*Inorg. Chem.* **1980**, *19*, 1835–1840

Contribution from the Department of Chemistry,
University of California, Santa Barbara, California 93106

# Photochemical Reactions of Iridium(III) Pentaammine and *trans*-Tetraammine Complexes in Aqueous Solution. Ligand-Field and Charge-Transfer Photochemistry

MEHDI TALEBINASAB-SARVARI, ANDREW W. ZANELLA, and PETER C. FORD*

*Received October 16, 1979*

The photochemical properties of the iridium(III) ammine complexes $Ir(NH_3)_5X^{2+}$ ($X^-$ = $Cl^-$, $Br^-$, $I^-$), $Ir(NH_3)_5L^{3+}$ (L = $NH_3$, $H_2O$, $CH_3CN$, $C_6H_5CN$), *trans*-$Ir(NH_3)_4I_2^+$, and *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$ in aqueous solution are reported and discussed. In general it is observed that photolysis into the ligand-field (LF) absorption band region leads to ligand photoaquations (only) with quantum yields and product distributions independent both of the irradiation wavelength and of whether the solutions are deaerated or air saturated. Since the wavelength range studied included both singlet bands and those assigned as the lowest energy "triplet" absorptions, it is concluded that LF excitation is followed by efficient conversion/intersystem crossing to give a common excited state, the lowest energy "triplet" LF state. For those species giving disubstituted products, the stereochemistry is exclusively trans. Irradiation at wavelengths corresponding to ligand to metal charge-transfer (LMCT) absorption bands also leads predominantly to ligand aquation as the net photoreaction. However, different reaction patterns are noted in aerated solutions than in deaerated solutions, suggesting a redox component to this photochemistry. Qualitatively, the photochemistry of the iridium(III) ammine complexes parallels that of the rhodium(III) analogues.

## Introduction

The photochemical properties of hexacoordinate $d^6$ transition-metal complexes have been the subject of considerable research interest in recent years. The reasons are severalfold, important ones certainly being the relative thermal inertness of the low-spin complexes and the reasonably well-understood spectroscopy of these species. A major goal of our laboratories has been to examine systematically the photochemistry and spectroscopy of complex ions of different metals to establish both the generalities and the discontinuities in the photochemical behavior of homologous systems.[1-6] Such studies provide tests of the theoretical models offered for both ligand-field (LF) and charge-transfer (CT) photochemistry[7] and provide guidelines for developing new or improved treatments. Previously, we reported[1] a quantitative investigation of the LF photochemistry of the iridium(III) ammine complexes $Ir(NH_3)_6^{3+}$, $Ir(NH_3)_5H_2O^{3+}$, and $Ir(NH_3)_5Cl^{2+}$ in aqueous solution. Described here are considerably more extensive photochemical investigations of the pentaammine complexes $Ir(NH_3)_5X^{2+}$ or $Ir(NH_3)_5X^{3+}$ (X = $Cl^-$, $Br^-$, $I^-$, acetonitrile (acn), or benzonitrile (bzn)) and of the synthesis and photochemistry of the tetraammine complexes *trans*-$Ir(NH_3)_4X_2^+$ (X = $Cl^-$, $Br^-$, $I^-$).

## Experimental Section

**Materials.** Reagent grade material and doubly distilled water were used throughout. $[Ir(NH_3)_5X](ClO_3)_2$ and *cis*- and *trans*-$[Ir(en)_2,X_2]X$ (X = $Cl^-$, $Br^-$, $I^-$) were synthesized and purified according to published procedures.[8,9] The electronic spectra quantitatively agreed with reported values.[9,10]

$[Ir(NH_3)_5L](ClO_4)_3$ (L = bzn, acn) complexes were prepared by a procedure similar to that used by Foust for Rh(III) analogues.[11,12] A solution of $[Ir(NH_3)_5H_2O](ClO_4)_3$ (100 mg) in the minimum amount of dry DMA to dissolve the complex plus L (bzn or acn, 2 mL) was placed in a sealed tube and heated at 130 °C for 30 h. The resulting product solution was added to 2-methyl-1-propanol (30 mL), and the mixture was refrigerated overnight. The precipitate formed was collected by filtration and then washed with ethanol and ether. This product was then recrystallized from hot water (pH adjusted to about 2 by $HClO_4$), washed with ethanol and ether, and dried under vacuum. The electronic spectra of these compounds are reported in Table I. The IR spectra display CN stretching bands at 2330 and 2285 $cm^{-1}$ for the acetonitrile and benzonitrile complexes, respectively, Analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Anal. Calcd for $C_2H_{18}N_6O_{12}Cl_3I_2$ ($[Ir(NH_3)_5acn](ClO_4)_3$): C, 3.94; H, 2.96; N, 13.47. Found: C, 3.89; H, 2.92; N, 13.62. Anal. Calcd for $C_7H_{20}N_6O_{12}Cl_3I_2$ ($[Ir(NH_3)_5bzn](ClO_4)_3$): C, 12.40: H, 2.97; N, 12.40. Found: C, 12.68; H, 3.25; N, 12,20.

The *trans*-diiodotetraammine complex was prepared by a photochemical procedure. An acidic aqueous solution of $[Ir(NH_3)_5I](ClO_4)_2$ ($2 \times 10^{-3}$ M) was irradiated with 366-nm light until no further spectral changes occurred. This solution is considered to contain *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$ as the only iridium product (see Results). To this solution was added concentrated HI and the mixture was then heated to boiling for 60 min to give *trans*-$Ir(NH_3)_4I_2^+$. Addition of concentrated $Na_2S_2O_6$ solution precipitated [*trans*-$Ir(NH_3)_4I_2]_2S_2O_6$ which was recrystallized from hot water. Anal. Calcd for $H_{24}N_8O_6S_2I_4Ir_2$: H, 2.04; N, 9.42; I, 42.8. Found: H, 2.13; N, 9.42; I, 42.9.

For preparation of the dibromo or dichloro analogues, an equivalent amount of $AgClO_4$ was added to the photosolution containing *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$, and this solution was heated at 100 °C for 30 min. After being cooled, this solution was filtered to remove the yellow AgI precipitate. To the filtrate solution (containing presumably *trans*-$Ir(NH_3)_4(H_2O)_2^{3+}$) was added concentrated HCl or HBr, and the resulting mixture was heated to boiling for 60 min to give *trans*-$Ir(NH_3)_4Cl_2^+$ or *trans*-$Ir(NH_3)_4Br_2^+$, respectively. These were precipitated from the cooled solutions by addition of concentrated $HClO_4$ to give the respective perchlorate salts, which were recrystallized. The electronic spectra in aqueous solution (see Results) were closely analogous to those of the known *trans*-$Ir(en)_2X_2^+$ ions.[9]

**Photolysis Procedures.** Photolyses were carried out according to the procedures described previously.[1] Typical irradiation intensities were $1.4 \times 10^{-7}$ einstein/(L s) (254 nm) and $1.8 \times 10^{-6}$ einstein/(L s) (313 nm) as determined by ferrioxalate actinometry. Reaction solutions were prepared from dilute perchloric acid (pH 3.0–4.0) with iridium complexes in the concentration range $2 \times 10^{-4}$ to $4 \times 10^{-3}$ M. Quantum yields for ammonia aquation ($\Phi_{NH_3}$) were determined from changes in the solution pH. In addition, spectral changes were used to evaluate the quantum yields for photoaquation of $NH_3$ from $Ir(NH_3)_5I^{2+}$ and $Cl^-$, bzn, and acn from $Ir(NH_3)_5Cl^{2+}$, $Ir(NH_3)_5bzn^{3+}$,

---

(1) A. W. Zanella, M. Talebinasab-Sarvari, and P. C. Ford, *Inorg. Chem.*, **15**, 1980 (1976).

(2) P. C. Ford, J. D. Petersen, and R. E. Hintze, *Coord. Chem. Rev.*, **14**, 67 (1974).

(3) T. Matsubara and P. C. Ford, *Inorg. Chem.*, **17**, 1747 (1978).

(4) T. Matsubara, M. Bergkamp, and P. C. Ford, *Inorg. Chem.*, **17**, 1604 (1978).

(5) A. W. Zanella, K. H. Ford, and P. C. Ford, *Inorg. Chem.*, **17**, 1051 (1978).

(6) J. D. Petersen, R. J. Watts, and P. C. Ford, *J. Am. Chem. Soc.*, **98**, 3188 (1976).

(7) (a) S. C. Pyke and R. G. Linck, *J. Am. Chem. Soc.*, **93**, 5281 (1971); (b) M. S. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 165 (1973); (c) J. I. Zink, *Inorg. Chem.*, **12**, 1018 (1973); (d) P. C. Ford, *ibid.*, **14**, 1440 (1975); (e) J. F. Endicott and G. J. Ferraudi, *J. Phys. Chem.*, **80**, 949 (1976); (f) L. G. Vanquickenborne and A. Ceulemans, *J. Am. Chem. Soc.*, **99**, 2208 (1977).

(8) H. H. Schmidtke, *Inorg. Synth.*, **12**, 243 (1970).

(9) (a) R. A. Bauer and F. Basolo, *Inorg. Chem.*, **8**, 2231 (1969); (b) I. B. Barnovskii, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **13**, 1708 (1968).

(10) H. H. Schmidtke, *Inorg. Chem.*, **5**, 1682 (1966).

(11) R. D. Foust and P. C. Ford, *Inorg. Chem.*, **11**, 899 (1972).

(12) These complexes were first prepared by A. W. Zanella of these laboratories.

0020-1669/80/1319-1835$01.00/0

**Table I.** Photoaquation Quantum Yields for the Haloammineiridium(III) Complexes

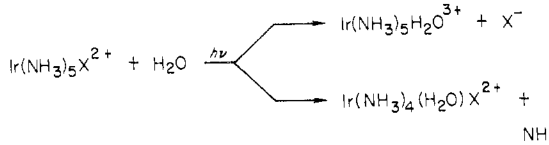
| | spectra[a] | | photochemistry[a] | | |
|---|---|---|---|---|---|
| complex | $\lambda_{max}$ ($\epsilon$)[b] | assignt[c] | $\lambda_{irr}$[b] | $\Phi_X$[d] | $\Phi_{NH_3}$[d] |
| $Ir(NH_3)_5Cl^{3+}$ | 365 (10) | $^3E, {}^3A_2 \leftarrow {}^1A_1$ | 366 | 0.13 | 0.023 |
| | 286 (73) | $^1E, {}^1A_2 \leftarrow {}^1A_1$ | 313 | 0.13[e] | 0.021 |
| | 227 (333) | $^1E, {}^1B_2 \leftarrow {}^1A_1$ | 254 | 0.15[e] | 0.020 |
| $Ir(NH_3)_5Br^{2+}$ | 385 sh (10) | $^3E, {}^3A_2 \leftarrow {}^1A_1$ | 366 | 0.020 | 0.050 |
| | 303 (100) | $^1E, {}^1A_2 \leftarrow {}^1A_1$ | 313 | 0.020 | 0.055 |
| | 230 (800) | LMCT | 254 | 0.021 | 0.052 |
| | | | 229 | 0.021 | 0.055 |
| $Ir(NH_3)_5I^{2+}$ | 417 sh (14) | $^3E, {}^3A_2 \leftarrow {}^1A_1$ | 405 | $<2 \times 10^{-4}$ | 0.56 |
| | 337 (372) | $^1E, {}^1A_2 \leftarrow {}^1A_1$ | 366 | $<2 \times 10^{-4}$ | 0.55 |
| | 234 (4600) | LMCT | 313 | $<2 \times 10^{-4}$ | 0.63 |
| | 215 (6700) | LMCT | 254 | $<2 \times 10^{-4}$ | 0.52 |
| | | | 229 | $<2 \times 10^{-4}$ | 0.30 |
| | | | 214 | | 0.35 |
| *trans*-$Ir(NH_3)_4I_2^+$ | 508 (19) | $^3E, {}^3A_2 \leftarrow {}^1A_1$[f] | 500 | 0.12 | <0.004 |
| | 403 (210) | $^1E, {}^1A_2 \leftarrow {}^1A_1$[f] | 405 | 0.13 | <0.003 |
| | 281 ($1.4 \times 10^4$) | LMCT[f] | 313 | 0.12 | <0.003 |
| | 230 ($4.0 \times 10^4$) | LMCT[f] | 254 | 0.11 | <0.01 |
| | | | 229 | 0.10 | |
| *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$ | 388 (387) | | 366 | 0.002 | <0.002 |
| | 240 (3530) | | 229 | ~0.005[g] | <0.005 |
| | 216 sh (5520) | | | | |

[a] In dilute aqueous solution; 25 °C; pH 3; *not deaerated* (see text). [b] λ in nm; ε in $M^{-1}$ $cm^{-1}$. [c] Reference 10. [d] Quantum yields for photoaquation in mol/einstein; values for three or more determinations; experimental reproducibility ±10% or better. [e] Reference 1. [f] Assigned in analogy to pentaammine complexes; ref 10. [g] Note that the value in deaerated solution differs considerably; see text.

and $Ir(NH_3)_5acn^{3+}$, respectively. The quantum yields for chloride and bromide aquation were confirmed independently by potentiometric titration with silver nitrate solution. The quantum yield for photoaquation of benzonitrile was confirmed independently by passing the photolysis solution through a cation-exchange (Bio-Rad AG 50W-X4, 200-400 mesh) column and measuring the absorbance at 223 nm ($\lambda_{max}$ for free bzn).[5] Control solutions in the dark displayed no spectral or pH changes, thus confirming the very low thermal reactivity of the iridium(III) complexes.[13,14]

## Results

**Halopentaammine Complexes.** Ligand aquations were the only net photoreactions seen in the course of examining the continuous photolyses of the various Ir(III) ammine complexes at wavelengths corresponding to the lower energy LF absorption bands. Two competing pathways are observed, halide aquation (eq 1a) and ammine aquation (eq 1b). Notably,



$$Ir(NH_3)_5X^{2+} + H_2O \xrightarrow{h\nu} Ir(NH_3)_5H_2O^{3+} + X^- \quad (1a)$$

$$Ir(NH_3)_5X^{2+} + H_2O \xrightarrow{h\nu} Ir(NH_3)_4(H_2O)X^{2+} + NH_3 \quad (1b)$$

the quantum yields for both pathways (Table I) are essentially independent of irradiation wavelength ($\lambda_{irr}$) over ranges including both triplet and singlet LF absorption. At these $\lambda_{irr}$ deaerating the reaction solutions had no effect on the quantum yields, suggesting that the LF excited states are too short-lived to be quenched by $O_2$. Notably, the relative importances of halide aquation (eq 1a) and ammine aquation (eq 1b) change dramatically with the latter becoming increasingly dominant as one proceeds down the series $Cl^-$, $Br^-$, $I^-$. Once one ligand has been replaced, there is very little secondary photoreaction observable spectrally. For $X^- = Cl^-$ this is consistent with the LF photoreactivity of $Ir(NH_3)_5H_2O^{2+}$ which undergoes photoexchange of coordinated and solvent $H_2O$ but no measurable $NH_3$ aquation.[1] The absence of spectrally significant secondary photoreactions when $NH_3$ aquation is the dominant primary photosubstitution pathway is illustrated by the LF photolysis of aqueous $Ir(NH_3)_5I^{2+}$ (Figure 1) which displays sharply defined isosbestic points at 361, 283, and 244 nm in the solution spectrum throughout the photolysis. This observation indicates that, with the exception of possible aquo exchange, the $Ir(NH_3)_4(H_2O)X^{2+}$ product is essentially photoinert to LF excitation in aqueous solution (vide infra).

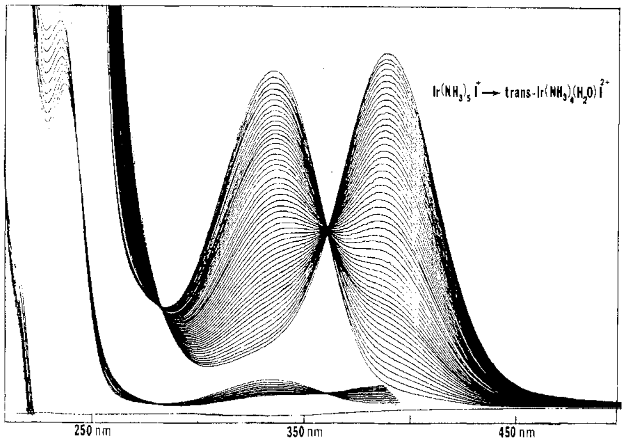


**Figure 1.** Upper curve: spectra recorded periodically during the 366-nm photolysis of $Ir(NH_3)_5I^{2+}$ in aqueous solution. Initial concentration of $Ir(NH_3)_5I^{2+}$ ($\lambda_{max}$ 337 nm) is $1.1 \times 10^{-3}$ M in pH 2 aqueous solution. Lower curve: spectra recorded periodically for 229-nm photolysis of $Ir(NH_3)_5I^{2+}$ (initial concentration $1.03 \times 10^{-4}$ M) in an equilibrated, pH 3 aqueous solution.

The following observations support the view that the $Ir(NH_3)_4(H_2O)X^{2+}$ species produced by $NH_3$ photoaquation from aqueous $Ir(NH_3)_5X^{2+}$ have the trans configuration. First, attempts to resolve the products into different stereoisomers by cation-exchange chromatography on Bio-Rad AG-50W (200–400 mesh) were unsuccessful, the aquo halo product in each case eluting as a single band. Much stronger evidence for the iodo complex was provided by heating the $Ir(NH_3)_4(H_2O)I^{2+}$ photoproduct in a solution to which concentrated HI had been added. When compared to the spectra of *cis*- and *trans*-$Ir(en)_2I_2^+$ (Table II), it is clear that there is a close correspondence with the spectrum of *trans*-$Ir(en)_2I_2^+$. Since the thermal substitution reactions of the Ir(III) ammines are stereoretentive,[9a,15] we conclude that *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$

---

(13) E. Borghi and F. Monacelli, *Inorg. Chim. Acta*, **5**, 211 (1971).
(14) F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, 1967.

**Table II.** Comparison of Spectra[a] of Dihalotetraammine Complexes "*trans*"-$Ir(NH_3)_4X_2^+$ Prepared by Initial Photochemical Labilization of $NH_3$ from $Ir(NH_3)_5I^{2+}$ (see Experimental Section) and the Known *trans*- and *cis*-$Ir(en)_2X_2^+$ Complexes[b]

| "*trans*"-$Ir(NH_3)_4X_2^+$ | | *trans*-$Ir(en)_2X_2^+$ | | *cis*-$Ir(en)_2X_2^+$ | |
|---|---|---|---|---|---|
| $\lambda_{max}$ | $\epsilon$ | $\lambda_{max}$ | $\epsilon$ | $\lambda_{max}$ | $\epsilon$ |
| | | $X^- = I^-$ | | | |
| 508 sh | 19 | 490 sh | 18 | | |
| 403 | 210 | 398 | 183 | 346 | 393 |
| 281 | $1.54 \times 10^4$ | 283 | $1.37 \times 10^4$ | 283 | $2.75 \times 10^3$ |
| 230 | $4.0 \times 10^4$ | 230 | $4.72 \times 10^4$ | 226 | $2.9 \times 10^4$ |
| | | $X^- = Br^-$ | | | |
| 472 | 6 | 450 | 13 | | |
| 372 | 48 | 360 | 74 | 310 | 205 |
| 302 | 27 | 285 sh | 47 | 265 | 210 |
| 226 sh | $2.62 \times 10^3$ | 230 sh | $3.01 \times 10^3$ | 230 | $1.73 \times 10^3$ |
| | | $X^- = Cl^-$ | | | |
| 460 | 6 | 425 | 13 | 380 | 17 |
| 357 | 45 | 345 | 52 | 315 | 92 |
| 274 | 44 | 272 sh | 58 | 293 | 120 |
| 244 sh | 166 | | | 255 | 127 |

[a] $\lambda$ in nm; $\epsilon$ in $M^{-1}\ cm^{-1}$; spectra in dilute aqueous solutions. [b] Reference 9a.

is the principal photoproduct from $Ir(NH_3)_5I^{2+}$. Notably, 313-nm photolysis of the *trans*-$Ir(NH_3)_4I_2^+$ prepared by the thermal anation of $Ir(NH_3)_4(H_2O)I^{2+}$ regenerates quantitatively the spectrum of the initial photoproduct from $Ir(NH_3)_5I^{2+}$ (see below). Similarly, when concentrated HBr or concentrated HCl was added, respectively, to the photoproduct solutions from the 313-nm photolyses of $Ir(NH_3)_5Br^{2+}$ or of $Ir(NH_3)_5Cl^{2+}$ and the resulting solutions were heated, the result was a mixture of monohalo- and dihaloammine complexes. Cation-exchange chromatography separated the unipositive dihalo complexes from the dipositive $Ir(NH_3)_5X^{2+}$ species. Electronic spectra of elution aliquots containing the monopositive ions were quantitatively identical with that of the dihalo $Ir(NH_3)_4X_2^+$ complexes, the syntheses of which are described below and of which are assigned a trans configuration on the basis of comparison of electronic spectra with those of the known bis(ethylenediamine) analogues (Table II). For the bromo species, the formation of *trans*-$Ir(NH_3)_4Br_2^+$ by the photoaquation of $NH_3$ followed by quantitative (assumed) anation with HBr and then ion-exchange chromatography gave an overall quantum yield of 0.068 mol/einstein on the basis of the extinction coefficients listed in Table II. This value compares favorably to the 0.055 determined for $NH_3$ aquation from solution pH changes (Table I).

Photolyses into the charge-transfer region give a somewhat different picture. The photochemistry of $Ir(NH_3)_5Br^{2+}$ resulting from 229-nm irradiation is quantitatively indistinguishable from that seen at longer wavlengths regardless of whether the solutions are deaerated or not. In contrast, LMCT photolysis of $Ir(NH_3)_5I^{2+}$ at 229 nm in aerated solution leads to smaller quantum yields for net $NH_3$ labilization (0.3 mol/einstein) than for LF excitation (0.6 mol/einstein) (Table III). Under these conditions, the photolysis solution spectra show well-defined isosbestic points, indicating little secondary photochemistry (Figure 1). A remarkable behavioral difference is found in deaerated solution. The periodic recorded spectra during the CT photolysis of deaerated aqueous $Ir(NH_3)_5I^+$ showed no isosbestic points, indicating significant thermal and/or photochemical secondary reactions even during the early stages of the photolysis. Best estimates for the primary quantum yields of photolabilization are $\Phi_{NH_3} = 0.32$ mol/einstein and $\Phi_{I^-} < 0.002$ mol/einstein on the basis of pH and spectral changes during the initial stages. Thus, the differences between aerated and deaerated solutions can be largely attributed to the secondary photoreactions of the initial *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$ product described in the next section.

**Tetraammine Complexes.** The dihalotetraammines $Ir(NH_3)_4X_2^+$ ($X = Cl^-, Br^-, I^-$) were all prepared via a photolysis procedure somewhat analogous to one described[9] earlier for the bis(ethylenediamine) complexes. Photolysis of aqueous $Ir(NH_3)_5I^{2+}$ leads to the formation of $Ir(NH_3)_4(H_2O)I^{2+}$ which can be converted by thermal anation with iodide ion (see Experimental Section) to a isolable diiodo complex $Ir(NH_3)_4I_2^+$ with a spectrum closely analogous to that of *trans*-$Ir(en)_2I_2^+$ (Table II). Thus, a trans configuration for $Ir(NH_3)_4I_2^+$ is implied, and, since the thermal substitution reactions of iridium(III) amines apparently are highly stereoretentive,[9a,15] a trans configuration is also implied for the $Ir(NH_3)_4(H_2O)I^{2+}$ photoproduct. When the latter material was heated in the presence of $Ag^+$ ion, a new species, presumably *trans*-$Ir(NH_3)_4(H_2O)_2^{3+}$, is formed in situ by the aquation of $I^-$. Heating the diaquo complex with HBr or HCl gives the respective dihalo species $Ir(NH_3)_4Br_2^+$ and $Ir(NH_3)_4Cl_2^+$. The electronic spectra of these ions are quite analogous to the spectra of the known *trans*-$Ir(en)_2X_2^+$ analogues and markedly different from the cis species (Table II). Thus, again, a trans configuration is assigned for each, consistent with the view that the sequence of thermal substitution reactions beginning with the *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$ photoproduct is stereoretentive. This synthetic sequence is illustrated in Scheme I for the dibromo species.

**Scheme I**

$$Ir(NH_3)_5I^{2+} + H_2O \xrightarrow{h\nu} trans\text{-}Ir(NH_3)_4(H_2O)I^{2+} + NH_3 \quad (2)$$

$$trans\text{-}Ir(NH_3)_4(H_2O)I^{2+} + Ag^+ + H_2O \rightarrow trans\text{-}Ir(NH_3)_4(H_2O)_2^{3+} + AgI \quad (3)$$

$$trans\text{-}Ir(NH_3)_4(H_2O)_2^{3+} + 2Br^- \rightarrow trans\text{-}Ir(NH_3)_4Br_2^+ + 2H_2O \quad (4)$$

The LF photolysis of *trans*-$Ir(NH_3)_4I_2^+$ in aqueous solution leads simply to the aquation of $I^-$ to give the same *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$ ion observed as the photoproduct of $Ir(NH_3)_5I^{2+}$ (eq 5). The absence of spectrally significant

$$trans\text{-}Ir(NH_3)_4I_2^+ + H_2O \xrightarrow{h\nu} trans\text{-}Ir(NH_3)_4(H_2O)I^{2+} + I^- \quad (5)$$

secondary photolysis is indicated by the observance of isosbestic points at 485, 322, and 204 nm throughout the photolysis run. Similarly, LF excitation (366 nm) of *trans*-$Ir(NH_3)_4Br_2^+$ or *trans*-$Ir(NH_3)_4Cl_2^+$ leads principally to halide photoaquation ($\Phi_{Br^-} = 0.23$ mol/einstein and $\Phi_{Cl^-} = 0.28$ mol/einstein) but, in contrast to the diiodo ion, some ammine aquation ($\Phi_{NH_3} = 0.013$ mol/einstein) is also seen for the dichloro ion.

As described above, the LF photolysis ($\lambda_{irr} = 366$ nm) of aqueous *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$ ($ClO_4^-$ salt) leads to no spectral or pH changes, an observation which confines the net photochemistry, if any, to the exchange of solvent and coordinated water. This species was comparably "photoinert" to LF irradiation in deaerated solutions. Irradiation of *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$ in the LMCT region (229 nm) gives a different result. In solutions equilibrated with air, $NH_3$ photoaquation is nil according to pH changes but a small $I^-$ photoaquation (about 0.01 mol/einstein) is seen via spectral changes. However, in deaerated solution, the system is considerably more photoactive under LMCT excitation. Long-term photolysis leads to a spectrum virtually identical with that of *trans*-$Ir(NH_3)_4I_2^+$ at a concentration corresponding to about 50% of the initial starting material concentration. Quantum yields for disappearance of *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$

---

(15) H. Ogino and J. C. Bailar, Jr., *Inorg. Chem.*, 17, 1118 (1978).

**Table III.** Electronic Spectra and Photoaquation Quantum Yields for Pentaammineiridium(III) Complexes $Ir(NH_3)_5L^{3+}$

| | spectra[a] | | photochemistry[a] | | |
|---|---|---|---|---|---|
| complex | $\lambda_{max}$ ($\epsilon$)[b] | assignt[c] | $\lambda_{irr}$[b] | $\Phi_x$[d] | $\Phi_{NH_3}$[d] |
| $Ir(NH_3)_6^{3+}$ | 315 sh (14) | $^3T_1 \leftarrow {}^1A_1$ | 313 | 0.090[e] | 0.093 |
| | 251 (92) | $^1T_1 \leftarrow {}^1A_1$ | 254 | 0.083[e] | 0.082 |
| | 214 (160) | $^1T_2 \leftarrow {}^1A_1$ | | | |
| $Ir(NH_3)_5H_2O^{3+}$ | 333 sh (12) | $^3E, {}^3A_2 \leftarrow {}^1A_1$ | 313 | 0.42[e] | <0.002 |
| | 258 (86) | $^1E, {}^1A_2 \leftarrow {}^1A_1$ | 254 | | <0.03 |
| | 213 (128) | $^1E, {}^1A_2 \leftarrow {}^1A_1$ | | | |
| $Ir(NH_3)_5acn^{3+}$ | 320 (22) | $^3E, {}^3A_2 \leftarrow {}^1A_1$ | 313 | 0.28 | <0.003 |
| | 246 (217) | $^1E, {}^1A_2 \leftarrow {}^1A_1$ | 254 | 0.27 | <0.002 |
| | 204 (1.36 × $10^3$) | | | | |
| $Ir(NH_3)_5bzn^{3+}$ | 283 (3 × $10^3$) | $\pi^* \leftarrow \pi$ | 313 | 0.16 | <0.001 |
| | 254 (9.73 × $10^3$) | $\pi^* \leftarrow \pi$ | 254 | 0.17 | 0.001 |
| | 236 (11.8 × $10^3$) | $\pi^* \leftarrow \pi$ | | | |

[a] In 25 °C dilute aqueous solution; pH 3. [b] $\lambda$ in nm; $\epsilon$ in $M^{-1}$ $cm^{-1}$. [c] Reference 10. [d] In mol/einstein; values for three or more determinations; experimental reproducibility better than ± 10% of the value listed. [e] Reference 1.

are about ~0.055 mol/einstein, but $NH_3$ labilization remains nil (<0.005 mol/einstein). The other products are unknown. (However, if the remainder of the iridium were in a species such as *trans*-$Ir(NH_3)_4(H_2O)_2^{3+}$, it would be obscured in the spectra by the more strongly absorbing diiodo species.)

**Other Pentaammine Complexes $Ir(NH_3)_5L^{3+}$.** For the neutral ligand complexes $Ir(NH_3)_5L^{3+}$, where L is $H_2O$, acn, bzn, or $NH_3$, the photoproduct in each case is $Ir(NH_3)_5H_2O^{3+}$ (eq 6). For L $\neq$ $NH_3$, ammine photoaquation is at most a

$$Ir(NH_3)_5L^{3+} + H_2O \xrightarrow{h\nu} Ir(NH_3)_5H_2O^{3+} + L \quad (6)$$

very minor path (Table III). Photolysis behavior in each case was quantitatively independent of whether the irradiation wavelength was 313 nm (corresponding to a "spin-forbidden" LF transition) or 254 nm (corresponding to "spin-allowed" LF transitions for L = $NH_3$, $H_2O$, or acn and to a $\pi$–$\pi^*$ intraligand transition for L = bzn). For 313-nm irradiation of $Ir(ND_3)_6^{3+}$ in $D_2O$ (25 °C), the quantum yield for ammine labilization is 0.21 mol/einstein, significantly higher than the 0.090 mol/einstein value seen for the analogous perprotio system in $H_2O$.

## Discussion

The following features of the Ir(III) photochemistry described here shall be the focus of our discussion: (1) Ligand labilization is the sole net photoreaction observed in the continuous photolysis studies. (2) For pentaammine species where products are disubstituted, product stereochemistry is exclusively trans. (3) Photoaquation quantum yields for individual complexes are independent of $\lambda_{irr}$ regardless of whether initial excitation corresponds to LF spin-allowed or -forbidden bands; however, excitation into LMCT absorptions leads to significant differences in the photoreaction behavior. Notably, the pattern emerging for the pentaammine- and the *trans*-tetraammineiridium(III) complexes $Ir(NH_3)_5X^{2+}$, $Ir(NH_3)_5L^{3+}$, and *trans*-$Ir(NH_3)_4X_2^+$ shows not only qualitative but also quantitative similarities to that seen for analogous Rh(III) complexes (Table IV).

Ligand photoaquation (point 1) would be the expected pathway for the LF excitation of the Ir(III) ammines given that luminescence spectra of complexes such as $Ir(en)_3^{3+}$ and *trans*-$Ir(en)_2Cl_2^+$ indicate the lowest energy excited states (es) to be LF in nature.[16] It is a well-established pattern[2,5,17] that the LF excitation of low-spin $d^6$ complexes (with the exception of the Co(III) ammines) generally leads to ligand labilization with moderate to high quantum yields.

**Table IV.** Comparison of the Quantitative LF Photoactivity of Iridium(III), Rhodium(III), and Cobalt(III) Ammine Complexes $M(NH_3)_5X^{n+}$ and *trans*-$M(NH_3)_4X_2^{n+}$ [a]

| | ligand preferentially aquated | | photoaquation quantum yield, $\Phi_T$[b] | |
|---|---|---|---|---|
| X | Rh(III)[c] | Ir(III) | Rh(III)[c] | Ir(III) |
| $Cl^-$ | $Cl^-$ | $Cl^-$ | 0.16 | 0.13 |
| $Br^-$ | $NH_3$ | $NH_3$ | 0.20 | 0.06 |
| $I^-$ | $NH_3$ | $NH_3$ | 0.82 | 0.63 |
| $H_2O$ | $H_2O$ | $H_2O$ | 0.42 | 0.42 |
| $NH_3$ | $NH_3$ | $NH_3$ | 0.08 | 0.09 |
| acn | acn | acn | 0.47 | 0.28 |
| bzn | bzn | bzn | 0.35 | 0.16 |
| *trans*-$(Cl^-)_2$ | $Cl^-$ | $Cl^-$ | 0.17 | 0.28 |
| *trans*-$(I^-)_2$ | $I^-$ | $I^-$ | 0.48 | 0.13 |

[a] $\lambda_{irr}$ corresponds to lowest energy, spin-allowed LF absorption maximum ($^1E, {}^1A_2 \leftarrow {}^1A_1$). [b] $\Phi_T = \Phi_X + \Phi_{NH_3}$. [c] Data from ref 2.

The photoaquation quantum yields for the Rh(III) ammine complexes have been found essentially independent of $\lambda_{irr}$ for excitation into the LF absorption bands.[6,18,19] This fact combined with results with triplet sensitizers[18,19] have led to the conclusion that the initial LF excitation is followed by rapid internal conversion/intersystem crossing to a common state, presumably the lowest energy LF triplet state, which is precursor to essentially all deactivation processes: nonradiative decay to ground state, radiative decay to ground state, or reactive decay to give substitution products. Experiments in this laboratory have now demonstrated by direct measurements of Rh(III) excited-state lifetimes in aqueous solution[17] that LF photoactivity is indeed the result of the high intrinsic lability of the lowest energy, thermally equilibrated excited state ($^3T_{1g}$ for an octahedral complex) as would be expected from the $(t_{2g})^5(e_g)^1$, i.e., $(\pi)^5(\sigma^*)^1$, configuration. The LF photochemistry of the Ir(III) homologues is also $\lambda_{irr}$ independent. Since the present studies include direct excitation of bands assigned[8] as transitions from a singlet ground state to a low-energy triplet LF state (Tables I and III), one can again conclude that the lowest energy LF triplet is a common-state precursor to reaction or deactivation[20] (Figure 2).

Notably, the cobalt(III) analogues display a similar pattern regarding the identity of the ligand labilized[5] but show two

---

(16) M. K. DeArmond and J. E. Hillis, *J. Chem. Phys.*, **54**, 2247 (1971).

(17) M. A. Bergkamp, J. Brannon, D. Magde, R. J. Watts, and P. D. Ford, *J. Am. Chem. Soc.*, **101**, 4549 (1979).

(18) T. L. Kelly and J. F. Endicott, *J. Phys. Chem.*, **76**, 1937 (1972).

(19) J. D. Petersen and P. C. Ford, *J. Phys. Chem.*, **78**, 1144 (1974).

(20) Notably, we have for convenience used the spin multiplicity term "triplet" to describe the lowest LF state. While such designations have been commonly used (e.g., see ref 10 and 18), it should be emphasized that the spin-orbit coupling constants for these Ir(III) complexes are large and the spin quantum number no longer provides a good description of electronic behavior.

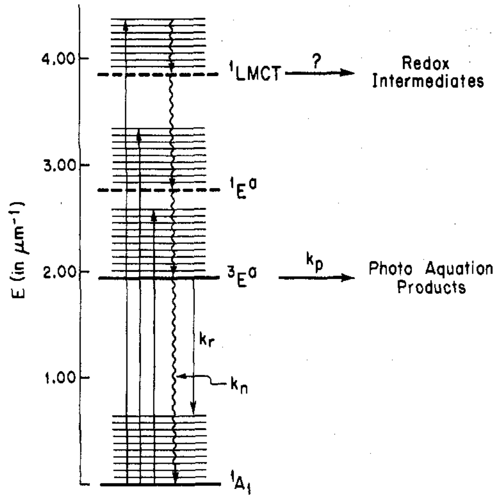


**Figure 2.** Qualitative energy level diagram for $Ir(NH_3)_5Br^{2+}$. LF excitation is depicted as resulting in rapid intersystem crossing/internal conversion of the lowest LF excited states which can undergo reactive ($k_p$), radiative ($k_r$), or nonradiative ($k_n$) deactivation. Charge-transfer excitation leads to the same products and quantum yields as LF excitation, suggesting the principal deactivation pathway via internal conversion to the LF excited-state manifold; however, some direct reaction to give redox intermediates cannot be excluded.

dramatic departures from the Ir(III) and Rh(III) systems when quantum yields resulting from LF excitation are compared.[1,5] The cobalt(III) photoaquation quantum yields are more than an order of magnitude smaller and are significantly $\lambda_{irr}$ dependent. Apparently these differences lie in the relatively weak ligand field splitting of the cobalt ammine complexes, since photosubstitution quantum yields resulting from LF excitation of the stronger field pentacyano complexes $Co(CN)_5X^{n-}$ are comparable to those of the Ir(III) and Rh(III) complexes and are much less $\lambda_{irr}$ dependent.[21] The reasons for such differences are unclear, conceivably these lie in different chemical mechanisms of the es reactions or in the facility of interconversion between upper and lower states. One marked difference is the recent spectroscopic demonstration that the quintet configuration is the lowest es of the Co(III) ammines,[22] a point which has been the subject of previous speculation.[23] Since the quintet would suffer less Jahn–Teller distortion than would the lowest triplet, it may be less active toward dissociative ligand loss. However, the energetic position and the proposed low reactivity of the quintet are not alone adequate criteria for explaining the anomalous $\lambda_{irr}$ dependence of the cobalt(III) ammine LF photosubstitutions.

When discernible, the stereochemistry of the photoproducts from eq 1b is exclusively trans, an observation which provides a pathway for synthesis of *trans*-diacido complexes starting with the iodopentaammine. Trans products are also seen for the analogous photoreactions of Rh(III), a fact consistent with the theoretical views that labilization should be focussed along the weak field axis of the three mutually perpendicular axes defined by the six ligands. However, when $NH_3$ is the leaving group from $M(NH_3)_5X^{n+}$, the stereochemical origin of the labilized $NH_3$ is not obvious, especially for the Rh(III) systems where photostereolability concomitant with photolabilization has been observed[24] for disubstituted Rh(III) tetraammine. Nonetheless, similar studies of dihalo Ir(III) complexes[25] show but small photostereomobility for the *cis*-dichloro and -dibromo complexes and only stereoretentive photoaquation of the trans analogues, suggesting that the trans products of eq 1b are indeed the result of labilizing the $NH_3$ trans to the unique ligand.

The marked increase in the ammonia photoaquation quantum yield resulting from the perdeuteration of hexaammineiridium(III) also duplicates the trend observed for Rh(III) complexes.[17,19] This quantum yield increase has been attributed to a longer lifetime for the reactive triplet state in the perdeuterio system owing to the suppression of the weak coupling contribution to nonradiative deactivation ($k_n$ in Figure 2). Decreases in $k_n$ allow more deactivation via the competitive reaction channel ($k_p$).[17,19] Some preliminary low-temperature (77 K) luminescence studies of the perprotio and perdeuterio Ir(III) ammine complexes support this view, the perdeuterio complexes displaying considerably longer lifetimes than the perprotio analogues under these conditions.[25]

For the benzonitrile complex, $Ir(NH_3)_5bzn^{3+}$, all the wavelengths studied correspond to absorptions which are intraligand in character. The observation of relatively high quantum yield photoaquation of benzonitrile alone suggests internal conversion from the IL excited states(s) to the labile LF states to occur efficiently. This type of intramolecular sensitization from the organic chromophore has been noted previously for the Rh(III) and Co(III) analogues.

The charge-transfer photochemistry reported here is a brief survey of the behavior of these complexes under continuous photolysis and is the subject of continuing study in these laboratories. For the bromo complex $Ir(NH_3)_5Br^{2+}$ and the diiodo species *trans*-$Ir(NH_3)_4I_2^+$, excitation into the LMCT absorption bands leads to photochemistry indistinguishable from that resulting from LF excitation. These similarities may be fortuitous; however, an alternative interpretation is that the LMCT states initially populated by 229-nm excitation undergo efficient internal conversion to the LF excited-state manifold. The same conclusion cannot be drawn for $Ir(NH_3)_5I^{2+}$. In this case, 229-nm photolysis in air-equilibrated solution gives the same Ir(III) products, *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$ as LF excitation (Figure 1), but $\Phi_{NH_3}$ values are half those seen for LF photolysis. Thus the LMCT state(s) must have available important deactivation pathways to the ground state not involving initial internal conversion to the more reactive LF states. This result is strikingly similar to the behavior reported for the rhodium(III) analogue $Rh(NH_3)_5I^{2+}$, for which it was concluded that at least part of the photolabilization occurred via a redox mechanism.[26]

The possible role of similar photoredox pathways in the Ir(III) complexes is indicated in the LMCT photolysis of *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$. When irradiated at 229 nm, this ion showed markedly different behavior in aerated and deaerated solutions, appearing nearly photoinert in aerated solution but undergoing significant photoreaction in deaerated solution to give an unexpected product *trans*-$Ir(NH_3)_4I_2^+$. While the differences might represent the result of $O_2$ quenching of the LMCT state, this seems unlikely given the failure of $O_2$ to affect noticeably either the LF or LMCT photochemistry of $Ir(NH_3)_5I^{2+}$. A more likely alternative is that $O_2$ quenches some intermediate, perhaps $Ir(NH_3)_4^{2+}$,

---

(21) (a) A. W. Adamson, A. Chiang, and E. Zinato *J. Am. Chem. Soc.*, **91**, 5467 (1969); (b) M. Wrighton, H. B. Gray, G. S. Hammond, and V. Miskowsi, *Inorg. Chem* **12**, 740 (1973).

(22) E. I. Solomon, paper presented at the 175th National Meeting of the American Chemical Society, Anaheim, CA, April 1978.

(23) (a) L. Viaene, J. D'Olieslager, A. Ceulemans, and L. G. Vanquickenborne, *J. Am. Chem. Soc.*, **101**, 1405 (1979); (b) C. H. Langford and C. P. J. Vuik, *ibid.*, **98**, 5409 (1976).

(24) (a) D. Strauss and P. C. Ford, *J. Chem. Soc., Chem. Commun.*, 194 (1977); (b) L. Skibsted, D. Strauss, and P. C. Ford, *Inorg. Chem.*, **18**, 3171 (1979); (c) L. Skibsted and P.C. Ford, *J. Chem. Soc., Chem. Commun.*, 853 (1979); (d) L. Skibsted and P. C. Ford, *Inorg. Chem.*, in press.

(25) M. Talebinasab-Sarvari and P. C. Ford, reported at the 1978 Pacific Conference on Chemistry and Spectroscopy, San Francisco, CA, Sept 1978; *Inorg. Chem.*, in press.

(26) T. L. Kelly and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 1797 (1972).

*Inorg. Chem.* **1980**, *19*, 1840–1846

which serves as a key link in a redox chain reaction.

**Acknowledgment.** This work was supported by the National Science Foundation. The iridium used in these studies was provided on loan by Matthey Bishop, Inc.

**Registry No.** $[Ir(NH_3)_5acn](ClO_4)_3$, 73453-89-1; $[Ir(NH_3)_5bzn](ClO_4)_3$, 73453-87-9; [*trans*-$Ir(NH_3)_4I_2]_2S_2O_6$, 73495-00-8; $[Ir(NH_3)_5H_2O](ClO_4)_3$, 31285-82-2; $[Ir(NH_3)_5I](ClO_4)_2$, 67573-09-5; $Ir(NH_3)_5Cl^{2+}$, 29589-09-1; $Ir(NH_3)_5Br^{2+}$, 35884-02-7; $Ir(NH_3)_5I^{2+}$, 25590-44-7; *trans*-$Ir(NH_3)_4I_2^+$, 62153-22-4; *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$, 73453-92-6; *trans*-$Ir(NH_3)_4Br_2^+$, 62153-21-3; *trans*-$Ir(NH_3)_4Cl_2^+$, 62153-20-2; $Ir(NH_3)_6^{3+}$, 24669-15-6; $Ir(NH_3)_5H_2O^{3+}$, 29589-08-0; $Ir(NH_3)_5acn^{3+}$, 73453-88-0; $Ir(NH_3)_5bzn^{3+}$, 53783-43-0; *trans*-$Ir(NH_3)_4(H_2O)Cl^{2+}$, 73453-91-5; *trans*-$Ir(NH_3)_4(H_2O)Br^{2+}$, 73453-90-4; *trans*-$Ir(NH_3)_4(H_2O)_2^{3+}$, 62153-23-5.

---

Contribution No. 3436 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

# Thermal and Photochemical Reactivity of $(C_5H_5)_2V_2(CO)_5$

LARRY N. LEWIS and KENNETH G. CAULTON*

*Received January 22, 1980*

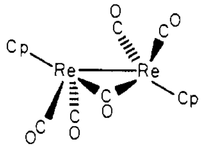
The complex $Cp_2V_2(CO)_5$ has been synthesized by photolysis of $CpV(CO)_4$ in tetrahydrofuran (THF). The sequence of reactions leading to dimerization has been shown to require photoinduced dimerization of the observed primary photoproduct $CpV(CO)_3(THF)$. The thermal and photochemical reactivity of $Cp_2V_2(CO)_5$ with CO and a variety of phosphines has been examined in order to assess the mechanistic significance of the V–V multiple bond and the carbonyl semibridges. On the basis of both chemical trapping experiments and low-temperature photolyses, it is found that strong nucleophiles may directly attack the pentacarbonyl dimer with displacement of the metal–metal double bond; monomeric products result. Weak nucleophiles effect net CO substitution on the intact dimer but do so via the species $Cp_2V_2(CO)_4$, which is in equilibrium with the pentacarbonyl; this equilibrium has been demonstrated by using $^{13}CO$. A THF adduct of this tetracarbonyl dimer has been observed directly at low temperatures and proves that the primary chemical consequence of irradiation of $Cp_2V_2(CO)_5$ is CO dissociation, not dimer scission. The reaction of $PEt_2Ph$ with dimeric, multiply bonded $Cp_2V_2(CO)_5$ thus exhibits a remarkable product dependence on the source of activation energy.

## Introduction

The photochemistry of dimeric transition-metal carbonyl complexes containing a metal–metal bond of unit order exhibits substantial complexity.[1] Irradiation at the absorption frequency assigned as $\sigma \rightarrow \sigma^*$ (with respect to the metal–metal bond) might reasonably be expected to destroy that bond. Photolysis in the presence of alkyl halides has indeed yielded products which are consistent with (but do not in every case uniquely require) the photoproduction of the radical monomer M·.

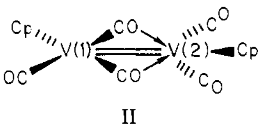
Photolysis of a complex containing a multiple metal–metal bond might well lead to distinctly different chemical consequences. Thus, a double-bonded dimer with a ground-state one-electron configuration $\sigma^2\pi^2$ will maintain a formal single bond following any one-electron excitation. In such a circumstance, ligand photodissociation, which dominates the photochemistry of monomeric metal carbonyls, might become competitive with or preferable to metal–metal bond homolysis. Even for the single-bonded dimer $[CpMo(CO)_3]_2$, a flash photolytic study has demonstrated[2] that Mo–Mo homolysis is accompanied by CO photodissociation. As indicated above, this complexity necessitates careful reconsideration of earlier studies which tended to demand a single and universal mechanism for the photochemistry of single-bonded dimers.

We report here a study of the thermal chemistry and photochemistry of $Cp_2V_2(CO)_5$.[3,4] We consider this to be an example of a complex with a double bond[5] between the metal atoms and thus a test case for our simple ideas on the photochemistry of this class. The intriguing geometric and electronic structure of $Cp_2V_2(CO)_5$[6] also motivated this study. The complex does not possess the symmetric structure of $Cp_2Re_2(CO)_5$[7] (I) but instead may be viewed as the fusion of $CpV(CO)_3$ and $CpV(CO)_2$ monomers. Two of the CO groups in the $CpV(CO)_3$ fragment participate in a structurally and spectroscopically significant interaction with the second metal atom ("carbonyl semibridges"[4,6]).

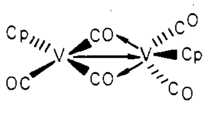


I

Detailed comparison of structural parameters for $Cp_2V_2(CO)_5$ and $Cp_2V_2(CO)_4(PPh_3)$ has been used[8] in an attempt to support the idea that the carbonyl semibridges in both of these molecules are performing a donor function toward V(2) (structure II). This model leads to an 18-electron configuration at both V(1) and V(2), provided the net effect of two donor semibridges is the donation of only two electrons. The acceptor semibridge model[6] (III), on the other hand, yields a 16-electron configuration at both metal atoms. The ex-



II



III

---

(1) Wrighton, M. S. *Top. Curr. Chem.* **1976**, *65*, 37.

(2) Hughey, J. L.; Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440.

(3) Fischer, E. O.; Schneider, R. J. *Chem. Ber.* **1970**, *103*, 3685.

(4) Cotton, F. A.; Frenz, B. A.; Kruczynski, L. *J. Am. Chem. Soc.* **1973**, *95*, 951.

(5) This statement contrasts with that published previously.[6] In support of our claim, the chromium–chromium triple-bond length in $Cp_2Cr_2(CO)_4$ is 2.22 Å. Since vanadium is intrinsically larger than chromium by as much as 0.08 Å (the difference between the M–C(Cp) distances in the two compounds), the V–V separation of 2.46 Å in $Cp_2V_2(CO)_5$ supports the idea of V–V multiple bonding.

(6) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

(7) Foust, A. S.; Hoyano, J. K.; Graham, W. A. G. *J. Organomet. Chem.* **1971**, *32*, C65.

(8) Huffman, J. C.; Lewis, L. N.; Caulton, K. G., submitted for publication in *Inorg. Chem.*