that of (bpy)Re(CO)$_3$-CH$_2$Ph, which we have previously demonstrated to feature a MLCT absorption band with $\lambda_{\max}$ = 450 nm.[33] The FTIR data also rule out the dimer as a possible photoproduct, for this species is reported to display four ν_{CO} bands.[32] Unfortunately, the IR spectrum of an authentic sample of (bpy)Re(CO)$_3$−CH$_2$Ph is unavailable; however, the fact that the ν_{CO} bands for the photoproduct mixture appear at lower frequency compared to those for (bpy)Re(CO)$_3$(py)$^+$ is consistent with −CH$_2$Ph being a stronger σ-donor ligand than py. Finally, the mass spectral data are in accord with (bpy)Re(CO)$_3$−CH$_2$Ph being a major photoproduct, since the prominent peak observed at m/e 517 is clearly the parent ion of the benzyl complex and the m/e 427 peak corresponds to (bpy)Re(CO)$_3^+$, which is the most likely daughter ion which would arise from fragmentation of (bpy)Re(CO)$_3$−CH$_2$Ph$^{+\bullet}$.

Discussion

Ion-Pair Charge Transfer Absorption. To a first approximation, the IPCT absorption band observed for THF solutions of **ReBo** derives from a transition involving the HOMO of the benzylborate donor and the LUMO of the Re(I) acceptor. Since the HOMO of the borate is the boron−benzyl carbon σ bonding orbital (i.e., $\sigma_{\mathrm{C-B}}$),[20] and the LUMO of the Re(I) complex is a π antibonding orbital localized predominately on bpy (i.e., π^*_{bpy}),[21a] in a one electron approximation the IPCT transition is $\sigma_{\mathrm{C-B}} \rightarrow \pi^*_{\mathrm{bpy}}$. Given the $\sigma_{\mathrm{C-B}} \rightarrow \pi^*_{\mathrm{bpy}}$ assignment, the orbital basis for the IPCT absorption in **ReBo** bears a close analogy to IPCT bands previously observed in ion-pairs comprising *organic* pyridinium and bipyridinium cations with organic or organometallic anions. For example, Sullivan et al. observed an IPCT absorption band at $\lambda_{\max}$ = 360 ($\epsilon_{\max}$ = 150 M^{-1} s^{-1}) for CH$_3$CN solutions of the salt 1,1′-dimethyl-4,4′-bipyridinium tetraphenylborate, [MV^{2+}][BPh$_4^-$]$_2$.[34] IPCT bands in salts comprising pyridinium cations paired with organometallic anions have also been reported by by Kochi and Bockman.[17]

The energy of an IPCT absorption band for a charge transfer salt in solution is given by[16]

$$\Delta E_{\mathrm{IPCT}} = \Delta E_{1/2} - \Delta G_{\mathrm{IP}} + \chi \qquad (15)$$

where ΔE_{IPCT} is the absorption band maximum, $\Delta E_{1/2}$ is the difference between the half-wave potentials for electrochemical oxidation and reduction of the anionic donor and cationic acceptor, respectively, ΔG_{IP} is the free energy for formation of the ion-pair from the free ions, and χ is the reorganization energy associated with the optical ion-pair charge transfer transition. For the **ReBo** system, it is possible to estimate $\chi \approx 1.0$ eV from experimental values of ΔE_{IPCT} = 3.54 eV, $E_{1/2}$(BzBPh$_3^-$/BzBPh$_3$) = 1.09 V, $E_{1/2}$(bpy/bpy$^{-\bullet}$) = −1.16 V and ΔG_{IP} = −0.23 eV. As noted above, Kochi and Bockman have investigated the spectroscopic properties ion-pair charge transfer in salts of the form A$^+$Co(CO)$_4^-$, where A is a cationic pyridinium or quinolinium cation.[17] Extrapolation of a plot of ΔE_{IPCT} vs $\Delta E_{1/2}$ for the A$^+$Co(CO)$_4^-$ series to $\Delta E_{1/2}$ = 0 leads to an estimate of χ = 0.9 eV after correction for ΔG_{IP}. Thus, there is good qualitative agreement between the values of χ calculated for the **ReBo** and A$^+$Co(CO)$_4^-$ systems, a fact which supports the IPCT assignment for the weak band seen for **ReBo** in THF.

It is also useful to draw an analogy between the IPCT salts examined herein and charge transfer complexes formed between neutral organic electron/donor acceptor pairs in solution. Recent detailed studies by Farid, Gould, and co-workers provide remarkable detail concerning the structure and electronic properties of organic charge transfer complexes.[35] From bandshape analysis of the charge transfer absorption and (exciplex) fluorescence of a series of complexes they have been able to extract χ values for the charge transfer processes in a variety of solvents. For charge transfer complexes formed from cyanoaromatic acceptors paired with alkylbenzene donors in moderately polar solvents such as CHCl$_3$, χ values ranging from 0.5 to 0.8 eV are typical.[32] Of interest is the fact that the χ estimated from the IPCT absorption of **ReBo** and A$^+$Co(CO)$_4^-$ salts in THF is larger than that observed for the organic complexes. A possible reason for the larger χ values observed for the organometallic ion-pairs is that the anion/cation pairs in the organometallic salts cannot approach as closely as the aromatic donor/acceptor complexes which are likely to exist in "sandwich" geometries to optimize the donor/acceptor electronic interaction.

Photochemical Mechanism. The luminescence and transient absorption data reveal that photoexcitation of **ReBo** under conditions where the salt exists as free ions or as ion-pairs leads to photoreduction of the (bpy)Re$^{\mathrm{I}}$(CO)$_3$(py)$^+$ acceptor with unit

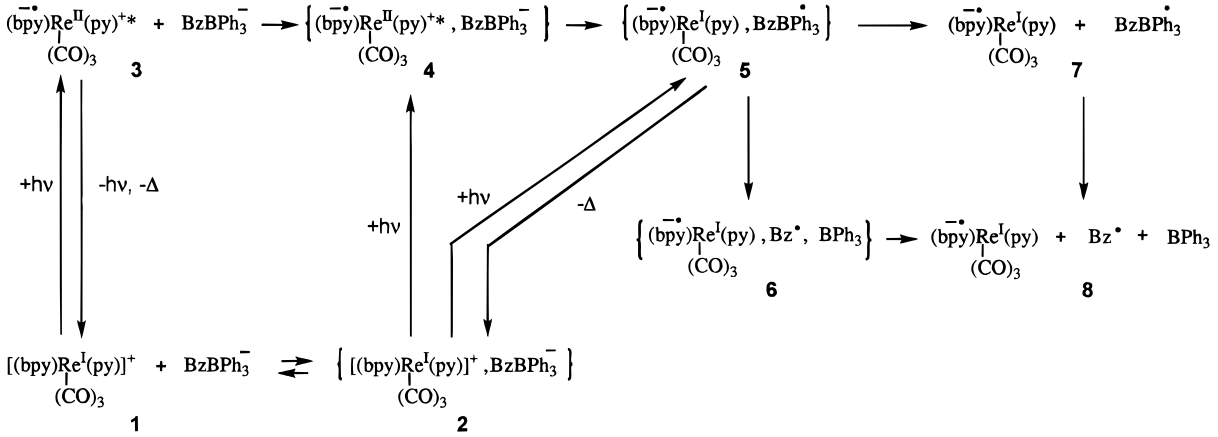
---

(33) Lucia, L. A. M.S. Thesis, University of Florida, 1993.

(34) Sullivan, B. P.; Dressick, W. J.; Meyer, T. J. *J. Phys. Chem.* **1982**, *86*, 1473.

(35) (a) Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7242. (b) Gould, I. R.; Farid, S. *J. Phys. Chem.* **1992**, *96*, 7635. (c) Gould, I. R.; Young, R. H.; Mueller, L. J.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8176. (d) Gould, I. R.; Young, R. H.; Mueller, L. J.; Albrecht, A. C.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8188.

Scheme 1



quantum efficiency. Scheme 1 illustrates a number of possible mechanistic pathways that could explain the experimental observations. In this scheme a variety of "states" are labeled with boldface numerals; for example the ground state free ions and ion-pair are labeled **1** and **2**, respectively.

It is important to note that some intermediate "states" in the photochemical mechanism may exist in one or more "forms". Specifically, two pathways are envisaged for formation of encounter complex **4**, which consists of the MLCT excited state Re(I) cation in close proximity to the benzylborate anion. Thus, **4** forms either by diffusion of the free ions together, **3** → **4**, or by direct MLCT photoexcitation of the ground state ion-pair, **2** → **4**. Although **4** has the same electronic configuration regardless of the pathway, details such as solvation state, ion-pair geometry, average separation distance, and donor−acceptor electronic coupling may be path dependent. In a like manner it is possible that geminate radical pair **5**, which is produced by electron transfer from the borate to the Re(I) complex, may exist in different solvation states and average inter-radical separation distance. For example, geminate pair **5**, which is formed by diffusional encounter followed by electron transfer (**3** → **4** → **5**), very likely has a greater average separation distance and weaker electronic coupling between the Re and boranyl radicals compared to the geminate pair which is formed by direct IPCT excitation (**2** + $h\nu$ → **5**).[35a]

On the basis of the experimental data obtained for solutions of **ReBo** in CH_3CN and THF, some conclusions can be drawn with regard to the pathways for formation of geminate radical pair **5**. First, in CH_3CN static quenching of the Re → bpy MLCT emission was not observed. This result indicates that in this solvent the predominant path to the geminate radical pair is diffusional encounter followed by electron transfer (**3** → **4** → **5**). By contrast, in THF solution **ReBo** exists predominantly as ion pair **2**. In this case, geminate radical pair **5** can be produced either via MLCT excitation followed by electron transfer (**2** + $h\nu$ → **4** → **5**) or by direct IPCT excitation (**2** + $h\nu$ → **5**). Unfortunately, due to overlap of the IPCT and MLCT transitions in **ReBo**, it is not possible to photoselect one of these two pathways. However, since the oscillator strength of the MLCT transition is 20- to 30-fold larger than that for the IPCT transition, it is likely that for **ReBo** in THF the geminate pair is formed almost exclusively via the MLCT state.

A significant point concerns the rate of electron transfer within encounter complex **4** (i.e., $k_{4\rightarrow5}$). In the luminesence lifetime studies of **ReBo** in THF a short-lived decay component that could be ascribed to **4** was not observed. Given the relatively low radiative rate of the Re → bpy MLCT state ($k_r \approx 10^5\ s^{-1}$)[21a] and the 500 ps time resolution of the single photon counting lifetime apparatus used for these studies, it is only possible to estimate a lower limit for $k_{4\rightarrow5} \geq 10^{10}\ s^{-1}$. However, it is important to note that even with $k_{4\rightarrow5} \approx 10^{10}\ s^{-1}$ the rate of electron transfer is sufficiently fast such that geminate pair **5** is formed with unit efficiency upon photoexcitation of ion-pair **2** (i.e., relaxation of **4** by radiative and/or nonradiative decay is not competitive with electron transfer).

Three channels are available for decay of geminate radical pair **5**. The first is return electron transfer (**5** → **2**) and leads back to starting materials without net photochemistry. The other two channels both lead to irreversible photoreduction of (bpy)-$Re^I(CO)_3(py)^+$. One channel involves C−B bond fragmentation within geminate radical pair **5** followed by cage escape (**5** → **6** → **8**), while the other is cage escape to form free radicals followed by C−B bond fragmentation (**5** → **7** → **8**). The quantitative transient absorption experiments indicate that (within experimental uncertainty) irreversible photoreduction of $(bpy)Re^I(CO)_3(py)^+$ occurs with unit quantum efficiency when corrected for the efficiency of MLCT quenching. This indicates that return electron transfer (**5** → **2**) does not occur and that **5** decays exclusively by one (or both) of the other channels. The fact that return electron transfer does not take place to a measurable extent in **5** indicates that the competing processes occur with (a sum of) rates that exceed the rate of return electron transfer by at least a factor of 20. Previous studies of the cage escape efficiency for bimolecular photoinduced electron transfer in the $(bpy)Re^I(CO)_3(py)^+$ system suggest that return electron transfer in **5** will occur with a rate in excess of $5 \times 10^8\ s^{-1}$.[21b] If this is correct, then the experimental observation that return electron transfer cannot compete with bond fragmentation and/or cage escape implies that the latter processes occur with a sum of rates that exceed $10^{10}\ s^{-1}$. We conclude that the dominant pathway for decay of geminate pair **5** is C−B bond fragmentation within geminate radical pair **5** followed by cage escape (**5** → **6** → **8**). This conclusion is based on observations by Schuster and co-workers which indicate that C−B bond fragmentation in boranyl radicals of the type $R{-}BPh_3^{\bullet}$ (R = alkyl or benzyl) occurs at a rate in excess of $10^{11}\ s^{-1}$.[20] The results of the present study are consistent with these findings, in that return electron transfer within geminate pair **5**, although expected to be competitive with cage escape, clearly cannot compete with the exceedingly fast bond fragmentation process.

Summary and Conclusions

The luminescence and transient absorption studies of **ReBo** indicate that the Re → bpy MLCT excited state is efficiently quenched by electron transfer from the benzylborate anion. Regardless of whether MLCT quenching occurs via a diffusional pathway or within a preformed ion-pair, return electron transfer within the geminate radical pair formed by electron transfer does not occur and therefore irreversible photoreduction of the acceptor cation occurs with unit quantum efficiency. Return electron transfer is precluded by ultrafast dissociation of the C−B bond in the boranyl radical.

Unfortunately, with the **ReBo** system it is not possible to use photoselection to compare the quantum efficency for photoreduction for IPCT and MLCT excitation of the ion-pair in THF, because the two optical transitions occur in the same wavelength range. Interest in this point is motivated by our recent observations concerning cage escape yields in ion-pairs of the type $[(bpy)Re^{I}(CO)_3(py)^{+}][Co(CO)_4^{-}]$,[36] which imply that return electron transfer is much more rapid in geminate pairs formed by IPCT excitation compared with those formed by excitation of the Re → bpy MLCT state in the ion-pair. Thus, current work on Re−borate ion-pairs is directed to preparation of ion-pairs in which the IPCT absorption is clearly red-shifted from the Re → bpy MLCT transition.

Acknowledgment. We gratefully acknowledge support for this project from the National Science Foundation (Grant No. CHE 94-01620). B.H.M. holds an NSF Minority Fellowship (1994−1997).

IC9605074

---

(36) Lucia, L. A. Ph.D. Dissertation, University of Florida, 1996.