(s, 18 H, $SiMe_3$), 1.34 (s, 18 H, *t*-Bu).

Bis(*tert*-butylimido)bis((trimethylsilyl)oxo)molybdenum, IIIb, was prepared analogously from 7.75 g of MoO_2Cl_2 and 26.0 mL (20.2 g) of *t*-$BuNH(SiMe_3)$ in 150 mL of hexane. The IIIb compound obtained on removal of the solvent (15.06 g, 93%) is apparently analytically pure but can be additionally sublimed in vacuo or recrystallized (hexamethyldisiloxane, −40 °C): mp 42–43 °C; NMR (toluene-d_8) δ 0.20 (s, 18 H, $SiMe_3$), 1.37 (s, 18 H, *t*-Bu).

trans-Bis(1-adamantylamido)tetrakis(trimethylsilyl)oxo)molybdenum was prepared by refluxing 1.0 g of MoO_2Cl_2 with 4.5 g of (1-adamantyl)(trimethylsilyl)amine in 25 mL of hexane for 4.5 h. The solvent was removed to afford a waxy solid which was redissolved in 20 mL of toluene. Cooling this solution to −40 °C yielded 0.75 g of pale yellow cubes of the compound suitable for X-ray diffraction.

Structural Details. Data were collected on a Syntex P3 diffractometer with the crystal cooled to −55 °C (graphite monochromator; Mo Kα radiation; $\lambda = 0.71069$ Å). Preliminary examination indicated the crystal to be monoclinic with space group $P2_1/c$. The unit-cell dimensions were refined from the Bragg angles (as determined by the Syntex centering routine) of 48 reflections: $a = 10.533$ (2) Å, $b = 18.217$ (3) Å, $c = 10.817$ (1) Å, $\beta = 103.08$ (1)°. The cell volume, 2022 Å^3, yields a calculated density of 1.240 g cm^{-3} for $Z = 2$.

Intensity data for 3553 reflections were collected by using the ω-scan technique ($4° < 2\theta < 55°$; scan width of 0.8°; variable scan rate of 2.0–5.0° min^{-1}; background measurements at both ends of the scan; total background time equal to scan time). The intensities of four standard reflections were monitored after every 200 reflections; only statistical fluctuations were noted. The intensity of one reflection was measured in 10° increments about the diffraction vector; no variation in the intensity was observed. No absorption correction was applied ($\mu = 0.78$ cm^{-1}).

Registry No. I, 72207-45-5; IIa, 72207-46-6; IIb, 72207-47-7; IIIa, 71851-94-0; IIIb, 71851-95-1; *trans*-$(AdNH)_2Mo(OSiMe_3)_4$, 72207-48-8; WCl_6, 13283-01-7; $(t\text{-}BuO)_4W(N\text{-}t\text{-}Bu)$, 72207-49-9; CrO_2Cl_2, 7791-14-2; MoO_2Cl_2, 13637-68-8; *t*-$BuNH(SiMe_3)$, 5577-67-3; (1-adamantyl)(trimethylsilyl)amine, 36960-58-4.

Supplementary Material Available: Tables of final positional parameters (as fractional coordinates), thermal parameters, and structure factor amplitudes (observed and calculated) (29 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Missouri—St. Louis, St. Louis, Missouri 63121

Photosubstitution of Cyclopentadienylvanadium Tetracarbonyl

Donna G. Alway and Kenneth W. Barnett*[1]

Received June 28, 1979

The lability of $CpV(CO)_4$ ($Cp = \eta^5\text{-}C_5H_5$) toward photosubstitution is well documented. A variety of diene,[2] acetylene,[3–5] and phosphine[5–10] derivatives have been prepared by irradiation of $CpV(CO)_4$ with the appropriate substrate. Photoreactions of $CpV(CO)_4$ with the monodentate phosphines PPh_3,[5,6] PBu_3,[7] or PH_3[8] (L) yield monosubstituted complexes $CpV(CO)_3(L)$, while reactions with $Ph_2P(CH_2)_nPPh_2$[9] (n = 1, 2, 4) or $PhP(CH_2CH_2PPh_2)_2$[10] (L_2) give the disubstituted complexes *cis*-$CpV(CO)_2L_2$. Photolysis of $CpV(CO)_4$ in tetrahydrofuran solutions containing X^- (X = Cl, Br, I) or BH_4^- is reported to yield $CpV(CO)_3X^-$ or mixtures of $CpV(CO)_3H^-$ and $CpV(CO)_2BH_4^-$, respectively.[6] Similarly, photolysis of tetrahydrofuran solutions containing $CpV(CO)_4$ and $CpV(CO)_3H^-$ gives the hydrogen-bridged dimeric complex, $[CpV(CO)_3]_2H^-$.[6]

The reactions cited above were promoted by irradiation of $CpV(CO)_4$ with unfiltered, high-intensity ultraviolet light. In some cases the photolyses were conducted for prolonged periods of time and/or at elevated temperatures. Although of synthetic value, such reactions provide little information about the excited-state decay processes available to the complex. We were prompted, therefore, to examine the photochemistry of $CpV(CO)_4$, using monochromatic irradiation.

Experimental Section

Materials. $CpV(CO)_4$ was purchased from Strem Chemicals, Inc., and recrystallized from chloroform/hexane prior to use. PPh_3 was obtained from Eastman Kodak Co. and used as received. High-purity carbon monoxide was purchased from Matheson Gas Products. Spectroscopic grade benzene was used after drying over molecular sieves. ^{13}CO (90%) was purchased from the Monsanto Chemical Co.

Spectra. Infrared spectra were recorded with Perkin-Elmer 337 or 521 grating spectrophotometers using matched 0.1- or 1.0-mm KBr solution cells. Proton NMR and UV–visible spectra were obtained with Varian T-60 and Beckman Acta MVI spectrophotometers, respectively.

Photolysis Procedures. All operations, except for the actual irradiations, were performed in the dark. Solutions of $CpV(CO)_4$ (5×10^{-4} M, 366 nm; 1×10^{-3} M, 436 nm) in 10-mL aliquots were placed in matched 10-mm i.d. Pyrex test tubes. The samples were deoxygenated by purging with prepurified argon for at least 10 min. The tubes were placed in a merry-go-round apparatus[11] of our own design. A 200-W Hanovia medium-pressure mercury-arc lamp was situated in an immersion well surrounded by two concentric cylindrical Pyrex jackets containing appropriate aqueous filter solutions to isolate the desired mercury emissions (336 nm: 0.125 M $NiSO_4$, 0.50 M $CoSO_4$ (l = 20 mm), and 6.4×10^{-4} M 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (l = 10 mm); 436 nm: 5.4 M $NaNO_2$ (l = 20 mm) and 0.18 M $CuSO_4$, 2.7 M NH_3 (l = 10 mm)). Light intensities (366 nm, 4.4×10^{-8} einstein/s; 436 nm, 5.5×10^{-8} einstein/s) were measured by ferrioxalate actinometry.[12] The photoproduct, $CpV(CO)_3(PPh_3)$, was characterized by infrared, proton NMR, and UV–visible spectroscopy and was identified by comparison to the spectra of an authentic sample. Reactions of $CpV(CO)_4$ with PPh_3 were analyzed quantitatively by proton NMR spectroscopy. Following irradiation, the solvent was removed from the reaction solution by rotary evaporation at room temperature or below and the remaining materials were dissolved in deuteriochloroform for NMR analysis. The percentage yield of the product was determined by integration of the relative intensities of the cyclopentadienyl proton resonances of the complexes present. Quantum yields (corrected for incomplete absorption by $CpV(CO)_4$ samples) are reported as the average of triplicate determinations. Conversions were limited to 15% or less and were linear with irradiation time. Thermal dark reactions were monitored and were negligible within the times required for irradiation and analysis.

Synthesis of $CpV(CO)_3(PPh_3)$. $CpV(CO)_4$ (1.14 g, 5.0 mmol) and PPh_3 (1.31 g, 5.0 mmol) were dissolved in 450 mL of benzene. The orange solution was photolyzed with a water-cooled 200-W Hanovia medium-pressure mercury-arc lamp for 1 h. The volume of the solution was reduced to ~20 mL by rotary evaporation. Chromatography

---

[1] To whom correspondence should be addressed at Ashland Chemical Co. Research and Development Department, P.O. Box 2219, Columbus, Ohio 43216.

[2] M. Wrighton, *Chem. Rev.*, **74**, 401 (1974), and references therein.

[3] A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. A. Pasynskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **3**, 727 (1970).

[4] A. N. Nesmeyanov, *Adv. Organomet. Chem.*, **10**, 56 (1972).

[5] R. Tsumura and N. Hagihara, *Bull. Chem. Soc. Jpn.*, **38**, 1901 (1965).

[6] R. J. Kinney, W. D. Jones, and R. G. Bergman, *J. Am. Chem. Soc.*, **100**, 7902 (1978).

[7] E. O. Fischer and R. J. J. Schneider, *Angew Chem., Int. Ed. Engl.*, **6**, 569 (1967).

[8] E. O. Fischer, E. Louis, and R. J. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **7**, 136 (1968).

[9] D. Rehder, L. Dahlenburg, and I. Müller, *J. Organomet. Chem.*, **122**, 53 (1976).

[10] I. Müller and D. Rehder, *J. Organomet. Chem.*, **139**, 293 (1977).

[11] J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, 1966.

[12] C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

Table I. Quantum Yields for the Reaction[a,b]

$$\mathrm{CpV(CO)_4 + PPh_3 \xrightarrow{h\nu} CpV(CO)_3(PPh_3) + CO}$$

$[PPh_3]/[CpV(CO)_4]$	Φ(366 nm)[c]	Φ(436 nm)[c]	$[PPh_3]/[CpV(CO)_4]$	Φ(366 nm)[c]	Φ(436 nm)[c]
0.5	0.42	0.35	7.5	0.78	0.79
1.0	0.49	0.41	10.0	0.83	0.79
2.5	0.71	0.59	1.0[d]	0.13	0.11
5.0	0.81	0.79			

[a] Irradiation in benzene solutions at 25 °C. [b] At 366 nm, $[CpV(CO)_4] = 0.50 \times 10^{-3}$ M. At 436 nm, $[CpV(CO)_4] = 1.00 \times 10^{-3}$ M. [c] Estimated error ±0.10 Φ unit. [d] Irradiation in benzene solutions saturated with carbon monoxide.

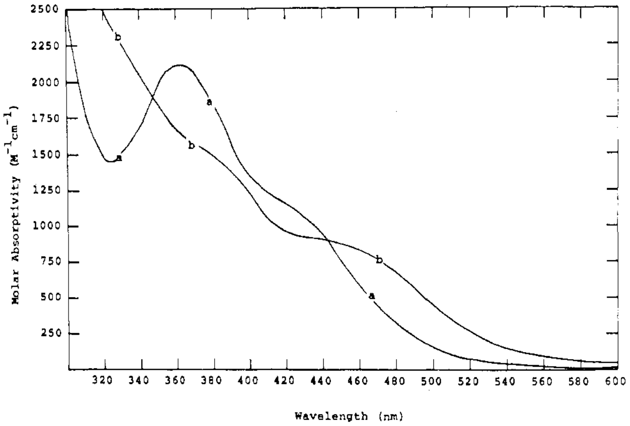

Figure 1. Electronic absorption spectra of $CpV(CO)_4$ (a) and $CpV(CO)_3(PPh_3)$ (b) in benzene solution.

on neutral alumina (Brockman Activity Grade I, 3 × 30 cm column), using 1:1 benzene/hexane as eluant, gave an orange band and a red band that remained on the upper portion of the column. The orange band was collected under argon and the solvent removed by rotary evaporation to leave an orange solid. This was recrystallized from chloroform/hexane, washed with hexane, and dried to yield 0.060 g of $CpV(CO)_3(PPh_3)$ (3%), mp 158–162 °C (lit.[13] 160–161 °C). ^1H NMR ($CDCl_3$ solvent, Me_4Si internal standard): δ(Cp) 4.87 (d, J(P–H) = 1 Hz), δ(Ph) 7.5 (m). IR ($CHCl_3$ solution): ν(CO) 1960, 1885, 1865 cm^{-1}.

Results and Discussion

Electronic absorption spectra of $CpV(CO)_4$ and $CpV(CO)_3(PPh_3)$ in benzene solution are shown in Figure 1. The spectrum of $CpV(CO)_4$ is dominated by an intense absorption band in the UV-visible region (λ_{max} 362 nm (ϵ 1230 M^{-1} cm^{-1})). The spectrum of $CpV(CO)_3(PPh_3)$ displays features similar to those exhibited by $CpV(CO)_4$, although the bands are shifted to longer wavelengths. There is currently no sound basis for assigning the observed transitions. While the ground and excited states in the present case are doubtless similar in nature to $CpMn(CO)_3$ and its substituted derivatives,[14] we hesitate to make such an extrapolation in the absence of considerable additional information.

Irradiation of $CpV(CO)_4$ at 366 or 436 nm in deoxygenated benzene solutions causes no change in the infrared, UV-visible, or proton NMR spectra of the complex, indicating that no net chemical reaction takes place in the absence of added ligand. The carbonyl-bridged dimer[15] $Cp_2V_2(CO)_5$ has been observed by Bergman et al.[6] following irradiation of $CpV(CO)_4$ in tetrahydrofuran solutions continuously purged with nitrogen (eq 1). The dimeric complex is not a photoproduct of $CpV(CO)_4$ under our reaction conditions.

$$2\mathrm{CpV(CO)_4} \xrightarrow[\mathrm{THF,\ N_2}]{h\nu} \mathrm{Cp_2V_2(CO)_5} + 3\mathrm{CO} \qquad (1)$$

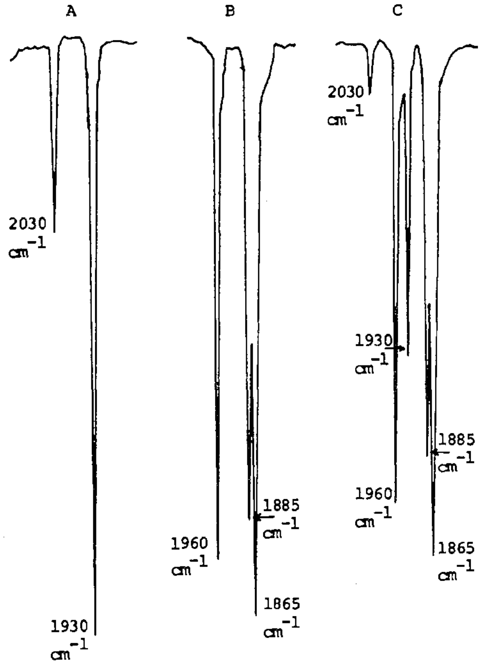

Figure 2. CO stretching region of the infrared spectra of (A) $CpV(CO)_4$, (B) $CpV(CO)_3(PPh_3)$, and (C) product mixture obtained by irradiating $CpV(CO)_4$ and PPh_3 in benzene solution at 366 nm. Spectra were recorded in cyclohexane solution.

In agreement with previous reports,[5,6] photolysis of $CpV(CO)_4$ in benzene solutions containing PPh_3 leads exclusively to formation of $CpV(CO)_3(PPh_3)$ (eq 2). Isosbestic points

$$\mathrm{CpV(CO)_4 + PPh_3 \xrightarrow{h\nu} CpV(CO)_3(PPh_3) + CO} \qquad (2)$$

at 348 and 442 nm (Figure 1) are preserved throughout irradiation, indicating the absence of secondary reactions. Further evidence that $CpV(CO)_3(PPh_3)$ is the sole product of the reaction is provided by infrared spectral changes observed during photolysis. The carbonyl stretching bands of $CpV(CO)_4$ decrease in intensity concurrent to the appearance and growth of absorption bands attributable to $CpV(CO)_3(PPh_3)$ (Figure 2). Proton NMR spectra of photolyzed samples show a singlet at δ 5.13 and a doublet at δ 4.87 (J(P–H) = 1 Hz) in $CDCl_3$ solution, characteristic of the cyclopentadienyl proton resonances of $CpV(CO)_4$ and $CpV(CO)_3(PPh_3)$, respectively. The disubstituted complex, $CpV(CO)_2(PPh_3)_2$, is not produced by irradiation of either $CpV(CO)_4$ or $CpV(CO)_3(PPh_3)$ with excess PPh_3 for periods of up to 2 h. This indicated to us either that $CpV(CO)_3PPh_3$ is not photoactive or that the phosphorus ligand is being dissociated preferentially. The latter is actually the case, as was demonstrated by photolyzing $CpV(CO)_3(PPh_3)$ in CO-saturated benzene and observing the rapid appearance of $CpV(CO)_4$, i.e., the reverse of eq 2. A small amount of decomposition occurred during this reaction, prohibiting accurate determination of the quantum yield for PPh_3 dissociation.

Quantum yields for photoreactions of $CpV(CO)_4$ with PPh_3 at 366 and 436 nm are given in the Table I. Within the

---

(13) E. Vitz and C. H. Brubaker, Jr., *J. Organomet. Chem.*, **104**, C33 (1976).
(14) P. J. Giordano and M. S. Wrighton, *Inorg. Chem.*, **16**, 160 (1977).
(15) E. O. Fischer and R. J. J. Schneider, *Chem. Ber.*, **103**, 3684 (1970).

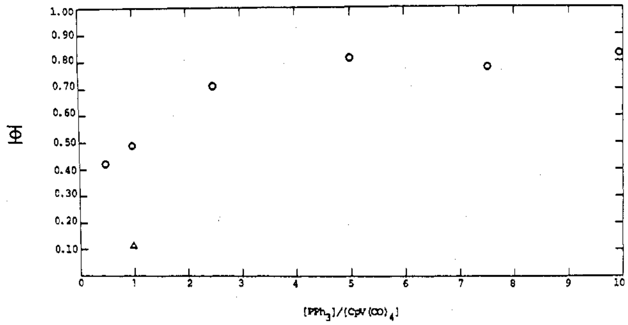

Figure 3. Effect of PPh_3 concentration on the quantum yield (366 nm) of photosubstitution for $CpV(CO)_4$. $[CpV(CO)_4]$ is constant at 0.5×10^{-3} M. Δ = solution saturated with CO.

accuracy of our experimental data, the values obtained are independent of irradiation wavelength. The absence of a wavelength effect on the quantum yield for a photochemical reaction is generally attributed to conversion of the initially populated excited states to a common chemically reactive excited state.[11,16–18]

The variation in quantum yields for substitution of $CpV(CO)_4$ as a function of PPh_3 concentration (Table I and Figure 3) parallels the results obtained for PPh_3 substitution of $CpFe(CO)_2Br$,[19,20] $CpFe(CO)_2I$,[19,20] and 1,1,1,1-tetracarbonyl-2,3,1-diazaferrole.[21] At low phosphine concentrations, the quantum yield increases with increasing ligand concentration. When PPh_3 is present in about fivefold molar excess of $CpV(CO)_4$, the quantum yield reaches a maximum value of 0.80 and becomes independent of entering ligand concentration. An increase in the concentration of free carbon monoxide decreases the quantum yield for phosphine substitution. These results are best accounted for by eq 3–7. Decay

$$CpV(CO)_4 \rightarrow CpV(CO)_4^* \qquad (3)$$

$$CpV(CO)_4^* \rightarrow CpV(CO)_4 \qquad (4)$$

$$CpV(CO)_4^* \rightarrow CpV(CO)_3 + CO \qquad (5)$$

$$CpV(CO)_3 + CO \rightarrow CpV(CO)_4 \qquad (6)$$

$$CpV(CO)_3 + PPh_3 \rightarrow CpV(CO)_3(PPh_3) \qquad (7)$$

of excited state $CpV(CO)_4^*$ by physical processes is represented by eq 4. Dissociation of carbon monoxide gives coordinatively unsaturated $CpV(CO)_3$ (eq 5), which may be stabilized by weak-bonding interactions with solvent molecules.[21,22] By analogy to other metal–carbonyl systems,[21–24] $CpV(CO)_3$ is expected to recombine rapidly with carbon monoxide, regenerating $CpV(CO)_4$ (eq 6). Thus, PPh_3 must compete with carbon monoxide for the vacant coordination site of the $CpV(CO)_3$ intermediate. As the phosphine concentration is increased, nucleophilic attack by PPh_3 becomes more favorable, and the quantum yield for substitution increases and approaches the quantum yield for formation of $CpV(CO)_3$ (eq 5). The limiting value of 0.80 reveals that loss of carbon monoxide from $CpV(CO)_4^*$ is highly efficient and that it is the dominant photochemical process for $CpV(CO)_4$.

At the suggestion of one of the reviewers we conducted the irradiation of $CpV(CO)_4$ at 366 nm under one atmosphere of ^{13}CO, as we had done for related systems.[19,25] New bands (not observed with ^{12}CO atmosphere) at 2020, 2015, 2000, 1945, 1930, and 1880 cm^{-1} grew in within 3 min. This is attributed to formation of $CpV(CO)_3(^{13}CO)$, *cis*- and *trans*-$CpV(CO)_2(^{13}CO)_2$, and perhaps more heavily ^{13}C enriched species. This result is consistent with the other behavior cited above and is readily explained by eq 5 and 6. Further work is required to definitively assign the infrared bands observed, and this will be undertaken as a separate project.

Although the data could be interpreted in terms of an associative substitution mechanism, it is unlikely that the reaction proceeds by formation of a crowded, eight-coordinate, 20-electron $CpV(CO)_4(PPh_3)$ intermediate. Kinetic studies of the thermal substitution reactions of $CpV(CO)_4$ with a variety of phosphines (including PPh_3) and phosphites have shown that the reactions proceed by a dissociative pathway in which loss of carbon monoxode is the rate determining step.[26] An S_N2 mechanism for nucleophilic substitution has been considered for the photoreaction of $Mn(CO)_4NO$ with PPh_3, but even in this case both dissociative and associative processes are invoked.[27,28]

Acknowledgment. A University of Missouri—St. Louis Graduate Research Fellowship (D.G.A.) is gratefully acknowledged.

Registry No. $CpV(CO)_4$, 12108-04-2; $CpV(CO)_3(PPh_3)$, 12213-09-1.

---

(16) D. L. Morse and M. S. Wrighton, *J. Am. Chem. Soc.*, **98**, 3931 (1976).
(17) J. Nasielski and A. Colas, *Inorg. Chem.*, **17**, 237 (1978).
(18) G. Malouf and P. C. Ford, *J. Am. Chem. Soc.*, **99**, 7213 (1977).
(19) D. G. Alway and K. W. Barnett, *Inorg. Chem.*, **17**, 2826 (1978).
(20) D. G. Alway and K. W. Barnett, *Adv. Chem. Ser.*, **No. 168**, 115 (1978).
(21) A. Albini and H. Kisch, *J. Am. Chem. Soc.*, **98**, 3869 (1976).
(22) J. M. Kelly, D. V. Bent, H. Hermann, D. Schultefrohlinde, and E. Koerner von Gustorf, *J. Organomet. Chem.*, **69**, 259 (1974).
(23) D. R. Kidd and T. L. Brown, *J. Am. Chem. Soc.*, **100**, 4095 (1978).
(24) J. L. Hughey IV, C. R. Bock and T. J. Meyer, *J. Am. Chem. Soc.*, **97**, 4440 (1975).
(25) D. G. Alway and K. W. Barnett, *Inorg. Chem.*, in press.
(26) G. C. Faber and R. J. Angelici, *Inorg. Chem.*, **9**, 1586 (1970).
(27) D. P. Keeton and F. Basolo, *Inorg. Chim. Acta*, **6**, 33 (1972).
(28) A. J. Rest, *Chem. Commun.*, **345** (1970).

Contribution from the Departments of Chemistry,
Indiana-Purdue University at Fort Wayne,
Fort Wayne, Indiana 46805, and
New Mexico State University, Las Cruces, New Mexico 88003

Long-Lived Intermediates in the Production of Hydrogen from Ultraviolet Photolysis of Acidic Di- and Trichlorocuprate(I) Ions[1]

Kenneth L. Stevenson,*[2a] David M. Kaehr,[2b] Dennis D. Davis,[2c] and Charles R. Davis[2d]

Received June 25, 1979

In our previous papers on the photooxidation of di- and trichlorocuprate ions in acid solution we reported on their use as photocatalysts for the oxidation of other species such as Ti^{3+},[3] in the production of $H_2(g)$ via solar energy,[4] and most recently on the primary processes which occur in the photooxidation of these anions.[5] This last report contains strong evidence that the absorption of light into the charge-transfer-to-solvent band of the $CuCl_3^{2-}$ ion results in the production

---

(1) Presented at the National Meeting of the American Chemical Society, Miami Beach, Fla., Aug 1978, and at the 11th Central Regional Meeting of the American Chemical Society, Columbus, Ohio, May 1979.
(2) (a) Indiana-Purdue University. (b) Graduate research assistant, Indiana-Purdue University. (c) New Mexico State University. (d) Graduate student, New Mexico State University.
(3) K. L. Stevenson and D. D. Davis, *Inorg. Nucl. Chem. Lett.*, **12**, 905 (1976).
(4) D. D. Davis, G. K. King, K. L. Stevenson, E. R. Birnbaum, and J. H. Hageman, *J. Solid State Chem.*, **22**, 63 (1977).
(5) D. D. Davis, K. L. Stevenson, and C. R. Davis, *J. Am. Chem. Soc.*, **100**, 5344 (1978).