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PHOTOCHEMISTRY OF ELECTRON DONOR-ACCEPTOR COMPLEXES OF THE BIS(FULVALENE) DICOBALT MONO- AND DICATIONS

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ABSTRACT

Addition of carbon tetrachloride or chloroform to acetonitrile solutions of the bis(fulvalene)dicobalt monocation results in the appearance of new absorption features which are attributed to formation of electron donor-acceptor complexes. The association constants of these complexes are 2.36 /mole fraction (carbon tetrachloride) and 2.74 /mole fraction (chloroform). Excitation in the absorption bands of the donor-acceptor complexes results in oxidation of the monocation to the dication with high quantum yields. A donor-acceptor complex is also formed when sodium tetraphenylborate is added to acetonitrile solutions of the bis(fulvalene)dicobalt dication. Spectroscopic determination of the association constant of the dication with tetraphenylborate yields a value of 26.3 /mole fraction. Excitation of the absorption bands of the ion-pair results in high quantum yields for formation of the bis(fulvalene) dicobalt monocation. Biphenyl is found in photolyzed solutions as a byproduct of the oxidation of the tetraphenylborate anion.

INTRODUCTION

The coupling of two metallocene moieties in bis(fulvalene)dimetal complexes $[(C_{10}H_8)_2M_2]^{n+}$ leads to materials which, in certain of their oxidation levels, display intense absorption bands in the near infrared region of the electromagnetic spectrum. Examples of complexes which display these bands include $[(C_{10}H_8)_2Fe_2]^{1+}$ (1550nm)(ref.1-5) $[(C_{10}H_8)_2Ni_2]^{0/1+/2+}$ (900-1000nm)(ref.6), and $[(C_{10}H_8)_2Co_2]^{0/1+}$ (980nm)(ref.6). Comparable absorption bands are notably absent (ref.4,5) in $[(C_{10}H_8)_2Fe_2]^{0/2+}$ as well as in the parent $Fe(Cp)_2{}^{0/1+}$, $Ni(Cp)_2{}^{0/1+}$, and $Co(Cp)_2{}^{0/1+}$ metallocenes (Cp=cyclopentadienyl)(ref.7-11). Although initial studies of $[(C_{10}H_8)_2Fe_2]^{1+}$ suggested (ref.1,2) that this band might be due to an intervalence charge-transfer (IT)(ref.12) in a class II mixed valence system (ref.13), later studies (ref.4,5) of this complex showed it to be a class III system. The appearance of similar bands in several oxidation levels in bis(fulvalene) complexes of Ni and Co further confirmed the inappropriateness of an IT assignment in these complexes. The extinction coefficients of the near infrared absorption bands in the $[(C_{10}H_8)_2Fe_2]^{1+}$ and $[(C_{10}H_8)_2Co_2]^{0/1+}$ complexes (10^3-10^4 $M^{-1}cm^{-1}$) clearly indicate their spin-allowed nature; however, the

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orbital character of this transition has been discussed in detail for only the iron complex (ref.5,14).

The position and intensity of the near infrared absorption band in the $[(C_{10}H_8)_2Co_2]^{1+}$ complex is of particular interest for its potential to absorb a large portion of the solar emission spectrum. Quantitative considerations of inherent energy losses associated with threshold solar energy converters indicate that losses due to non-absorption of wavelengths longer than the threshold and vibrational deactivation at wavelengths shorter than the threshold are minimized for a threshold wavelength of about 1110nm at AM 1.2 (ref.15,16). Although the optimum threshold wavelength is somewhat shorter when radiative losses are included (ref.16,17), threshold wavelengths greater than 800nm are clearly required for near-maximum conversion of solar energy to internal energy at a threshold. Few discrete, solvated molecular species have electronic absorption features in this low energy region, and, when observed, these transitions are often low intensity IT bands which lead to rapid conversion of the excitation energy to heat via vibrational deactivation processes.

In addition to its favorable near infrared absorption properties, the bis(fulvalene)dicobalt monocation is known to be both oxidizable and reducible to the dication and neutral species, respectively (ref.18). Reduction potentials for these processes, which are each polarographically reversible in acetonitrile, are at +0.17v (2+/1+) and -0.71v (1+/0) vs NHE. Thus, both the spectroscopic absorption and electrochemical properties of the bis (fulvalene)dicobalt complexes suggest that they might participate in photoredox processes under long-wavelength illumination. These considerations have led us to study the spectroscopic and photochemical properties of the bis (fulvalene)dicobalt mono- and dications under a variety of conditions. Extended Huckel calculations have been performed in conjunction with these studies in order to clarify further the orbital character of the intense near infrared absorption band of the monocation.

EXPERIMENTAL TECHNIQUES

Synthetic Procedures

Bis(fulvalene) dicobalt dihexachlorophosphate. The hexachlorophosphate salt of the dicationic species was prepared by the Davison and Smart method (ref.18). Purification was achieved by repeated recrystallizations from ethanol/acetonitrile mixtures followed by column chromatography on Sephadex LH-20. Elution with acetonitrile gave clean separations of the copper-red dication from traces of the dark-green monocation which remained in the recrystallized samples prior to column chromatography. Other, unidentified impurities remained near the top of the column during elution with acetonitrile.

Bis(fulvalene) dicobalt hexachlorophosphate. The hexachlorophosphate salt of the monocationic species was prepared by reduction of the dication with hydrazine hydrate in acetonitrile according to the method of Smart (ref.19,20). Slow cooling of the dark green solution resulting from reduction of the orange dication gave dark green microcrystals of the monocation. These were collected and washed with absolute ethanol and then dry ether, and dried under vacuum. Purification was accomplished by recrystallization from acetonitrile followed by column chromatography as described above for the dication.

Absorption Measurements

Absorption spectra in the visible/ultraviolet and in the near-infrared regions were monitored with Cary model 15 and model 14 spectrophotometers, respectively. Metal complex concentrations were typically 3.5×10^{-4} M for $[(C_{10}H_8)_2Co_2]^{1+}$ and 5.5×10^{-4} M for $[(C_{10}H_8)_2Co_2]^{2+}$; however, conformance to Beer's law could be demonstrated for each complex in acetonitrile over the range 10^{-3}-10^{-5} M. Due to the photoactivity of several of the solutions which were studied, sample preparations were, in these cases, performed in a darkroom. In order to prevent photolysis during absorption measurements with the Cary model 14 in the near-infrared region, a Corning 2-58 filter was placed between the tungsten analysis lamp and the sample. This filter removed wavelengths shorter than 630nm. Association constants were determined with samples prepared in the dark from a stock solution of the metal complex in acetonitrile and the appropriate donor or acceptor. Halocarbon (acceptor) concentrations were adjusted to 20, 30, 40, or 50% by volume, while sodium tetraphenylborate (donor) concentrations of 1:1, 5:1, or 20:1 mole ratio of donor:complex were employed. Absorption measurements of the photoactive donor/complex and acceptor/complex solutions were obtained by changing samples after each 200nm increment of spectral scanning in order to minimize sample photolysis in the analyzing beam. Association constants were calculated according to the method of Borrell and Henderson (ref.21).

Studies of the pressure dependence of the absorption spectrum of $[(C_{10}H_8)_2Co_2]^{1+}$ were performed with a high pressure apparatus described by Dawson and Offen (ref.22). The body of the pressure cell, which was constructed from a "Berylco 25" Be/Cu alloy, was fitted with Linde synthetic sapphire windows. The sample capsule was constructed from a cylindrical quartz tube which was cut to the desired length and sealed at one end with a quartz disc. After filling with the sample solution, the other end was sealed with a stainless steel piston fitted with a teflon O-ring. Hexanes were used as the pressure transmitting fluid in the cell. A Cary model 14 spectrophotometer modified to accomodate the high pressure cell was used for absorption measurements at 1-5 Kbar.

Photolysis Apparatus and Procedures

Photoredox quantum yields were determined with a continuous-beam photolysis system which utilized a 200 W high pressure mercury lamp (Illuminations Industries) in a PEK 911 lamp housing as an excitation source. A water-filled quartz cell was used as an infrared filter on the source, and the 365nm mercury line was isolated with an Oriel narrow band pass interference filter. The filtered lamp output was collimated with a supracil lens and passed through a manual shutter into a 1cm pyrex sample cell. The temperature of the photolysis solution was maintained at 25°C in a hollow brass cell holder with a Forma model 2095-2 constant temperature circulator. Light intensities at the irradiation wavelength, determined by ferrioxalate actinometry (ref.23), were approximately $1.6x10^{-6}$ Einsteins/min. Quantum yields were determined from changes in the electronic absorption spectrum of the starting material, monitored with a Cary model 118 spectrophotometer, as a function of irradiation time. Photolysis products were identified by electronic absorption spectroscopy, or, when appropriate, ^{13}C NMR spectroscopy, from samples photolyzed to completion. ^{13}C NMR spectra were obtained with a Nicolet NT-300 FT spectrometer.

Laser flash photolysis experiments were performed with pulses from a Quanta-Ray DCR-1 Nd/YAG laser. Absorption changes in the sample, which was contained in a 1cm quartz fluorescence cell, were followed by monitoring the intensity of light from an ILC Technology tungsten analyzing source, transmitted by the sample, as a function of time following pulsed laser excitation of the sample. Light from the analyzing source was passed through a Spex Minimate-2 single monochromator and focused by quartz lenses to intersect the pulsed laser beam in the sample. After passing through the sample, additional quartz lenses were used to focus the transmitted light onto the input slit of a Spex Spectramate double monochromator. An RCA 8852 photomultiplier at the output of this monochromator was used to monitor the intensity of transmitted light whose time dependence was analyzed with a Tektronix WP2110 transient digitizer system. This system employs a 7912AD digitizer and 4052 desktop computer to digitize and analyze the time dependence of transients generated by single laser pulses.

RESULTS

Absorption Spectroscopy

The ultraviolet/visible/near-infrared absorption spectrum of $[(C_{10}H_8)_2Co_2]^{1+}$ in acetonitrile is shown in Figure 1. Three well-defined absorption maxima are observed at 346nm ($5.8x10^3M^{-1}cm^{-1}$), 416nm ($1.2x10^3M^{-1}cm^{-1}$) and at 937nm ($7.3x10^3M^{-1}cm^{-1}$). The positions and intensities of these bands were not significantly affected when the solvent was changed to N,N-dimethylformamide. However, dissolution of the monocation in acetonitrile/carbon tetrachloride or acetonitrile/chloroform mixtures was found to cause large changes in the absorption spectrum in the visible and ultraviolet regions. These effects are illustrated for a 50% solution of CCl_4 in acetonitrile in Figure 1. Although initial measurements suggested some changes in the near-infrared absorption band in the presence of the halocarbon solvents, later studies showed these changes to be associated with photolysis of the complex in the halocarbon-containing solvent. Samples prepared in the dark and protected from excessive visible or ultraviolet irradiation during absorption measurements were found to show no solvent-halocarbon shifts in their near-infrared absorption features, but did show the shifts in the visible and ultraviolet regions illustrated in Figure 1.

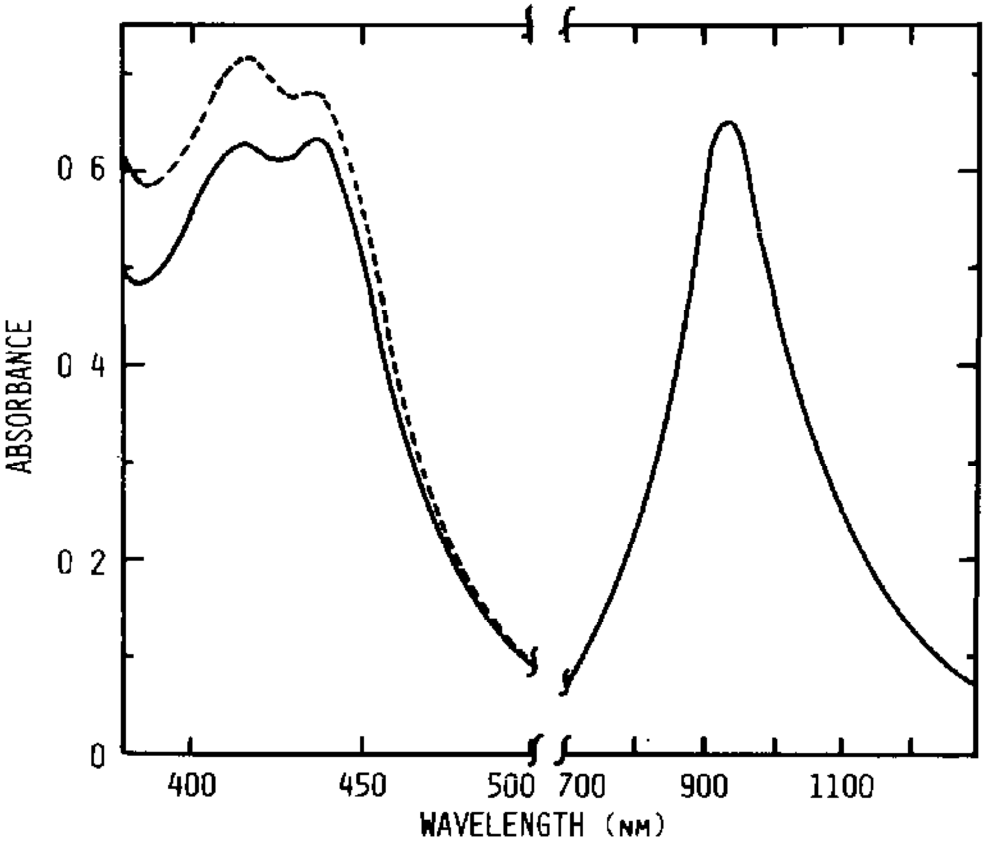

Fig. 1. Visible and near-infrared absorption spectra of 3.5 x 10^{-4} M solutions of the bis(fulvalene) dicobalt monocation (hexachlorophosphate salt) in acetonitrile (———) and in 50% carbon tetrachloride/acetonitrile (- - - -).

The ultraviolet/visible absorption spectrum of $[(C_{10}H_8)_2Co_2]^{2+}$ in acetonitrile is shown in Figure 2 on the following page. Two prominent absorption features are seen at 420nm ($4.3\times10^2 M^{-1}cm^{-1}$) and at 342nm ($1.5\times10^3 M^{-1}cm^{-1}$). No absorption features are seen in the near-infrared region, and addition of halocarbon solvents does not alter the positions or intensities in the absorption spectrum. However, addition of sodium tetraphenylborate to acetonitrile solutions of $[(C_{10}H_8)_2Co_2]^{2+}$ results in large changes in positions and intensities of the absorption bands, illustrated in Figure 2. Due to the photoactivity of solutions containing sodium tetraphenylborate (see below), they had to be protected from excess irradiation during absorption measurements in order to obtain reproducible absorption data.

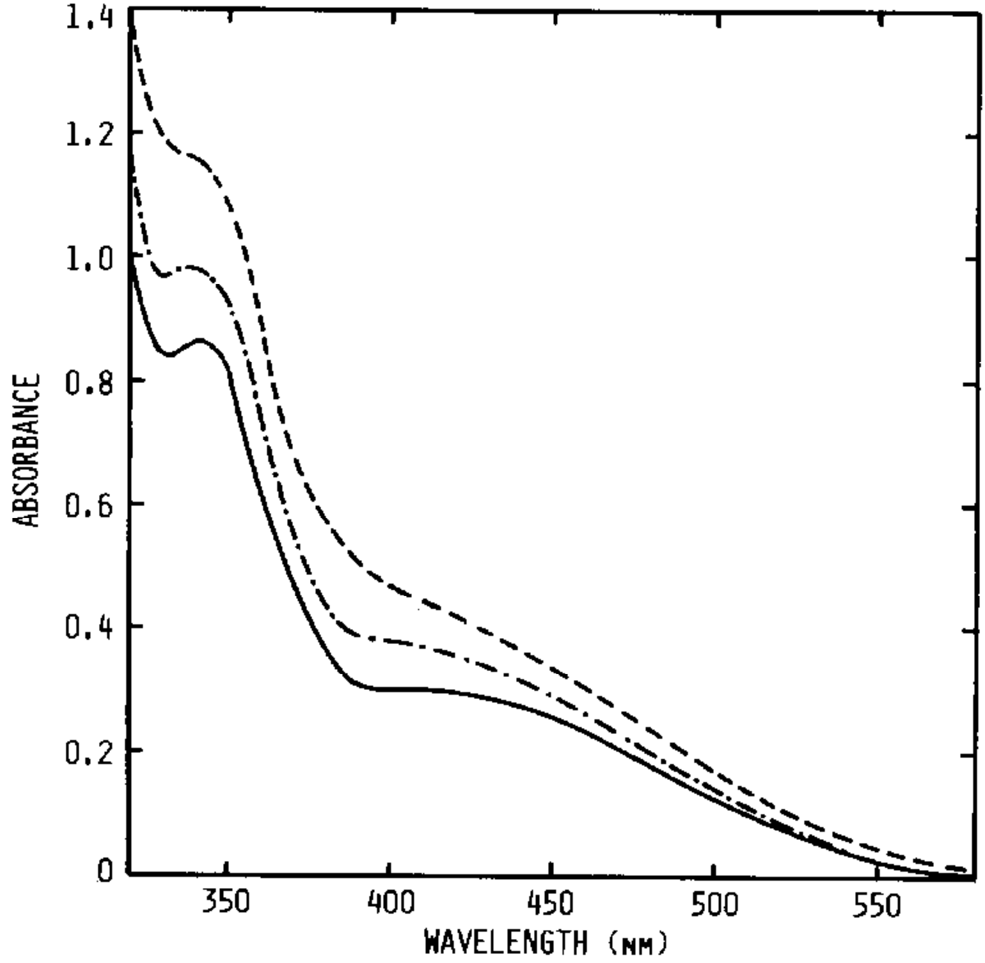

Fig. 2. Visible absorption spectra of the bis(fulvalene) dicobalt dication (5.50×10^{-5} M, hexachlorophosphate salt) in acetonitrile (———); in acetonitrile with 2.75×10^{-4} M added sodium tetraphenylborate (-·-·-·-); in acetonitrile with 1.38×10^{-3} M added sodium tetraphenylborate (- - - -).

Results of application of high pressures to solutions of $[(C_{10}H_8)_2Co_2]^{1+}$ in acetonitrile and in a solvent composed of 30% CCl_4 in acetonitrile are illustrated in Figure 3 on the following page. Application of pressure to 3 Kbars did not alter the position or intensity of any of the absorption features in acetonitrile. However, in 30% CCl_4/acetonitrile the position of the near-infrared absorption feature, which is not affected by the halocarbon at ambient pressure, is affected by the application of 3 Kbars pressure. Under these conditions the band maximum red shifts from 939nm to 958nm and decreases slightly in its intensity.

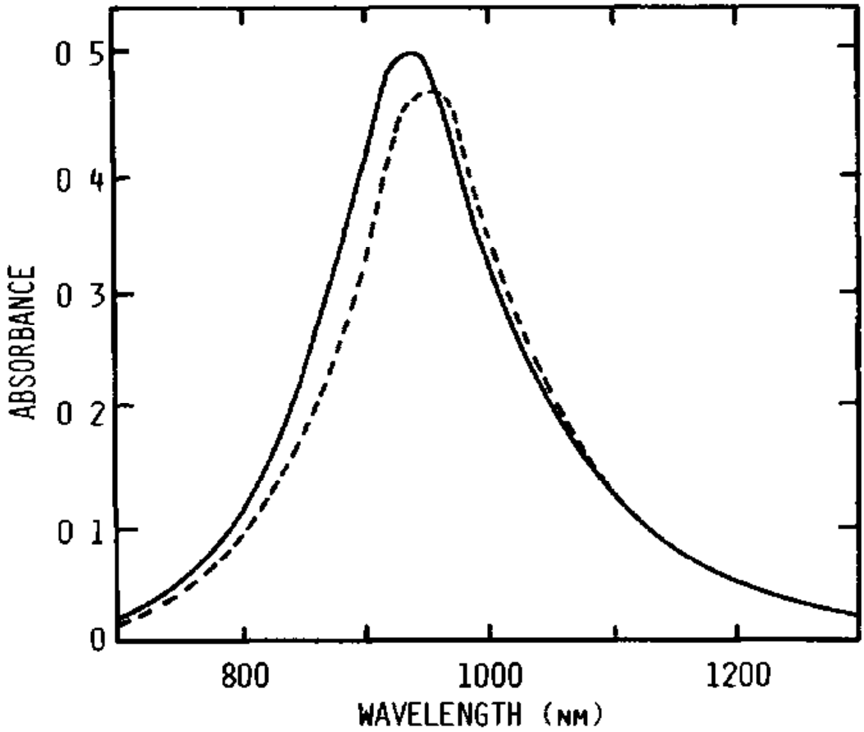

Fig. 3. Near-infrared absorption spectrum of the bis(fulvalene) dicobalt monocation (hexachlorophosphate salt) in 30% chloroform in acetonitrile at ambient pressure (———) and at 3 Kbar applied pressure (- - - -).

Determination of Association Constants

Previous studies of the ultraviolet/visible absorption spectra of $Fe(Cp)_2$ (ref.24), $Ru(Cp)_2$ (ref.21), $Ni(Cp)_2$ (ref.25), and $Co(Cp)_2$ (ref.25) have established the tendency of these species to form intermolecular charge-transfer complexes with halocarbon solvents. The effects of added halocarbons on the absorption spectrum of $[(C_{10}H_8)_2Co_2]^{1+}$ are similar to those observed previously for the metallocenes, and are similarly ascribed to formation of an intermolecular complex as illustrated in equation (1) below.

$$[(C_{10}H_8)_2Co_2]^{1+} + \underset{(X=CCl_4 \text{ or } CHCl_3)}{X} \xrightleftharpoons{K} [(C_{10}H_8)_2Co_2:X]^{1+} \qquad (1)$$

The spectral effects induced by CCl_4 and $CHCl_3$ are distinct; absorption changes due to added CCl_4 occur at wavelengths shorter than 450nm, whereas spectral changes due to added $CHCl_3$ are limited to the region below 370nm. The changes in the apparent molar absorptivities for addition of these halocarbons to acetonitrile solutions of the bis(fulvalene) dicobalt monocation are listed in Table 1 below for a few representative wavelengths.

TABLE 1
Variation of the apparent absorptivity of the bis(fulvalene) dicobalt monocation in mixtures of halocarbons and acetonitrile

Sovent composition (% by volume)		Molar Absorptivity ($M^{-1}cm^{-1}$) 416 nm	346 nm	300 nm
CH_3CN	100%	1210	5800	6450
$CHCl_3$	20%	"	5840	6840
$CHCl_3$	30%	"	5900	6930
$CHCl_3$	40%	"	6050	7080
$CHCl_3$	50%	"	6100	7210
CCl_4	20%	1260	6020	7020
CCl_4	30%	1280	6090	7200
CCl_4	40%	1320	6130	7490
CCl_4	50%	1340	6190	7610

The difference in the molar absorptivity in acetonitrile solutions ($\varepsilon[\lambda,B]$) and the molar absorptivity in halocarbon/acetonitrile mixtures ($\varepsilon[\lambda,A]$) can be expressed (ref.21,24,26) as

$$(\varepsilon[\lambda,A]-\varepsilon[\lambda,B])^{-1} = (\varepsilon[\lambda,C]-\varepsilon[\lambda,B])^{-1}(1+(K[A])^{-1}) \qquad (2)$$

where $\varepsilon[\lambda,C]$ is the molar absorptivity of the charge transfer complex, K is the equilibrium constant for association (eq (1)), and [A] is the mole fraction of added halocarbon. According to equation (2), K can be determined from the ratio of the intercept to the slope of a plot of $(\varepsilon[\lambda,A]-\varepsilon[\lambda,B])^{-1}$ versus $[A]^{-1}$. Evaluation of K from absorption data at an analysis wavelength of 300nm yields values of 2.36 mole fraction^{-1} (0.12 M^{-1}) for association of the bis(fulvalene) dicobalt monocation with CCl_4 and 2.74 mole fraction^{-1} (0.14 M^{-1}) for association with $CHCl_3$.

The changes in the absorption spectrum of the bis(fulvalene) dicobalt dication induced by addition of sodium tetraphenylborate were treated in a manner analogous to that described above for monocation/ halocarbon association. Apparent molar absorptivities for the dication/tetraphenylborate system at several representative wavelengths are listed in Table 2. Analysis of these data at 420nm according to Equation (2) yields a value of 26.3 mole fraction^{-1} for the association constant of the $[(C_{10}H_8)_2Co_2{:}B(Ph)_4]^{1+}$ ion pair.

TABLE 2
Variation of the apparent absorptivity of the bis(fulvalene) dicobalt dication in mixtures of sodium tetraphenylborate and acetonitrile

Mole ratio, $B(Ph)_4^-:[Co(ful)]_2^{2+}$	Molar absorptivity ($M^{-1}cm^{-1}$) 500 nm	440 nm	420 nm
0 : 1	171	428	468
1 : 1	184	457	506
5 : 1	202	495	565
20 : 1	259	605	709

Photochemical Results

Results of photolysis of the bis(fulvalene) dicobalt monocation in halocarbon solvents are illustrated in Figure 4 below for a photolysis at 365nm in 50% CCl_4 in acetonitrile. The spectral changes observed during photolysis are consistent

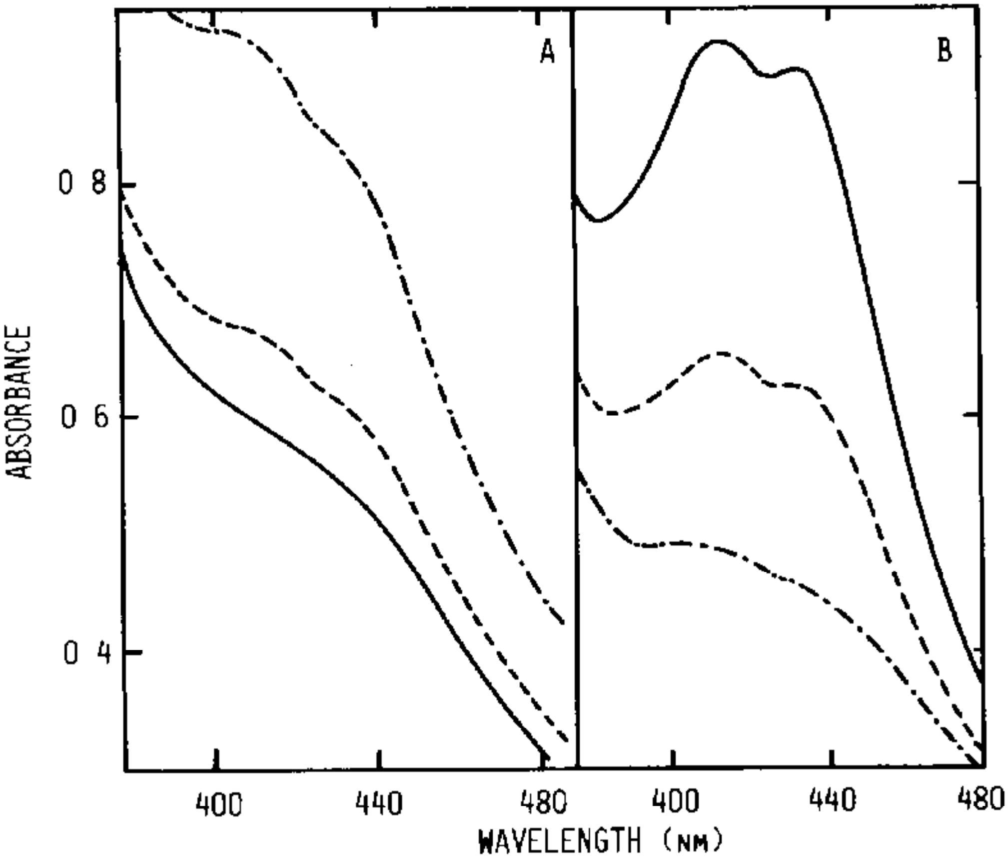

Fig. 4. Absorption spectra of: A) The bis(fulvalene) dicobalt dication and sodium tetraphenylborate in acetonitrile; and B) The bis(fulvalene) dicobalt monocation in 50% carbon tetrachloride/acetonitrile as a function of photolysis time at 365 nm. (———), prior to photolysis; (- - -), after 30 minutes photolysis; (-·-·-), after 60 minutes photolysis.

with formation of the bis(fulvalene) dicobalt dication. The formation of this species after extensive photolysis was further confirmed by its isolation and subsequent identification with ^{13}C NMR spectroscopy. Attempts to isolate and identify, by gas chromatographic techniques, decomposition products formed after photoreduction of the halocarbons, were unsuccessful. Quantum yield data for irradiation at 365nm in both CCl_4/acetonitrile and $CHCl_3$/acetonitrile solvent mixtures are compiled in Table 3 below. Irradiation of solutions of $[(C_{10}H_8)_2Co_2]^{1+}$ at wavelengths in the near infrared absorption band (> 700nm) resulted in no net photolysis, suggesting that the unassociated species is not photoactive, and that the photoredox reaction results only from irradiation of the charge-transfer complex. Since quantum yields based on the total absorption at 365nm include absorption by both the unassociated and associated species, these values were corrected to reflect yields based on the net absorption by the associated charge-transfer complex. The results of this correction, which can be accomplished (ref.26) by dividing apparent quantum yields by $(\varepsilon_{app}-\varepsilon)/\varepsilon_{app}$ (ε_{app} is the apparent molar extinction coefficient in the mixed halocarbon/acetonitrile solvent and ε is the molar extinction coefficient in acetonitrile), are also compiled in Table 3.

TABLE 3
Quantum yields for photo-oxidation of the bis(fulvalene) dicobalt monocation by halocarbons

Percent halocarbon in acetonitrile	Apparent quantum yield (ein/mol)	Corrected quantum yield (ein/mol)
30% $CHCl_3$	0.040	----
50% $CHCl_3$	0.053	0.61
30% CCl_4	0.236	2.71
50% CCl_4	0.302	1.97

Photolysis of the bis(fulvalene) dicobalt dication in acetonitrile solutions containing sodium tetraphenylborate results in spectral changes illustrated in Figure 4. These changes, which include the growth of the distinctive near-infrared absorption band in the region around 939 nm, provide evidence for photoreduction of the dication to the bis(fulvalene) dicobalt monocation. After extensive photolysis, evaporation of the solvent, and extraction of the solid residue with ethanol, biphenyl could be identified, by its ultraviolet absorption spectrum, as a product of the photoinduced decomposition of the tetraphenylborate ion. Irradiation of mixtures of the dication and sodium tetraphenylborate in dimethylforamide solvent gave results qualitatively similar to those observed in acetonitrile solvent systems.

Quantum yield data for formation of the monocation in photolysis of the dication in tetraphenylborate/acetonitrile mixtures based on total absorption of the excitation by both the unpaired and ion-paired species in solution are tabulated in Table 4. These yields were corrected as described above to give values based only on the net absorption of the excitation by the ion-paired species. The corrected yields, based upon the assumption that photoactivity arises only from absorption by the ion pair, are also compiled in Table 4.

TABLE 4
Quantum yields for photoreduction of the bis(fulvalene) dicobalt dication by tetraphenylborate anion

Mole ratio, $B(Ph)_4^-$: $[Co(ful)]_2^{2+}$	Apparent quantum yield (ein/mol)	Corrected quantum yield (ein/mol)
1 : 1	0.0058	0.118
5 : 1	0.0136	0.096
20 : 1	0.0360	0.121

Attempts to Monitor Emissions and Flash Photolysis Transients

Several attempts were made to monitor light emission by the bis(fulvalene) dicobalt mono- and dications over the range 300-1100nm. Both acetonitrile and dimethylformamide solvents were employed at room temperature, and glasses prepared by addition of 50% (by volume) glycerol to these solvents were used for attempts to measure emissions at 77K. Excitation sources for these attempts included conventional lamps and both Nd/YAG and N_2 pulsed lasers. Excitation wavelengths used with the conventional sources ranged throughout the visible and ultraviolet absorption bands; the fundamental 1064nm Nd/YAG and 337nm N_2 laser wavelengths were also employed. A variety of photomultipliers, capable of monitoring light emissions in the visible and near-infrared were utilized in these attempts. Several commercial spectrophotofluorimeters as well as a boxcar averager and transient digitizer (used in conjunction with the pulsed lasers) were used to analyze potential emission data. All attempts to monitor light emissions led to the conclusion that the complexes do not emit a measurable fraction of the absorbed radiation.

Similar attempts to monitor absorption changes following pulsed excitation of $[(C_{10}H_8)_2Co_2]^{1+}$ in acetonitrile with the full output of the Nd/YAG fundamental (1064nm) were made at several analyzing wavelengths throughout the near-infrared and visible absorption bands. No reproducible transients were observed in these attempts. Laser flash photolysis with added methylviologen dichloride similarly led to no observable transients even though wavelengths appropriate for monitoring the build-up of the anticipated methylviologen monocation as well as wavelengths appropriate for monitoring disappearance of the bis(fulvalene) dicobalt monocation were employed. Continuous photolysis with added methylviologen dichloride indicated that no net photolysis products were formed.

Laser flash photolysis of acetonitrile solutions of the bis(fulvalene) dicobalt dication with third harmonic pulses (354nm) in the presence of sodium tetraphenylborate showed a rapid increase in absorption during the laser pulse at analyzing wavelengths in the range 700-900nm. No disappearance of this absorption due to back reactions was observed.

DISCUSSION

Assignment of the Absorption Bands of the Bis(fulvalene) Dicobalt Mono- and Dications

A partial set of molecular orbitals depicting contributions from Co(3d) and C($2p_z$) atomic orbitals are illustrated in Figure 5. These orbitals, which are similar to those derived in prior molecular orbital treatments of bis(fulvalene) diiron (ref.14) and bis(fulvalene) dinickel (ref.27) complexes, provide a convenient basis for discussion of the visible and near-infrared absorption bands of $[(C_{10}H_8)_2Co_2]^{2+/1+}$. According to this scheme, the configuration of the ground state of the dication is $9a_g^2, 6b_{2u}^2, 6b_{1g}^2, 7b_{3u}^2, 10a_g^2, 9b_{3u}^2$, and the monocation results from addition of a single electron to the $9b_{1u}$ LUMO of the dication. The metal d-orbitals contributing to the ground state configuration of the dication are the d_{xy}, $d_{x^2-y^2}$, and d_{z^2} orbitals; the b_{1u} orbital occupied by the extra electron in the monocation is composed largely of Co(d_{xz}) metal orbitals. Three low energy orbital promotions may occur in the monocation. Of these, $b_{1u} \rightarrow a_u$ is Laporte forbidden and $b_{1u} \rightarrow b_{3g}$ and $b_{1u} \rightarrow b_{2g}$ are symmetry allowed. However, the redistribution of angular momentum associated with promotion from the $d_{xz}(b_{1u})$ to $d_{yz}(b_{3g})$ atomic orbitals will result in a low-intensity transition. Promotion from $d_{xz}-d_{xz}'(b_{1u})$ to $d_{xz}+d_{xz}'(b_{2g})$ should, on the other hand, result in an intense ${}^2B_{2g} \leftarrow {}^2B_{1u}$ transition. On this basis, the intense near-infrared band observed in the absorption spectrum of the monocation is assigned as the ${}^2B_{2g} \leftarrow {}^2B_{1u}$ transition. A comparable band should occur in the absorption spectrum of the doubly reduced neutral bis(fulvalene) dicobalt due to double occupation of the b_{1u} orbital, and, indeed, such a band has been reported(ref.6). This band should be absent in the bis(fulvalene) dicobalt dication, in agreement with its absorption spectrum (Fig.2).

The electron density changes accompanying the ${}^2B_{2g} \leftarrow {}^2B_{1u}$ transition, based upon the changes in mixing coefficients in the b_{1u} and b_{2g} orbitals, suggest that this transition resembles a d,pi-d,pi* transition of a metal-metal bonded binuclear complex. However, the metal-metal distance has been determined in similar bis(fulvalene) dimetal complexes of Fe (ref.28) and Ni (ref.27) as well as in $[(C_{10}H_8)_2Co_2]^{2+}$ (ref.20), and is too large (391-416pm) to indicate any significant metal-metal pi interaction. Furthermore, a near infrared absorption band, similar to the one observed in the bis(fulvalene) diiron monocation, is

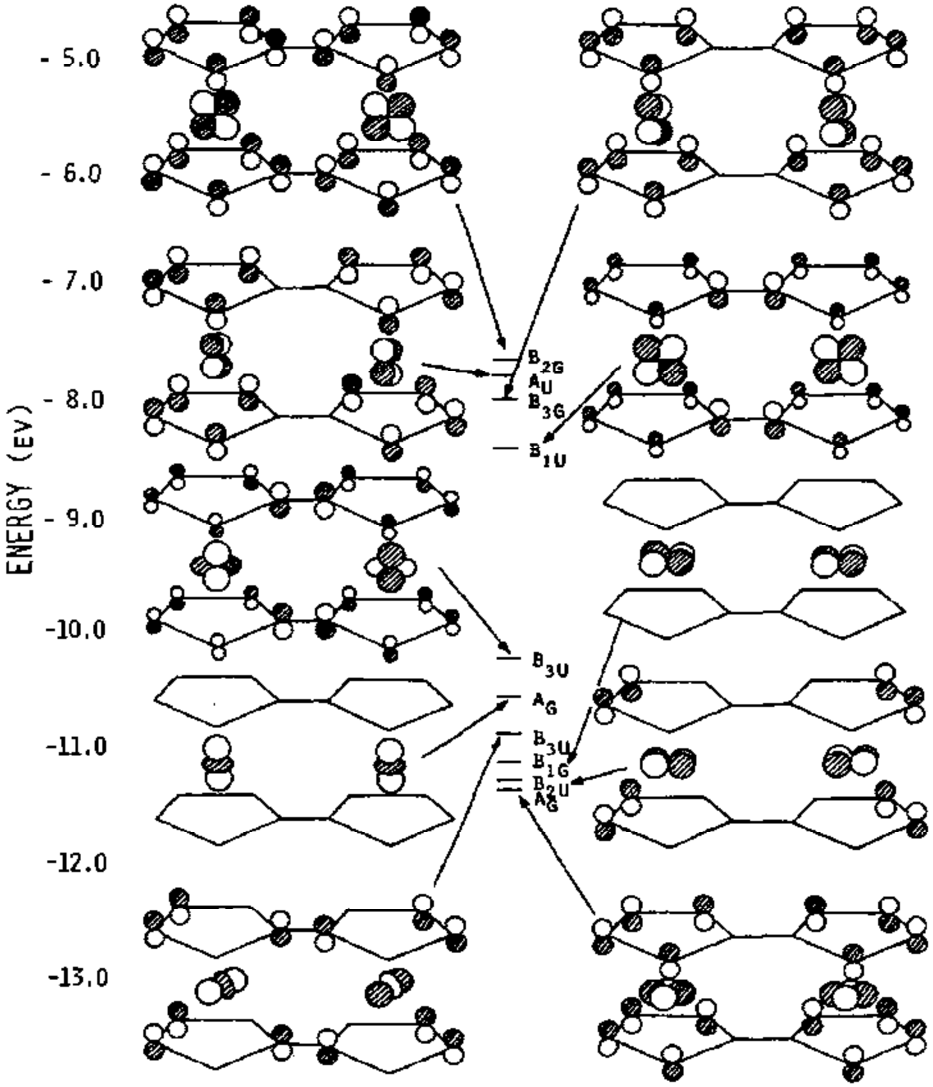

Fig. 5. Molecular orbitals of bis(fulvalene) dimetal complexes

also seen (ref.29) in [2.2] ferrocenophane-1,13-diyne, where the Fe-Fe distance is estimated to be 650pm. This band is absent, however, in the mono-oxidized [1.1] ferricenophanium and 1,12-dimethyl [1.1] ferricenophanium cations (ref.30) which contain saturated bridges. These observations each suggest that the near-infrared absorption band is not the result of a direct metal-metal interaction. Rather, an indirect interaction of the two metals through conjugated bridging ligands is implicated.

This point of view is, in fact, consistent with the result of the molecular orbital calculation. A small decrease in the electron density on Co and a small increase in the electron density on fulvalene results from a $^2B_{2g} \leftarrow {}^2B_{1u}$ transition. This is accompanied by a decrease in the pi electron density along the bridging (C_3-C_8) fulvalene bonds and an increase in the pi electron density in each of the cyclopentadienyl rings. Reference to the molecular orbital diagram (Fig 5) further illustrates the bonding changes which occur in the bridging fulvalene bonds as a result of promotion of an electron from the b_{1u} orbital (pi-bonding along the bridge bonds) to the b_{2g} orbital (pi*-antibonding along the bridge bonds). The net transition may thus be viewed as the result of two primary redistributions of electron density; 1) a small metal-to-ligand charge-transfer component, and 2) a change in the relative phasing of the d_{xz} orbitals accompanied by a cooperative change of phasing in the $C(p_z)$ orbitals along the bridging fulvalene bonds. These two effects work together to enhance the electron density in the cyclopentadienyl rings and to reduce the bonding between these rings.

In addition to the intense near-infrared absorption band at 940nm in the absorption spectrum of the bis(fulvalene) dicobalt monocation, a second weak shoulder, not seen in the dication absorption spectrum, is also seen in the monocation. The absence of this band in the dication suggests that it arises from a transition from the half-filled $9b_{1u}$ orbital of the monocation, which is vacant in the dication. As noted above, a weak transition would result from an orbital promotion to either the $6b_{3g}$ or $6a_u$ orbital. The visible absorption spectra of both the mono- and dicationic complexes are dominated by a broad, moderately intense band in the region 400-450nm. The similarity of this band in both species suggests that it arises from an orbital promotion from the filled $9b_{3u}$ orbital to an empty $6b_{3g}$ or $8b_{2g}$ orbital.

Lifetime of the $^2B_{2g}$ Excited State of the Bis(fulvalene) Dicobalt Monocation

Calculation of the radiative lifetime of the near-infrared absorption band of the bis(fulvalene)dicobalt monocation from its integrated absorption intensity (ref.31) yields a value of about 50 ns. In spite of this short radiative lifetime and the probable absence of an intervening excited state between the $^2B_{2g}$ excited state and the $^2B_{1u}$ ground state, all attempts to monitor emission from the $^2B_{2g} \longleftarrow {}^2B_{1u}$ excitation have failed. Although an intense Nd/YAG laser excitation source was used in several of these attempts, the sensitivity of the near infrared photomultipliers which were employed is severely restricted. A conservative estimate of the upper limit for the emission quantum yield from the $^2B_{2g}$ excited state of about 10^{-3} suggests that the lifetime of this state could be no more than 50ps. This estimate is further confirmed by the apparent absence of bleaching of the ground state in attempts to monitor transient absorption changes induced by pulsed excitation with the Nd/YAG laser fundamental.

The short excited state lifetime (50ps) would severely limit the extent of ground state depletion during the relatively long (10ns) laser pulse.

Spectroscopic Effects of Added Halocarbons and Tetraphenylborate Anion

The absorption spectral shifts induced by addition of halocarbons to acetonitrile solutions of the bis(fulvalene) dicobalt monocation are restricted to the visible and ultraviolet regions. The absence of comparable effects on the near-infrared absorption band indicates that the visible-ultraviolet shifts are not due to simple solvation effects, but are due to transitions within the association complex, $[(C_{10}H_8)_2Co_2:X]^{1+}$ (Equation (1), $X=CCl_4$ or $CHCl_3$). Previous descriptions of similar observations in several metallocenes (ref.21,24,25) suggest that these new absorption phenomena may be described as donor-acceptor charge transfer (ref.32,33) bands. In addition to structural similarities in the bis (fulvalene) and metallocene complexes, which suggest the likelihood of a similar assignment, several current observations are consistent with this formulation. (1) Although no discrete band maxima are observed, absorption changes induced by CCl_4 occur below 450nm whereas absorption changes due to added $CHCl_3$ are restricted to the region below 370nm. This apparent increase in the absorption energy is consistent with previous correlations (ref.24) of the energy of dissociative charge-transfer with $E_{½}$ values for reduction of halocarbon solvents (ref.34). A recent discussion (ref.35) provides a clear theoretical justification, based upon a dipole-in-a-sphere model (ref.36), for a linear correlation of the intermolecular charge-transfer energy and $E_{½}$ values for the acceptor in donor-acceptor complexes. (2) Excitation in the region where absorption changes occur results in oxidation of the bis(fulvalene) dicobalt monocation to the dication. This observation, in conjunction with the absence of photo-oxidation of the monocation for excitation in the near-infrared absorption band, is indicative of the dissociative charge-transfer nature of the halocarbon-induced absorption changes. (3) The absorption spectrum of the bis(fulvalene) dicobalt dication is not affected by halocarbons, even though the features in the 400-500nm region are thought to arise from orbital promotions similar to those responsible for comparable absorption bands of the monocation. (4) The association constant of the monocation with CCl_4 in acetonitrile ($0.12\ M^{-1}$) is about a factor of 10^3 smaller than the reported association constant for cobaltocene with CCl_4 in ethanol ($119\ M^{-1}$) and over 10^4 smaller than the association constant of nickelocene with CCl_4 in ethanol ($3795M^{-1}$) (ref.25). Assuming that the primary interactions leading to association are due to charge transfer between the electrophilic halocarbon and the metal center (see below), a smaller association constant is consistent with the anticipated reduction of metal electron density in the monocation relative to neutral cobaltocene and nickelocene.

The detailed nature of the charge transfer interactions of halocarbons with metallocenes may be viewed as the result of association of the electrophilic halocarbon with either the pi-cloud of the fulvalene ligand (ref.37) or with d-electron density (ref.38-41) "concentrated in an equatorial belt perpendicular to the C_5 axis" (ref.24). Considerations (3) and (4) above are both relevant to this point. According to the molecular orbital description of the bis (fulvalene) dicobalt complexes, reduction of the dication results from addition of an electron to a b_{1u} orbital which is largely composed of $Co(d_{xz})$ atomic orbitals. This suggests that the primary halocarbon/complex interactions occur at the metal center rather than the pi-cloud of the ligand (ref.42). These interactions are apparently insufficient to alter the energy of the near-infrared absorption band at atmospheric pressure, consistent with its rather small metal-to-ligand charge transfer component. The observed red-shift in this band at elevated pressures is taken as evidence for an increase in the association constant; however, the shift to lower energy appears to be inconsistent with withdrawal of electron density from the metal center. The origin of this effect is not presently understood.

We are not aware of any previous studies of ion-pairing of the tetraphenylborate anion (BPh_4) with metal complexes. The absorption spectrum of ferriceneium tetraphenylborate in acidic ethanol, for example, has been reported (ref.26) to be identical to that of ferricenium chloride in aqueous acid. However, BPh_4^- is known (ref.43) to form a charge-transfer ion pair with the methylviologen dication (MV^{2+}), and it is also known (ref.44-50) to act as an η^6-bonded ligand in metal complexes. Its charge-transfer complex with MV^{2+} is characterized by a broad absorption band which extends to about 550nm and has a slight shoulder at 330-335nm (ref.43). Excitation in this intermolecular charge-transfer region was reported to result in a photoredox process leading to formation of the methylviologen monocation, triphenylborane, and biphenyl.

The ability of the BPh_4 to participate in both associative ion-pairing and in bonding as a ligand in transition metal complexes is indicative of its electron-donor qualities. Its addition to acetonitrile solutions of the bis (fulvalene) dicobalt dication leads to absorption changes which are similar in nature to the previously reported[43] absorption of the $[MV^{2+}:BPh_4]^{1+}$ charge-transfer complex. These observations, as well as the observed photoredox properties (see below) are consistent with formation of a charge-transfer ion-pair, $[(C_{10}H_8)_2Co_2:BPh_4]^{1+}$. The b_{1u} LUMO of the bis(fulvalene) dicobalt dication, as discussed above, is composed largely of metal d-orbitals. While this would suggest eletron-donation from the pi-system of one of the phenyl groups of BPh_4^- into the Co d-orbitals in the charge-transfer ion pair, this type of direct interaction might be severely sterically-hindered. Therefore, a sterically-favored indirect interaction of BPh_4^- with Co, moderated by the fulvalene ligand, must also be considered as a reasonable possibility. Contributions from C $2p_z$ orbitals to the LUMO of bis(fulvalene) dicobalt dication, particularly in the region of the fulvalene bridge bonds, would presumably facilitate this type of indirect interaction with the metal centers.

Photo-induced Oxidation and Reduction Processes

Although both ultraviolet-visible absorption and ^{13}C NMR evidence positively identify the bis(fulvalene) dicobalt dication as a photoproduct in the photolysis of the charge-transfer region of $[(C_{10}H_8)Co_2{:}CCl_4]^+$, attempts to identify probable halocarbon reduction products,such as C_2Cl_6, have proved to be unsuccessful. Previous reports of similar attempts in the photolysis of ruthenocene in CCl_4 also failed to provide positive identification of halocarbon reduction products (ref.21). This is probably due to some diversity in the nature of the final secondary or tertiary reduction products formed subsequent to the primary photochemical process. As suggested in previous studies of the photolysis of metallocenes in halocarbons (ref.21,24-26,51-53) the most probable primary photolysis products of dissociative charge-transfer excitation in CCl_4 are described in Equation (3) below.

$$[(C_{10}H_8)_2Co_2{:}CCl_4]^{1+} \xrightarrow{h\nu} [(C_{10}H_8)_2Co_2]^{2+} + Cl^- + {\cdot}CCl_3 \qquad (3)$$

An analogous process would lead to the formation of $\cdot CHCl_2$ radicals when $CHCl_3$ is used in place of CCl_4. The larger-than-unity quantum yields observed in photolysis of the CCl_4 complex are consistent with formation of free radicals, such as $\cdot CCl_3$, which could participate in secondary thermal oxidation of the bis (fulvalene) dicobalt monocation to the dication. The ^{13}C NMR results show no evidence of attack of the halocarbon radicals on the fulvalene rings; processes of this type are believed to lead to formation of $FeCl_4^-$ and/or ring-substituted products in the photolysis of ferrocene in CCl_4 (ref.51,53) and in CCl_4-ethanol mixtures (ref.52,54). The lower quantum yields for photo-oxidation of the bis(fulvalene) dicobalt monocation in $CHCl_3$ are consistent with its higher reduction potential in comparison to that of CCl_4. Similar effects were noted in the photolysis of ferrocene in these two halocarbons (ref.26), and the result lends further support to the charge-transfer nature of the interaction of the bis(fulvalene) dicobalt monocation with halocarbon solvents.

The appearance of the distinctive near-infrared absorption band during photolysis of $[(C_{10}H_8)_2Co_2{:}BPh_4]^+$ in acetonitrile provides clear evidence for photoreduction of the bis(fulvalene) dicobalt dication to the monocation. Furthermore, identification of biphenyl as a photolysis biproduct from decomposition of BPh_4^- is consistent with previous reports (ref.55) identifying biphenyl as a biproduct of oxidation of the tetraphenylborate anion by Cu(II). These considerations suggest that the primary photochemical process may be described as in Equation (4) below.

$$[(C_{10}H_8)_2Co_2{:}BPh_4]^{1+} \rightarrow [(C_{10}H_8)_2Co_2]^{1+} + BPh_4 \qquad (4)$$

This is followed by the thermal coupling process in Equation (5) below to yield biphenyl.

$$2\ BPh_4 \rightarrow BPh_3 + Ph\text{-}Ph \qquad (5)$$

Laser flash photolysis of the $[(C_{10}H_8)_2Co_2{:}BPh_4]^{1+}$ ion pair indicates that formation of the bis(fulvalene) dicobalt monocation occurs in less than the 10ns width of the laser pulse.

SUMMARY AND CONCLUSIONS

Excitation in the intense near-infrared absorption band of the bis (fulvalene) dicobalt monocation produces a $^2B_{2g}$ excited state which, according to estimates based upon its large oscillator strength and low emission quantum yield, relaxes in < 50ps. Our inability to observe photoreduction of the methyl viologen dication following excitation of $[(C_{10}H_8)_2Co_2]^{1+}$ appears to be a result of this prohibitively short excited state lifetime; diffusion rates are insufficient to assure collisional interactions of MV^{2+} with the excited monocation. While this result does not entirely discount the possibility that near-infrared excitation of $[(C_{10}H_8)_2Co_2]^{1+}$ could lead to photoredox processes, it does appear to indicate that there is little likelihood for intercepting the $^2B_{2g}$ excited state prior to its relaxation with quenchers which operate by a diffusional pathway.

The well-established donor-acceptor interactions of metallocenes with halocarbons are found also to occur in solutions of $[(C_{10}H_8)_2Co_2]^{1+}$ with added CCl_4 and $CHCl_3$. Excitation of the charge-transfer absorption bands of these complexes leads to oxidation of the bis(fulvalene) dicobalt monocation to the dication with high yields; the near-infrared $^2B_{2g}$ absorption band is photoinactive under these conditions. A donor-acceptor complex is also formed in solutions of the bis(fulvalene) dicobalt dication with sodium tetraphenylborate. Photolysis in the charge-transfer absorption bands of this complex result in reduction of the dication to the monocation in high yields, and to the formation of biphenyl.

These processes illustrate that $[(C_{10}H_8)_2Co_2]^{2+/1+}$ can, in principle, participate as a photocatalyst in the net redox reaction which oxidizes BPh_4^- and reduces CCl_4 or $CHCl_3$ (Equation 6).

$$CCl_4 + BPh_4^- \xrightarrow{h\nu} Cl^- + \cdot CCl_3 + BPh_3 + 1/2\ Ph_2 \qquad (6)$$

The oxidation and reduction steps depend upon donor-acceptor association processes in the ground state prior to excitation, and photoactivity is restricted to excitation wavelengths within the charge-transfer region of the donor-acceptor complexes.

It would be possible to design a photochemical cell which would operate in a manner analogous to the previously described (ref.43) cell based upon excitation of the $[MV:BPh_4]^{1+}$ donor-acceptor complex. However the small potential for the bis(fulvalene) dicobalt 2+/1+ couple (+0.17 V), which would provide the driving force for operation of the cell, would utilize only a small fraction of the equivalent solar input potential. This small ground state potential suggests that the primary potential for solar energy utilization in these complexes is either in direct photoreduction of subtrates by the monocation or in photoreduction of the monocation to form the highly reactive zero-valent species for use in subsequent thermal reduction processes. Examples of the latter process have not yet been reported. In each instance it appears that ground state associative processes with redox substrates will be a necessary prerequisite to avoid rapid relaxation of the excited monocation to its ground state. Utilization of the intense near-infrared absorption properties of $[(C_{10}H_8)_2Co_2]^{1+}$ appears to depend upon the discovery of substrates which can associate with the monocation and introduce new donor-acceptor absorption features into this low-energy region.

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