Inorg. Chem. **1980**, *19*, 1533-1543 **1533**

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Photochemistry of Cyclopentadienylmolybdenum and Cyclopentadienyltungsten Carbonyl Halide Complexes

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Received July 10, 1979

The primary photochemical process for $\eta^5\text{-}C_5H_5M(CO)_3X$ complexes (M = Mo, X = Br or I; M = W, X = Cl, Br, or I) at 366 or 436 nm is dissociation of a carbon monoxide ligand. Irradiations of benzene solutions containing triphenylphosphine lead stereospecifically to *cis*-$(\eta^5\text{-}C_5H_5)M(CO)_2(PPh_3)X$. Quantum yields vary as a function of irradiation wavelength ($\Phi_{366} > \Phi_{436}$), central metal ($\Phi_{Mo} > \Phi_W$) and halogen ($\Phi_{Cl} > \Phi_{Br} > \Phi_I$) but are relatively insensitive to PPh_3 concentration. The substituted complexes $\eta^5\text{-}C_5H_5Mo(CO)_2(PPh_3)X$ undergo cis ⇄ trans isomerization and ligand-exchange reactions leading to $\eta^5\text{-}C_5H_5Mo(CO)(PPh_3)_2X$ and $\eta^5\text{-}C_5H_5Mo(CO)_3X$.

Introduction

The solid state and solution structures[1-3] of $CpM(CO)_3X$ (M = Cr, Mo, W; Cp = $\eta^5\text{-}C_5H_5$) complexes are best regarded as pseudo square pyramidal, with the three carbonyl ligands and the halogen occupying basal positions of the square pyramid and the center of mass of the cyclopentadienyl ligand occupying the apical position. Substituted derivatives of general formulas $CpM(CO)_2(L)X$ and $CpM(CO)(L)_2X$ maintain this basic geometry and exist in cis and trans geometric forms[2-7] (Figure 1). In solution, the isomers are readily distinguished by infrared,[6,7] ^1H NMR,[5,7] and ^{13}C NMR spectroscopy.[3] These complexes thus comprise a system ideally suited for investigating the stereochemistry of photosubstitution and photoisomerization processes in cyclopentadienylmetal carbonyls, as well as extending our earlier investigations of $CpFe(CO)_2X$[8] and $CpV(CO)_4$.[9]

Prior to this study, the photochemical reactions reported[10-13] for $CpM(CO)_3X$ complexes were limited to the preparation of substituted derivatives, while mechanistic aspects of the photochemical reactions were neglected. Photoinduced reactions of $CpMo(CO)_3X$ with a variety of two-electron-donor ligands have afforded numerous covalent substitution products (eq 1), examples being $CpMo(CO)_2(L)Cl$[12] (L = PPh_3, $AsPh_3$, $SbPh_3$) and $CpMo(CO)_2(L)I$[12] (L = PEt_3, PPh_3, PCx_3, $P(OPh)_3$, $AsPh_3$, $AsMePh_2$, $SbPh_3$).

$$CpM(CO)_3X + L \xrightarrow{h\nu} CpM(CO)_2(L)X + CO \qquad (1)$$

Substituted derivatives of $CpM(CO)_3X$ have also been prepared by thermal reactions of the complexes with two-electron-donor ligands.[6,7] Disubstituted complexes of general formula $CpM(CO)(L)_2X$ have been obtained by prolonged irradiation of $CpM(CO)_3X$ with excess ligand,[12] suggesting that the monosubstituted complexes are themselves susceptible to photosubstitution (eq 2).

$$CpM(CO)_2(L)X + L \xrightarrow{h\nu} CpM(CO)(L)_2X + CO \quad (2)$$

Similarly, $CpM(CO)_3X$ complexes are reported to react photochemically with the bidentate ligands $Me_2P(CH_2)_2PMe_2$ and *cis*-$Ph_2PCH{=}CHPPh_2$ (L_2) to yield disubstituted $CpM(CO)(L_2)X$ complexes.[13]

Although it would appear at first glance that the above reactions involve simple substitution of carbon monoxide, King et al.[13] suggested that the photoreactions of $CpMo(CO)_3Cl$ with bidentate phosphine ligands proceed via initial formation of the ionic complexes, $[CpMo(CO)_2(L_2)]Cl$, and subsequent displacement of a carbonyl ligand by chloride ion (eq 3 and 4). The proposed scheme was based on the observations that the ionic complexes are produced by thermal reactions of $CpM(CO)_3Cl$ with bidentate ligands and that ultraviolet photolysis of the ionic derivatives leads to formation of the covalent substitution products.[14] However, it has not been verified experimentally that the ionic derivatives are intermediates in the overall photosubstitution processes.

$$CpMo(CO)_3Cl + L_2 \xrightarrow{h\nu} [CpMo(CO)_2(L_2)]Cl + CO \quad (3)$$

$$[CpMo(CO)_2(L_2)]Cl \xrightarrow{h\nu} CpMo(CO)(L_2)Cl + CO \qquad (4)$$

The photochemistry of the dimeric complexes $[CpMo(CO)_3]_2$ and $[CpW(CO)_3]_2$ has received considerable attention.[15-27] The dominant photoprocess for these complexes is

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(1) S. Chaiwasie and R. H. Fenn, *Acta Crystallogr., Sect. B*, **24**, 525 (1968).
(2) K. W. Barnett and D. W. Slocum, *J. Organomet. Chem.*, **44**, 1 (1972), and references therein.
(3) L. J. Todd, J. R. Wilkinson, J. P. Hickey, D. L. Beach, and K. W. Barnett, *J. Organomet. Chem.*, **154**, 151 (1978).
(4) R. J. Mawby and G. Wright, *J. Organomet. Chem.*, **21**, 169 (1970).
(5) J. W. Faller and A. S. Anderson, *J. Am. Chem. Soc.*, **92**, 5852 (1970).
(6) D. L. Beach and K. W. Barnett, *J. Organomet. Chem.*, **97**, C27 (1975).
(7) D. L. Beach, M. Dattilo, and K. W. Barnett, *J. Organomet. Chem.*, **140**, 47 (1977).
(8) D. G. Alway and K. W. Barnett, *Inorg. Chem.*, **17**, 2826 (1978).
(9) D. G. Alway and K. W. Barnett, *Inorg. Chem.*, **19**, 779 (1980).
(10) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974), and references therein.
(11) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, 1970, and references therein.
(12) R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. A*, 94 (1967).
(13) R. B. King, L. W. Houk, and K. H. Pannell, *Inorg. Chem.*, **8**, 1042 (1969).
(14) R. B. King, K. H. Pannell, C. A. Eggers, and L. W. Houk, *Inorg. Chem.*, **7**, 2353 (1968).
(15) M. S. Wrighton, *Top. Curr. Chem.*, **65**, 37 (1976).
(16) D. S. Ginley and M. S. Wrighton, *J. Am. Chem. Soc.*, **97**, 4908 (1975).
(17) D. S. Ginley, C. R. Bock, and M. S. Wrighton, *Inorg. Chim. Acta*, **23**, 85 (1977).
(18) R. M. Laine and P. C. Ford, *Inorg. Chem.*, **16**, 388 (1977).
(19) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 4246 (1975).
(20) A. R. Burkett, T. J. Meyer, and D. G. Whitten, *J. Organomet. Chem.*, **67**, 67 (1974).
(21) J. L. Hughey IV, C. R. Bock, and T. J. Meyer, *J. Am. Chem. Soc.*, **97**, 4440 (1975).
(22) J. L. Hughey and T. J. Meyer, *Inorg. Chem.*, **14**, 947 (1975).
(23) C. Giannotti and G. Merle, *J. Organomet. Chem.*, **105**, 97 (1976).
(24) D. M. Allen, A. Cox, T. J. Kemp, Q. Sultana, and R. B. Pitts, *J. Chem. Soc., Dalton Trans.*, 1189 (1976).
(25) R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. A*, 43, 1968.

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homolytic cleavage of the metal–metal bond (eq 5).[15-19]

$$[CpM(CO)_3]_2 \xrightarrow{h\nu} 2CpM(CO)_3\cdot \qquad (5)$$

$$[CpMo(CO)_3]_2 \xrightarrow{h\nu} Cp_2Mo_2(CO)_5 + CO \qquad (6)$$

Studies of $[CpMo(CO)_3]_2$ by flash photolysis in cyclohexane, tetrahydrofuran, and acetonitrile solutions have shown that both ultraviolet and visible irradiation of the complex results in metal–metal bond cleavage as the primary photoprocess, with dissociation of carbon monoxide (eq 6) being a minor photoprocess.[21] Irradiation of $[CpMo(CO)_3]_2$ with equimolar amounts of PPh_3 yields the monosubstituted dimeric complex $Cp_2Mo_2(CO)_5(PPh_3)$.[26] However, irradiation of $[CpMo(CO)_3]_2$ with an excess of PPh_3 for prolonged periods of time (~3 days) affords the ionic compound $[CpMo(CO)_2(PPh_3)_2][CpMo(CO)_3]$.[25] Photolysis of $[CpMo(CO)_3]_2$ and $[CpW(CO)_3]_2$ in the polar coordinating solvents pyridine, dimethyl sulfoxide, and dimethylformamide produces $CpMo(CO)_3^-$ and $CpW(CO)_3^-$, respectively.[24] $[CpMo(CO)_3]_2$ undergoes net disproportionation upon photolysis in acetone, acetonitrile, and tetrahydrofuran solutions that contain X^- (X = Cl, Br, SCN)[20] (eq 7).

$$[CpMo(CO)_3]_2 + X^- \xrightarrow{h\nu} CpMo(CO)_3X + CpMo(CO)_3^- \qquad (7)$$

Photochemical reactions of $CpM(CO)_3X$ and related complexes suggest a variety of possible deactivation pathways for excited-state $CpM(CO)_3X$ complexes. They include carbon monoxide dissociation (eq 8), heterolytic cleavage of the metal–halogen bond (eq 9) and homolytic cleavage of the metal–halogen bond (eq 10). For the substituted derivatives, $CpM(CO)_2(PPh_3)X$, dissociation of the phosphine ligand (eq 11) and geometric isomerization (eq 12 and 13) are also possible processes for excited-state decay. This paper describes the results of our investigation of the photochemical behavior (λ = 366 and 436 nm) of $CpM(CO)_3X$ and $CpM(CO)_2(PPh_3)X$ (M = Mo, W) in benzene solutions. The chromium analogues were excluded from this study, owing to their thermal instability.[2] A preliminary account of portions of this work has been published.[28]

$$CpM(CO)_3X \xrightarrow{h\nu} CpM(CO)_2X + CO \qquad (8)$$

$$CpM(CO)_3X \xrightarrow{h\nu} CpM(CO)_3^+ + X^- \qquad (9)$$

$$CpM(CO)_3X \xrightarrow{h\nu} CpM(CO)_3\cdot + X\cdot \qquad (10)$$

$$CpM(CO)_2(PPh_3)X \xrightarrow{h\nu} CpM(CO)_2X + PPh_3 \qquad (11)$$

$$cis\text{-}CpM(CO)_2(PPh_3)X \xrightarrow{h\nu} trans\text{-}CpM(CO)_2(PPh_3)X \qquad (12)$$

$$trans\text{-}CpM(CO)_2(PPh_3)X \xrightarrow{h\nu} cis\text{-}CpM(CO)_2(PPh_3)X \qquad (13)$$

Experimental Section

Materials. $[CpMo(CO)_3]_2$ and $[MeCpMo(CO)_3]_2$ were purchased from Strem Chemical Co. and recrystallized from chloroform/hexane prior to use. Other compounds were synthesized by standard literature methods[6,7,19,29-32] and characterized by infrared, ^1H NMR, and mass spectral data. By analogy to Wrighton's procedure for the synthesis of $CpW(CO)_3Cl$,[19] $CpW(CO)_3Br$ was prepared by ultraviolet irradiation of $[CpW(CO)_3]_2$ in benzene solution containing CBr_4 (55% yield). $CpW(CO)_3I$ was prepared by cleavage of $CpW(CO)_3CH_2Ph$ with iodine[7] at 0 °C in methylene chloride solution (72% yield). Spectroscopic-grade benzene, chloroform, cyclohexane, hexane, and carbon tetrachloride were stored over Davision 4-Å molecular sieves. Methylene chloride was washed successively with concentrated H_2SO_4, 5% NaOH solution, and distilled water, dried over anhydrous $MgSO_4$ overnight, and distilled from P_4O_{10} under argon prior to use. High-purity carbon monoxide was obtained from Matheson Scientific. ^{13}CO (90% enriched) was purchased from Monsanto Chemical Co. PPh_3, Ph_3CCl, $NaBPh_4$, 2,6-di-*tert*-butylphenol, CBr_4, and $(n\text{-}Bu)_4NBr$ were used as commercially available reagent-grade chemicals.

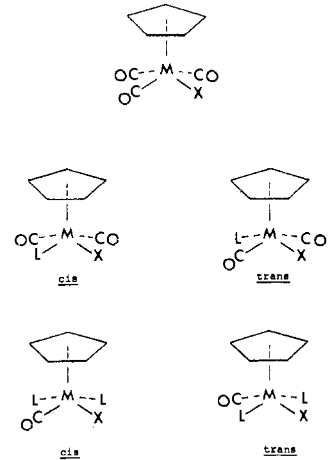

Figure 1. Structures of $CpM(CO)_{3-n}L_nX$ (n = 0–2) complexes.

Spectra. UV–visible spectra were recorded with a Beckman Acta M-VI spectrophotometer using matched 10.0-mm or 1.0-mm quartz cuvettes, purchased from Markson Science, Inc. Infrared spectra were obtained with Perkin-Elmer 337 or 521 grating spectrophotometers using matched 0.10-mm or 1.0-mm KBr solution cells, purchased from International Crystal Laboratories. The spectra were calibrated with the 1601-cm^{-1} band of polystyrene film. Infrared spectra of $CpMo(CO)_3Br$ and $CpMo(CO)_2(^{13}CO)Br$ were recorded on a Beckman 4240 spectrophotometer at the University of Illinois, Urbana, IL. ^1H NMR spectra were recorded with a Varian T-60 spectrophotometer using deuteriochloroform as solvent and tetramethylsilane as the internal standard. Mass spectra were obtained with an Associated Electrical Industries MS-1201 B spectrometer at a 70-eV ionizing voltage. Samples were introduced directly into the probe. Field-desorption mass spectra of $CpMo(CO)_2(PPh_3)X$ complexes in acetone solution were recorded with a Varian 731 mass spectrometer by Mr. J. C. Cook, Jr., at the University of Illinois, Urbana, IL.

Photolysis Apparatus. A 200-W Hanovia medium-pressure mercury-arc lamp was situated in a water-cooled Pyrex immersion well. The immersion well was surrounded by two concentric cylindrical Pyrex jackets containing appropriate aqueous filter solutions to isolate the desired mercury emissions [366 nm: 0.12 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.[33] Reaction vessels were matched 10-mm i.d. Pyrex tubes which were either covered with serum caps or hermetically sealed. The tubes were situated in a merry-go-round apparatus[34] of our design, external to the light source and filter jackets.

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(26) K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967).

(27) L. H. Ali, A. Cox, and T. J. Kemp, *J. Chem. Soc., Dalton Trans.*, 1475 (1973).

(28) D. G. Alway and K. W. Barnett, *J. Organomet. Chem.*, **99**, C52 (1975).

(29) R. B. King, "Organometallic Synthesis", Vol. 1, Academic Press, New York, 1965.

(30) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(31) P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organomet. Chem.*, **7**, 449 (1967).

(32) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

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

(34) J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, 1966.

Table I. Electronic Spectral Data for $CpM(CO)_n(PPh_3)_{3-n}X$ Complexes[a]

complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	solvent
$CpMo(CO)_3Cl$	320 (1980, sh), 470 (504)	C_6H_6
cis-$CpMo(CO)_2(PPh_3)Cl$	360 (936, sh), 473 (689)	C_6H_6
$CpMo(CO)(PPh_3)_2Cl$	*b*, 467 (704)	C_6H_6
$CpMo(CO)_3Br$	*b*, 475 (471)	C_6H_6
$CpMo(CO)_3Br$	330 (1253, sh), 478 (465)	CH_2Cl_2
cis-$CpMo(CO)_2(PPh_3)Br$	365 (820, sh), 475 (488)	C_6H_6
cis-$CpMo(CO)_2(PPh_3)Br$	360 (750, sh), 478 (450)	CH_2Cl_2
trans-$CpMo(CO)_2(PPh_3)Br$	314 (2210, sh), 470 (252)	C_6H_6
trans-$CpMo(CO)_2(PPh_3)Br$	312 (2660, sh), 475 (183)	CH_2Cl_2
$CpMo(CO)_3I$	315 (3810, sh), 482 (560)	C_6H_6
$CpMo(CO)_3I$	314 (3831), 484 (576)	CH_2Cl_2
cis-$CpMo(CO)_2(PPh_3)I$	300 (4260, sh), 484 (562)	C_6H_6
cis-$CpMo(CO)_2(PPh_3)I$	305 (3750, sh), 476 (492)	CH_2Cl_2
trans-$CpMo(CO)_2(PPh_3)I$	308 (5960), 475 (567)	C_6H_6
trans-$CpMo(CO)_2(PPh_3)I$	306 (5372), 476 (534)	CH_2Cl_2
$CpMo(CO)(PPh_3)_2I$	284 (5620), 470 (1112)	C_6H_6
$CpW(CO)_3Cl$	312 (2700), 457 (530)	C_6H_6
$CpW(CO)_3Cl$	312 (2770), 458 (495)	CH_2Cl_2
$CpW(CO)_3Br$	310 (1980, sh), 460 (520)	C_6H_6
$CpW(CO)_3Br$	312 (2240), 461 (593)	CH_2Cl_2
$CpW(CO)_3I$	306 (3440), 467 (778)	C_6H_6
$CpW(CO)_3I$	300 (3820), 466 (759)	CH_2Cl_2

[a] All complexes exhibit an intense absorption near 250 nm; λ_{max} is obscured by the solvent. [b] Absorption in this region was not resolved.

Typical Photolysis Procedures. All operations, except for the actual irradiations, were performed in the dark. Solutions of the cyclopentadienylmetal carbonyl complexes, and substrates when appropriate, were degassed by purging with prepurified argon for at least 10 min. The optical densities of the solutions at the irradiation wavelength were recorded by using 1.00 cm path length cuvettes. Aliquots (10 mL) of the solutions were transferred into argon-flushed reaction tubes. For reactions with carbon monoxide, the solutions were purged with the gas for 5 min prior to photolysis. Alternatively, the solutions were repurged with argon or degassed by three freeze-pump-thaw cycles. Photoproducts were characterized by infrared, ^1H NMR, and UV-visible spectroscopy and were identified by comparison to spectra of authentic samples.

Quantum Yield Measurements. Reactions were analyzed quantitatively by ^1H NMR spectroscopy. Following photolysis, the solvents were removed from the reaction solutions by rotary evaporation at room temperature or below, and the remaining materials were dissolved in deuteriochloroform for ^1H 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. The molar concentration of the product in the reaction solution was calculated by multiplying the initial reactant concentration by the percentage yield of product. The absence of secondary photolysis products was confirmed by infrared as well as ^1H NMR spectral data. Quantum yields are reported as the average of at least triplicate determinations. Conversions were limited to 15% or less and were linear with irradiation time. Thermal dark reactions were monitored in all cases and were found to be negligible during the time required for photolysis and analysis.

Results and Discussion

Electronic absorption spectral data for $CpM(CO)_3X$, $CpM(CO)_2(PPh_3)X$, and $CpM(CO)(PPh_3)_2X$ complexes are given in Table I. The spectra of $CpMo(CO)_3X$ and $CpW(CO)_3X$ are very similar, consisting of an intense absorption band near 470 nm. The spectra of $CpM(CO)_2(PPh_3)X$ and $CpM(CO)(PPh_3)_2X$ also display these features, although the absorption bands in the near-ultraviolet spectral region are more intense than those of $CpM(CO)_3X$ (Figure 2). The positions and intensities of the absorption bands of these complexes are not significantly effected by changing the solvent from benzene to methylene chloride.

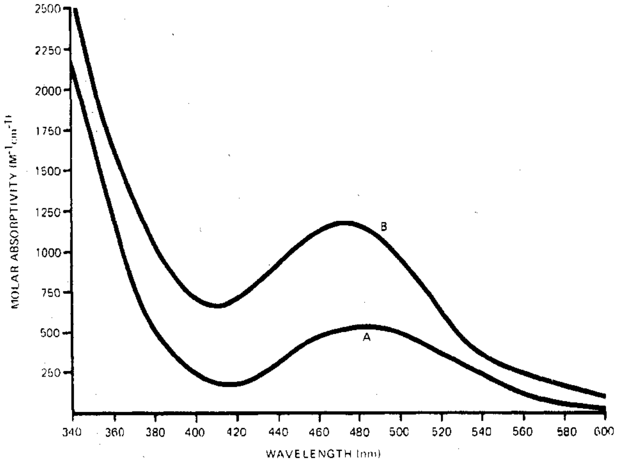

Figure 2. Electronic absorption spectra of $CpMo(CO)_3I$ (A) and $CpMo(CO)(PPh_3)_2I$ (B) in benzene solution.

Although definite assignments for the absorption bands in the electronic spectra of $CpM(CO)_{3-n}(PPh_3)_nX$ (n = 0, 1, 2) are not possible at present, the strong near-ultraviolet absorptions are most likely charge transfer in nature.[10,15] The visible absorption bands observed in the electronic spectra of these complexes are also present in the spectrum of $CpMo(CO)_2Br_2^-$ [20] and have been ascribed to ligand-field transitions.[10,21] The corresponding visible absorption bands in the electronic spectra of the dimeric complexes $[CpMo(CO)_3]_2$[19] and $[CpW(CO)_3]_2$[18,19] have been assigned[15,19] to transitions from metal πd orbitals to the σ^* antibonding orbitals associated with the metal-metal bonds.

$CpMo(CO)_3X$ and $CpW(CO)_3X$ undergo no net chemical reaction upon 366- or 436-nm irradiation in deoxygenated benzene or methylene chloride solutions, as observed by UV-visible, infrared, and ^1H NMR spectroscopy. Photolysis of $CpMo(CO)_3X$ and $CpW(CO)_3X$ in the presence of PPh_3 yields the monosubstituted complexes $CpMo(CO)_2(PPh_3)X$ and $CpW(CO)_2(PPh_3)X$, respectively. Although both cis and trans isomers of these complexes are known,[6,7] the complexes of cis geometry are formed stereospecifically by the photosubstitution reactions (eq 14). Infrared spectra of photolyzed samples show carbonyl stretching bands at ca. 2030, 1980, and 1890 cm^{-1}, characteristic of a mixture of $CpM(CO)_3X$ and $CpM(CO)_2(PPh_3)X$ complexes (Table II).

$$CpM(CO)_3X + PPh_3 \xrightarrow[M = Mo,\ W]{h\nu} cis\text{-}CpM(CO)_2(PPh_3)X \quad (14)$$

Evidence for formation of the complexes of cis geometry is provided by ^1H NMR spectroscopy. The spectra of photolyzed samples exhibit two singlet peaks in the cyclopentadienyl proton region, ca. δ 5.6 and δ 5.4, attributable to $CpM(CO)_3X$ and *cis*-$CpM(CO)_2(PPh_3)X$, respectively (Table II). Doublet peaks, ca. δ 5.1, characteristic of *trans*-$CpM(CO)_2(PPh_3)X$ complexes, are not observed, with the following exceptions. When the photoreactions of $CpMo(CO)_3Br$, $CpMo(CO)_3I$, or $CpW(CO)_3I$ with PPh_3 are allowed to go to 50, 35, or 60% completion, respectively, the monosubstituted complexes of trans geometry are formed in 3-5% yield. These complexes are produced by secondary photoreactions of the corresponding *cis*-$CpM(CO)_2(PPh_3)X$ complexes (vide infra).

Reproducible measurements of the quantum yields for PPh_3 substitution of $CpMo(CO)_3Cl$ could not be made, since the complex reacts slowly with PPh_3 in the dark at room temperature to yield *cis*-$CpMo(CO)_2(PPh_3)Cl$. Quantum yields for PPh_3 substitution of $CpMo(CO)_3X$ (X = Br, I) and $CpW(CO)_3X$ (X = Cl, Br, I) are given in Tables III and IV. The values vary as a function of irradiation wavelength ($\Phi_{366} > \Phi_{436}$), central metal ($\Phi_{Mo} > \Phi_W$), and halogen ($\Phi_{Cl} > \Phi_{Br} > \Phi_I$). Higher energy irradiation yields more efficient photosubstitution, although quantum yields for the reactions of

Table II. Infrared and ^{1}H NMR Spectral Data for η^5-Cyclopentadienylmolybdenum and η^5-Cyclopentadienyltungsten Carbonyl Complexes

complex	ν_{CO}, cm^{-1} [a]	δ_{Cp} [b,c]
$CpMo(CO)_3Cl$	2035, 1985	5.63
	2055, 1980, 1960[d]	
cis-$CpMo(CO)_2(PPh_3)Cl$	1975, 1885	5.42
$CpMo(CO)(PPh_3)_2Cl$	1795	4.88 m
$CpMo(CO)_3Br$	2050, 1980	5.62
	2055, 1986, 1965[d]	
cis-$CpMo(CO)_2(PPh_3)Br$	1980, 1890	5.42
trans-$CpMo(CO)_2(PPh_3)Br$	1980, 1890	5.08 d
$CpMo(CO)(PPh_3)_2Br$	1795	4.82 m
$CpMo(CO)_3I$	2045, 1975	5.57
	2040, 1970, 1955[d]	
cis-$CpMo(CO)_2(PPh_3)I$	1972, 1890	5.33
trans-$CpMo(CO)_2(PPh_3)I$	1972, 1890	5.07 d
$CpMo(CO)(PPh_3)_2I$	1795	4.83 m
$[CpMo(CO)_3]_2$	1960, 1920	5.33
$Cp_2Mo_2(CO)_5(PPh_3)$[g]	1972, 1895, 1820	5.11, 4.82 d
$[CpMo(CO)_2(PPh_3)]_2$[h]	1853 sh, 1830[e]	
$[CpMo(CO)_2(PPh_3)_2]$-$[CpMo(CO)_3]$[h]	1974, 1895, 1771[f]	
$[CpMo(CO)_4]BF_4$[i]	2128, 2041, 1980[e]	
$[CpMo(CO)_3(PPh_3)]PF_6$[i]	2025, 1995, 1955[e]	
$CpW(CO)_3Cl$	2050, 1965	5.82
cis-$CpW(CO)_2(PPh_3)Cl$	1965, 1870	5.60
$CpW(CO)_3Br$	2040, 1960	5.80
cis-$CpW(CO)_2(PPh_3)Br$	1960, 1865	5.55
$CpW(CO)_3I$	2040, 1960	5.68
cis-$CpW(CO)_2(PPh_3)I$	1960, 1860	5.47
trans-$CpW(CO)_2(PPh_3)I$	1960, 1860	5.13 d
$[CpW(CO)_3]_2$	1955, 1905	5.47
$[CpW(CO)_4]BF_4$[i]	2128, 2028, 1965[e]	

[a] Chloroform solution unless noted otherwise. [b] Deuteriochloroform solution with tetramethylsilane as internal standard. [c] Singlet unless noted otherwise; d = doublet, $J_{P-H} = 1.5$-2.0 Hz; m = multiplet. [d] Cyclohexane solution. [e] Nujol mull. [f] Methylene chloride solution. [g] Reference 26. [h] Reference 25. [i] Reference 31.

Table III. Quantum Yields for the Reactions $CpM(CO)_3X + PPh_3 \rightarrow$ *cis*-$CpM(CO)_2(PPh_3)X + CO$[a,b]

complex	solvent/added reagent	irradn λ, nm	Φ (±0.10Φ)
$CpMo(CO)_3Br$	C_6H_6	366	0.74
	C_6H_6/CO[c]	366	0.16
	$C_6H_6/C_{12}H_{22}O$[d]	366	0.70
	CH_2Cl_2	366	0.79
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	366	0.67
	C_6H_6	436	0.51
	C_6H_6/CO[c]	436	0.17
	$C_6H_6/C_{12}H_{22}O$[d]	436	0.54
	CH_2Cl_2	436	0.52
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	436	0.47
$CpMo(CO)_3I$	C_6H_6	366	0.39
	C_6H_6/CO[c]	366	0.091
	$C_6H_6/C_{12}H_{22}O$[d]	366	0.47
	CH_2Cl_2	366	0.40
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	366	0.43
	C_6H_6	436	0.22
	C_6H_6/CO[c]	436	0.046
	$C_6H_6/C_{12}H_{22}O$[d]	436	0.28
	CH_2Cl_2	436	0.18
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	436	0.35
$CpW(CO)_3Cl$	C_6H_6	366	0.44
	C_6H_6/CO[c]	366	0.16
	$C_6H_6/C_{12}H_{22}O$[d]	366	0.43
	CH_2Cl_2	366	0.41
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	366	0.37
	C_6H_6	436	0.11
	C_6H_6/CO[c]	436	0.060
	$C_6H_6/C_{12}H_{22}O$[d]	436	0.11
	CH_2Cl_2	436	0.085
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	436	0.094
$CpW(CO)_3Br$	C_6H_6	366	0.41
	C_6H_6/CO[c]	366	0.31
	$C_6H_6/C_{12}H_{22}O$[d]	366	0.40
	CH_2Cl_2	366	0.43
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	366	0.43
	C_6H_6	436	0.080
	C_6H_6/CO[c]	436	0.053
	$C_6H_6/C_{12}H_{22}O$[d]	436	0.083
	CH_2Cl_2	436	0.060
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	436	0.060
$CpW(CO)_3I$	C_6H_6	366	0.23
	C_6H_6/CO[c]	366	0.14
	$C_6H_6/C_{12}H_{22}O$[d]	366	0.24
	CH_2Cl_2	366	0.24
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	366	0.26
	C_6H_6	436	0.029
	C_6H_6/CO[c]	436	0.024
	$C_6H_6/C_{12}H_{22}O$[d]	436	0.029
	CH_2Cl_2	436	0.033
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	436	0.030

[a] Determined by integration of the cyclopentadienyl region in the proton NMR spectra. [b] $[CpM(CO)_3X] = [PPh_3] = 1.00 \times 10^{-3}$ M. [c] One atmosphere of CO pressure. [d] $C_{12}H_{22}O$ = 2,6-di-*tert*-butylphenol.

the molybdenum complexes are less sensitive to the wavelength of the exciting light than are those for the analogous tungsten complexes.

Quantum yields reported[35,37] for the photoreactions of $M(CO)_5(\text{amine})$ (M = Mo, W) with free amines (eq 15) show

$$M(CO)_5(\text{amine}) + \text{amine} \xrightarrow{h\nu} cis\text{-}M(CO)_4(\text{amine})_2 + CO \quad (15)$$

wavelength dependences similar to those observed in this system. The wavelength effect has been attributed to the existence of at least two reactive excited states.[35-38] A similar interpretation is suggested for the subject complexes. It seems reasonable that irradiations into the near-ultraviolet and visible bands of these complexes lead to different chemically reactive excited states and hence to different efficiencies in photoreactivity. Alternatively, the wavelength dependence may arise from population of higher energy nonreactive excited states which decay to a lower energy reactive excited state with less than 100% efficiency.[39] This behavior contrasts with that of $CpFe(CO)_2X$[8] and $CpV(CO)_4$[9] and is not well understood at present.

Quantum yields for appearance of *cis*-$CpM(CO)_2(PPh_3)X$ are consistently greater for the molybdenum complexes as compared to their tungsten analogues and decrease for both metals as the size of the halogen increases. The effect of the central metal and the halogen on the quantum yields is more pronounced for 436-nm irradiation than for 366-nm irradiation. Similar results were obtained by other workers for the photoreactions of $M(CO)_5(\text{amine})$ complexes with amines[36] (eq 15). The observed decrease in quantum yields for substitution of $CpM(CO)_3X$ complexes containing heavy atoms may possibly be attributed to shorter lifetimes of the chemically reactive excited states, since physical deactivation is expected to be more rapid owing to enhanced spin–orbit coupling.[40-44]

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(35) M. Wrighton, G. S. Hammond, and H. B. Gray, *Mol. Photochem.*, **5**, 179 (1973).
(36) M. Wrighton, *Inorg. Chem.*, **13**, 905 (1974).
(37) R. M. Dahlgren and J. I. Zink, *Inorg. Chem.*, **16**, 3154 (1977).
(38) H. B. Abrahamson and M. S. Wrighton, *Inorg. Chem.*, **17**, 3385 (1978).
(39) G. Malouf and P. C. Ford, *J. Am. Chem. Soc.*, **99**, 7213 (1977).
(40) J. Nasielski and A. Colas, *Inorg. Chem.*, **17**, 237 (1978).
(41) M. S. Wrighton, D. L. Morse, H. B. Gray, and D. K. Ottesen, *J. Am. Chem. Soc.*, **98**, 1111 (1976).
(42) K. M. Mann, H. B. Gray, and G. S. Hammond, *J. Am. Chem. Soc.*, **99**, 306 (1977).
(43) D. J. Darensbourg and M. A. Murphy, *Inorg. Chem.*, **17**, 884 (1978).
(44) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 4336 (1971).

Table IV. Effect of PPh_3 Concentration on the Quantum Yields for Photosubstitution of $CpM(CO)_3X$ Complexes[a]

complex	$10^3[PPh_3]$, M	irradn λ, nm	Φ^b (±0.10Φ)
$CpMo(CO)_3Br$	0.5	366	0.64
	1.0	366	0.74
	5.0	366	0.72
	10.0	366	0.66
	0.5	436	0.45
	1.0	436	0.51
	5.0	436	0.54
	10.0	436	0.51
$CpMo(CO)_3I$	0.5	366	0.32
	1.0	366	0.39
	5.0	366	0.33
	10.0	366	0.38
	0.5	436	0.21
	1.0	436	0.22
	5.0	436	0.26
	10.0	436	0.26
$CpW(CO)_3Cl$	0.5	366	0.36
	1.0	366	0.44
	5.0	366	0.38
	10.0	366	0.46
	0.5	436	0.11
	1.0	436	0.11
	5.0	436	0.11
	10.0	436	0.11
$CpW(CO)_3Br$	0.5	366	0.40
	1.0	366	0.41
	5.0	366	0.42
	10.0	366	0.35
	0.5	436	0.073
	1.0	436	0.080
	5.0	436	0.078
	10.0	436	0.078
$CpW(CO)_3I$	0.5	366	0.19
	1.0	366	0.23
	5.0	366	0.20
	10.0	366	0.23
	0.5	436	0.030
	1.0	436	0.029
	5.0	436	0.034
	10.0	436	0.034

[a] Irradiation in benzene solutions at 25 °C. $[CpM(CO)_3X] = 1.00 \times 10^{-3}$ M. [b] Quantum yield for appearance of *cis*-$CpM(CO)_2(PPh_3)X$.

Alternatively, the trends in quantum yields may reflect differences in metal–carbonyl bond strengths.[36] Tungsten forms stronger bonds with carbon monoxide than does molybdenum.[2,45,46] Kinetic studies of the thermal substitution reactions of $CpMo(CO)_3X$ with PPh_3 have shown[47] that the reactions proceed by a dissociative mechanism, with loss of carbon monoxide as the rate-determining step (eq 16 and 17).

$$CpMo(CO)_3X \xrightarrow[\text{slow}]{} CpMo(CO)_2X + CO \qquad (16)$$

$$CpMo(CO)_2X + PPh_3 \xrightarrow[\text{fast}]{} CpMo(CO)_2(PPh_3)X \qquad (17)$$

Rates of reaction decrease down the series Cl > Br > I and correlate with molybdenum–carbonyl bond strengths (Cl < Br < I), as indicated by infrared carbonyl-stretching frequencies and force constants.[47] If the relative metal–carbonyl bond strengths in the ground-state complexes persist in the excited states, then ease of loss of carbon monoxide is expected to decrease in the order Cl > Br > I. This rationale is likely to be an oversimplification, as illustrated by the trends in the photochemical reactivity of the related complexes $Re(CO)_5X$.[41] Although the metal–carbonyl bond strengths in the ground-state complexes increase in the order Cl < Br < I,[48,49] 366-nm quantum yields for PPh_3 substitution of $Re(CO)_5X$ (eq 18) decrease in the order Br > Cl > I.[41]

$$Re(CO)_5X + PPh_3 \xrightarrow{h\nu} cis\text{-}Re(CO)_4(PPh_3)X + CO \qquad (18)$$

As shown in Table IV, 366- and 436-nm quantum yields for PPh_3 substitution of $CpM(CO)_3X$ complexes are independent of entering ligand concentration over the range 5.0×10^{-4}–10.0×10^{-3} M, the metal complex concentration being 1.0×10^{-3} M. The quantum yields decrease markedly for solutions saturated with carbon monoxide (Table III), paralleling the observations made for PPh_3 substitution of $CpFe(CO)_2X$[8] and $CpV(CO)_4$.[9] These results strongly suggest that photosubstitution of $CpM(CO)_3X$ involves dissociation of carbon monoxide and are best accounted for by eq 19–23.

$$CpM(CO)_3X \xrightarrow{h\nu} CpM(CO)_3X^* \qquad (19)$$

$$CpM(CO)_3X^* \rightarrow CpM(CO)_3X \qquad (20)$$

$$CpM(CO)_3X^* \rightarrow CpM(CO)_2X + CO \qquad (21)$$

$$CpM(CO)_2X + CO \rightarrow CpM(CO)_3X \qquad (22)$$

$$CpM(CO)_2X + PPh_3 \rightarrow cis\text{-}CpM(CO)_2(PPh_3)X \qquad (23)$$

Absorption of light yields the electronically excited molecules $CpM(CO)_3X^*$ (eq 19). Radiative and nonradiative transitions leading back to the ground state are represented by eq 20. Dissociative loss of carbon monoxide from the excited-state molecules yields coordinatively unsaturated $CpM(CO)_2X$ (eq 21). These intermediates may be stabilized by weak bonding interactions with solvent molecules.[50,51] As observed in similar systems,[19,50-53] recombination of $CpM(CO)_2X$ with carbon monoxide (eq 22) is expected to proceed rapidly, resulting in no net chemical reaction in the absence of added ligands. Nucleophilic attack on the coordinatively unsaturated metal centers by PPh_3 to give the monosubstituted complexes (eq 23) is likely to be competitive with the recombination reactions.[51,52]

Quantum yields for PPh_3 substitution of $CpM(CO)_3X$ are less than 0.5 in most instances (Table III), indicating that dissociation of carbon monoxide is not a very efficient photoprocess for these complexes. This contention is consistent with the observation that limiting quantum yields are obtained at low phosphine concentrations (Table IV), since the concentration of free carbon monoxide is much less than that of PPh_3. Thus, the rate of reaction of $CpM(CO)_2X$ with PPh_3 (eq 23) must be greater than the rate of recombination with carbon monoxide (eq 22). This behavior is in contrast to that of $CpV(CO)_4$[9] and $CpFe(CO)_2X$[8] where limiting quantum yields for substitution are high (0.8–0.9) and require PPh_3 concentrations to be in excess of metal complex concentrations for effective competition with carbon monoxide.

In principle, photolysis of $CpM(CO)_3X$ complexes with PPh_3 could yield a cis/trans isomeric product mixture. There are two stereochemical environments for the carbonyl ligands in $CpM(CO)_3X$;[1-3] two of the carbonyl groups are cis to the halogen, and one is trans to the halogen. As shown in Figure 3, loss of cis and trans carbonyl ligands affords two stereochemically different coordinatively unsaturated $CpM(CO)_2X$ intermediates. Interconversion of I and II via intermediate

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(45) R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).

(46) F. A. Cotton and G. W. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1972, and references therein.

(47) C. White and R. J. Mawby, *Inorg. Chim. Acta*, **4**, 261 (1970).

(48) P. M. Treichel, *J. Organomet. Chem.*, **83**, 427 (1974).

(49) H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967).

(50) J. M. Kelley, D. V. Bent, H. Hermann, D. Schultefrohlinde, and E. Koerner von Gustorf, *J. Organomet. Chem.*, **69**, 259 (1974).

(51) A. Albini and H. Kisch, *J. Am. Chem. Soc.*, **98**, 3869 (1976).

(52) D. R. Kidd and T. L. Brown, *J. Am. Chem. Soc.*, **100**, 4095 (1978).

(53) J. M. Kelly, H. Hermann, and E. Koerner von Gustorf, *J. Chem. Soc., Chem. Commun.*, **105**, (1973).

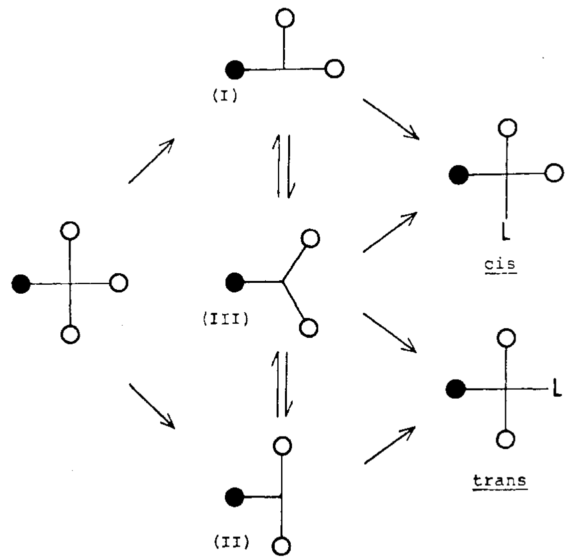

Figure 3. Stereochemical consequences of selective loss of CO from $\mathrm{CpM(CO)_3X}$ in the formation of $\mathrm{CpM(CO)_2LX}$, including the possibility of rearrangement of intermediates. The metal and cyclopentadienyl ligand have been omitted for clarity: ● = halide, ○ = CO, L = $\mathrm{PPh_3}$.

III may be possible, depending upon the energy barriers for rearrangement. Attack at intermediates I and II by $\mathrm{PPh_3}$ would yield *cis*- and *trans*-$\mathrm{CpM(CO)_2(PPh_3)X}$, respectively. Capture of intermediate III by $\mathrm{PPh_3}$ should afford an approximately 67% *cis*- and 33% *trans*-$\mathrm{CpM(CO)_2(PPh_3)X}$ isomeric mixture, since attack between carbon monoxide and the halogen is twice as probable as attack between the two carbonyl ligands.[6]

Monosubstituted complexes having cis geometry are formed exclusively as the primary products of the photoreactions of $\mathrm{CpM(CO)_3X}$ with $\mathrm{PPh_3}$ (eq 14). It is tempting to suggest that selective formation of *cis*-$\mathrm{CpM(CO)_2(PPh_3)X}$ is the result of stereospecific loss of carbon monoxide cis to the halogen from $\mathrm{CpM(CO)_3X}$. This interpretation would require that the $\mathrm{CpM(CO)_2X}$ intermediates be stereochemically rigid during their solution lifetime prior to capture by $\mathrm{PPh_3}$. Infrared[54] and ^{13}C NMR[3] spectral data for ground-state $\mathrm{CpM(CO)_3X}$ complexes indicate that the bond between the metal and the trans carbonyl ligand is stronger than the bonds between the metal and the cis carbonyl ligands. If these relative metal–carbonyl bond strengths persist in the excited-state complexes, then preferential loss of carbonyl ligands cis to the halogen is expected. However, it is possible that, following loss of a trans carbonyl ligand from $\mathrm{CpM(CO)_3X}$, intermediate II undergoes facile rearrangement to I prior to attack by $\mathrm{PPh_3}$ (Figure 3). Since the electronic properties and steric requirements of $\mathrm{PPh_3}$ differ from those of carbon monoxide, the original location of the carbonyl ligands that dissociate is not necessarily reflected by the stereochemistry of the substituted products.[55]

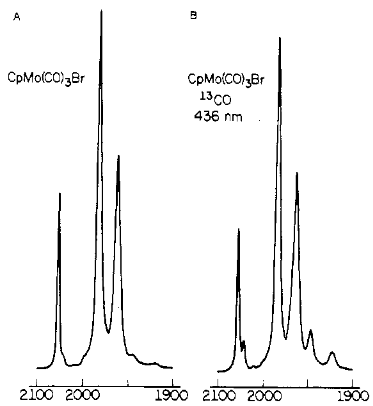

Figure 4. The ν_{CO} stretching region (cm^{-1}) of the infrared spectrum of $\mathrm{CpMo(CO)_3Br}$ before (A) and after (B) 436-nm irradiation of the complex in ^{13}CO-saturated benzene solution. Spectra were recorded in cyclohexane solution.

Table V. Carbonyl Infrared Spectral Data for $\mathrm{CpMo(CO)_3Br}$ and $\mathrm{CpMo(CO)_2(^{13}CO)Br}$

complex	obsd[a] ν_{CO}, cm^{-1}	calcd[b] ν_{CO}, cm^{-1}
$\mathrm{CpMo(CO)_3Br}$	2055, 1986, 1964.5	
cis-$\mathrm{CpMo(CO)_2(^{13}CO)Br}$	2020,[c] 1948	2030.5, 1970.7, 1952.4
trans-$\mathrm{CpMo(CO)_2(^{13}CO)Br}$	2042,[c] 1924.5	2043.1, 1988.8, 1922.7

[a] Spectra recorded in cyclohexane solution with 1.0-mm NaCl cells on a Beckman IR-4240 spectrophotometer. [b] Calculated by Professor D. J. Darensbourg, Tulane University, using ν_{CO} $\mathrm{CpMo(CO)_3Br}$ = 2045, 1989, and 1968 cm^{-1}.[54] [c] Absorption in this region obscured by the 1986-cm^{-1} absorption band of $\mathrm{CpMo(CO)_3Br}$.

In an attempt to overcome these differences between the entering and departing ligands, we irradiated $\mathrm{CpMo(CO)_3Br}$ at 436 nm in benzene solutions saturated with ^{13}CO. The ν(CO) regions of the infrared spectra of the complex obtained before and after irradiation are shown in Figure 4. As a consequence of photolysis, the weak bands at 2042, 2020, 1948, and 1925 cm^{-1} grow in intensity at the expense of the bands at 2055, 1986, and 1965 cm^{-1}. Calculated positions of the bands for $\mathrm{CpMo(^{13}CO)(CO)_2Br}$, isotopically enriched at positions cis and trans to bromine, are shown in Table V. The data clearly demonstrate that ^{13}CO is incorporated into the complex at both positions (eq 24) but do not reveal the cis/

$$\mathrm{CpMo(CO)_3Br} + {}^{13}\mathrm{CO} \xrightarrow{h\nu} \textit{cis-}\text{ or }\textit{trans-}\mathrm{CpMo(CO)_2(^{13}CO)Br} + \mathrm{CO} \quad (24)$$

trans ratio. This experiment was repeated with different partial pressures of ^{13}CO and with shorter irradiation times in hopes of revealing any stereochemical bias in product formation. In all cases, however, the above result was confirmed. It is thus not possible at present to state whether the two isomers of $\mathrm{CpMo(CO)_2(^{13}CO)Br}$ are produced independently or result from a rapid subsequent photoisomerization similar to that observed for $\mathrm{CpMo(CO)_2(PPh_3)X}$ (vide infra).

While the experimental results presented thus far are consistent with photoinduced dissociation of carbon monoxide from $\mathrm{CpM(CO)_3X}$, they do not exclude the possibility of scission of the metal–halogen bond as an excited-state decay process for the subject complexes. It is appropriate, therefore, to address the following discussion to the results of experiments designed to detect heterolytic or homolytic cleavage of the metal–halogen bond.

Loss of halide anions from $\mathrm{CpM(CO)_3X}$ would result in formation of the 16-electron cationic complexes $\mathrm{CpM(CO)_3}^+$ (eq 9). In benzene solutions, the ions should recombine rapidly to give the starting complexes. In the presence of free carbon monoxide or $\mathrm{PPh_3}$, the cations are expected to react to give the coordinatively saturated complexes $\mathrm{CpM(CO)_4}^+$[56] or $\mathrm{CpM(CO)_3(PPh_3)}^+$,[31] respectively, which should precipitate out of solution as the halide salts. No precipitates are observed following irradiation of $\mathrm{CpM(CO)_3X}$ with carbon monoxide

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(54) R. B. King and L. W. Houk, *Can. J. Chem.*, **47**, 2959 (1969).
(55) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 3160 (1976).
(56) E. O. Fischer, K. Fichtel, and K. Ofele, *Chem. Ber.*, **95**, 249 (1962).

or PPh_3 in benzene solutions. Furthermore, the ionic derivatives are not observed in the infrared and ^1H NMR spectra of photolyzed samples (Table II).

An argument could be made that the ionic derivatives are formed initially but that they undergo secondary photochemical reactions involving displacement of a carbonyl ligand from the coordination sphere of the metal by halide ion (eq 25 and 26). A similar scheme has been proposed[13] for the photochemical reactions of $CpMo(CO)_3Cl$ with bidentate phosphine ligands. Quantum yields for photochemical reactions that involve ionic intermediates should be influenced by the nature of the solvent medium.[57,58] Quantum yields for PPh_3 substitution of $CpM(CO)_3X$ are not significantly effected by changing the solvent from benzene to methylene chloride. They are also not effected by increasing the ionic strength of the solvent medium by addition of the inert electrolyte $(n\text{-}Bu)_4N^+BPh_4^-$ (Table III), thus ruling out an ionic photosubstitution mechanism.[21] These observations parallel those made for the photochemical reactions of $CpFe(CO)_2X$ complexes with PPh_3.[8]

$$CpM(CO)_3X + L \xrightarrow[L\,=\,CO\text{ or }PPh_3]{h\nu} CpM(CO)_3(L)^+ + X^- \tag{25}$$

$$CpM(CO)_3(L)^+ + X^- \xrightarrow{h\nu} CpM(CO)_2(L)X + CO \tag{26}$$

The consequence of homolytic cleavage of the metal–halogen bond of $CpM(CO)_3X$ complexes would be formation of the radical species $CpM(CO)_3\cdot$ and $X\cdot$ (eq 10). The $CpMo(CO)_3\cdot$ and $CpW(CO)_3\cdot$ radicals are primary photoproducts of the metal–metal-bonded dimers $[CpMo(CO)_3]_2$ and $[CpW(CO)_3]_2$, respectively.[15–19] These radicals undergo facile substitution by tertiary phosphines,[59] as do several other 17-electron metal carbonyl radicals.[60–63] Photosubstitution of $CpM(CO)_3X$ complexes by PPh_3 could, in principle, proceed by the pathway outlined by eq 27–30. The $CpM(CO)_3\cdot$ radicals generated by photolysis of $CpM(CO)_3X$ (eq 27) could either recombine with halogen radicals (eq 28) or undergo substitution by PPh_3 to give $CpM(CO)_2(PPh_3)\cdot$ (eq 29). Coupling of the substituted radicals with the halogen ($X\cdot$) would yield the mononuclear substitution products (eq 30). A similar scheme has been proposed[59] for the photosubstitution of $CpW(CO)_3H$ by PBu_3.

$$CpM(CO)_3X \xrightarrow{h\nu} CpM(CO)_3\cdot + X\cdot \tag{27}$$

$$CpM(CO)_3\cdot + X\cdot \rightarrow CpM(CO)_3X \tag{28}$$

$$CpM(CO)_3\cdot + PPh_3 \rightarrow CpM(CO)_2(PPh_3)\cdot + CO \tag{29}$$

$$CpM(CO)_2(PPh_3)\cdot + X\cdot \rightarrow cis\text{-}CpM(CO)_2(PPh_3)X \tag{30}$$

In accord with the scheme above, the dimeric complexes $[CpM(CO)_3]_2$, $Cp_2M_2(CO)_5(PPh_3)$, and possibly $[CpM(CO)_2(PPh_3)]_2$ are expected to form as the consequence of cross-coupling of the metal-based radicals (eq 31–33). The monosubstituted dimer is reported to be a product of photolysis of $[CpMo(CO)_3]_2$ with PPh_3.[25,26] Irradiation of $Mn_2(CO)_{10}$, which generates $Mn(CO)_5\cdot$ radicals, in the presence of PBu_3 is reported[62] to yield disubstituted $Mn_2(CO)_8(PBu_3)_2$ as the final product (eq 34). However, none of the dimeric complexes above (eq 31–33) are produced by irradiation of $CpM(CO)_3X$ with PPh_3, as monitored by infrared and ^1H NMR spectroscopy (Table II).

$$2CpM(CO)_3\cdot \rightarrow [CpM(CO)_3]_2 \tag{31}$$

$$CpM(CO)_3\cdot + CpM(CO)_2(PPh_3)\cdot \rightarrow Cp_2M_2(CO)_5(PPh_3) \tag{32}$$

$$2CpM(CO)_2(PPh_3)\cdot \rightarrow [CpM(CO)_2(PPh_3)]_2 \tag{33}$$

$$Mn_2(CO)_{10} + 2PBu_3 \xrightarrow{h\nu} Mn_2(CO)_8(PBu_3)_2 + 2CO \tag{34}$$

Table VI. Effect of $[CpMo(CO)_3]_2$ on the Photoreactions of $CpMo(CO)_3X$ with PPh_3[a,b]

X	$[[CpMo(CO)_3]_2]$, M	irradn time, s	$CpMo(CO)_2(PPh_3)X$ product distrib[c,d]	
			% cis (Φ)	% trans (Φ)
Br		80	12 (0.51)	. . .
Br	2.0×10^{-4}	80	23 (0.80)	8 (0.27)
I		100	7 (0.22)	. . .
I	2.0×10^{-4}	100	31 (0.68)	38 (0.81)

[a] Irradiation at 436 nm in benzene solutions at 25 °C. [b] $[CpMo(CO)_3X] = [PPh_3] = 1.00 \times 10^{-3}$ M. [c] Determined by integration of the cyclopentadienyl region in the proton NMR spectra. [d] Quantum yield for appearance of *cis*- or *trans*-$CpMo(CO)_2(PPh_3)X$.

Addition of $[CpMo(CO)_3]_2$ to benzene solutions containing $CpMo(CO)_3X$ (X = Br or I) and PPh_3 causes a drastic change in the yield and stereochemistry of the $CpMo(CO)_2(PPh_3)X$ photoproducts. For example, under conditions where 436-nm photolysis of $CpMo(CO)_3I$ with PPh_3 yields *cis*-$CpMo(CO)_2(PPh_3)I$ in 7% yield ($\Phi = 0.22$), addition of $[CpMo(CO)_3]_2$ affords *cis*-$CpMo(CO)_2(PPh_3)I$ in 31% yield ($\Phi = 0.68$) and *trans*-$CpMo(CO)_2(PPh_3)I$ in 38% yield ($\Phi = 0.81$), on the basis of the initial concentration of $CpMo(CO)_3I$. The concentration of $[CpMo(CO)_3]_2$ following irradiation is equal to its initial concentration, as determined by integration of the relative intensities of the cyclopentadienyl resonances in the ^1H NMR spectra of the samples. A similar product distribution was obtained upon 436-nm irradiation of benzene solutions containing $CpMo(CO)_3Br$, $[CpMo(CO)_3]_2$, and PPh_3 (Table VI).

The results may reasonably be accounted for by the reaction sequence of eq 35–44. Absorption of light by $CpMo(CO)_3X$ leads to formation of $CpMo(CO)_2X$ (eq 35) which may either recombine with carbon monoxide (eq 37) or react with PPh_3 to give *cis*-$CpMo(CO)_2(PPh_3)X$ (eq 37). Light absorption by $[CpMo(CO)_3]_2$ results in homolytic cleavage of the metal–metal bond and formation of $CpMo(CO)_3\cdot$ radicals[17,19,21] (eq 36). These radicals may recouple (eq 44) or lose carbon monoxide to generate the 15-electron complex $CpMo(CO)_2\cdot$ (eq 39).[15] Once formed, the $CpM(CO)_2\cdot$ radicals may undergo back-reactions with carbon monoxide (eq 40) or react with PPh_3 to give $CpMo(CO)_2(PPh_3)\cdot$ radicals (eq 41). Halogen

$$CpMo(CO)_3X \xrightarrow{h\nu} CpMo(CO)_2X + CO \tag{35}$$

$$[CpMo(CO)_3]_2 \xrightarrow{h\nu} 2CpMo(CO)_3\cdot \tag{36}$$

$$CpMo(CO)_2X + CO \rightarrow CpMo(CO)_3X \tag{37}$$

$$CpMo(CO)_2X + PPh_3 \rightarrow cis\text{-}CpMo(CO)_2(PPh_3)X \tag{38}$$

$$CpMo(CO)_3\cdot \rightarrow CpMo(CO)_2\cdot + CO \tag{39}$$

$$CpMo(CO)_2\cdot + CO \rightarrow CpMo(CO)_3\cdot \tag{40}$$

$$CpMo(CO)_2\cdot + PPh_3 \rightarrow CpMo(CO)_2(PPh_3)\cdot \tag{41}$$

$$CpMo(CO)_3\cdot + CpMo(CO)_3X \rightarrow CpMo(CO)_3X + CpMo(CO)_3\cdot \tag{42}$$

$$CpMo(CO)_2(PPh_3)\cdot + CpMo(CO)_3X \rightarrow cis\text{- or }trans\text{-}CpMo(CO)_2(PPh_3)X + CpMo(CO)_3\cdot \tag{43}$$

$$2CpMo(CO)_3\cdot \rightarrow [CpMo(CO)_3]_2 \tag{44}$$

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(57) P. H. Liu and J. I. Zink, *J. Am. Chem. Soc.*, **99**, 2155 (1977).
(58) J. Van Houten and R. J. Watts, *Inorg. Chem.*, **17**, 3381 (1978).
(59) N. W. Hoffman and T. L. Brown, *Inorg. Chem.*, **17**, 613 (1978).
(60) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 2065 (1975).
(61) B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, **99**, 2527 (1977).
(62) D. R. Kidd and T. L. Brown, *J. Am. Chem. Soc.*, **100**, 4095 (1978).
(63) D. R. Kidd, C. P. Cheng, and T. L. Brown, *J. Am. Chem. Soc.*, **100**, 4103 (1978).

abstraction from $CpM(CO)_3X$ by $CpMo(CO)_3\cdot$ and $CpMo(CO)_2(PPh_3)\cdot$ affords $CpMo(CO)_3X$ (eq 42) and *cis*- or *trans*-$CpMo(CO)_2(PPh_3)X$ (eq 43), respectively. Reactions 42 and 43 are chain-propagating steps, since the $CpMo(CO)_3\cdot$ radical is regenerated. The observation that the quantum yields for disappearance of $CpMo(CO)_3X$, i.e., the sum of the quantum yields for appearance of *cis*- and *trans*-$CpMo(CO)_2(PPh_3)X$ (Table VI), exceed 1.0 is wholly consistent with this interpretation. Thus, the radical chain-reaction sequence accounts for formation of *cis*- and *trans*-$CpMo(CO)_2(PPh_3)X$ in higher yields as a consequence of addition of $[CpMo(CO)_3]_2$ to solutions containing $CpMo(CO)_3X$ and PPh_3.

Support for the halogen-abstraction reactions is given by the report that $CpW(CO)_3\cdot$ radicals, generated by photolysis of $[CpW(CO)_3]_2$, abstract hydrogen atoms from $CpMo(CO)_3H$ to afford $CpW(CO)_3H$ and $[CpMo(CO)_3]_2$[59] (eq 45–47). More compelling evidence in this regard is provided

$$[CpW(CO)_3]_2 \xrightarrow{h\nu} 2CpW(CO)_3\cdot \tag{45}$$

$$CpW(CO)_3\cdot + CpMo(CO)_3H \rightarrow CpW(CO)_3H + CpMo(CO)_3\cdot \tag{46}$$

$$2CpMo(CO)_3\cdot \rightarrow [CpMo(CO)_3]_2 \tag{47}$$

by our observation that 436-nm irradiation of benzene solutions containing $CpMo(CO)_3I$ and $[MeCpMo(CO)_3]_2$ (MeCp = η^5-$CH_3C_5H_4$) yields $MeCpMo(CO)_3I$ and $[CpMo(CO)_3]_2$. The reaction seemingly must involve abstraction of iodine from $CpMo(CO)_3I$ by the $MeCpMo(CO)_3\cdot$ radical (eq 48–50).

$$[MeCpMo(CO)_3]_2 \xrightarrow{h\nu} 2MeCpMo(CO)_3\cdot \tag{48}$$

$$MeCpMo(CO)_3\cdot + CpMo(CO)_3I \rightarrow MeCpMo(CO)_3I + CpMo(CO)_3\cdot \tag{49}$$

$$2CpMo(CO)_3\cdot \rightarrow [CpMo(CO)_3]_2 \tag{50}$$

Studies conducted in other laboratories have shown that $CpM(CO)_3\cdot$ radicals (M = Mo, W), generated by photolysis of $[CpM(CO)_3]_2$[18,19] or $CpM(CO)_3Fe(CO)_2Cp$,[64] abstract chlorine from carbon tetrachloride to give $CpM(CO)_3Cl$. Irradiation of $CpM(CO)_3X$ in the presence of CX'_4 (X = Cl, X′ = Br; X = Br, I, X′ = Cl), however, does *not* afford $CpM(CO)_3X'$, as evidenced by mass spectral analysis of photolyzed complexes.

The absence of radical photoprocesses for $CpM(CO)_3X$ complexes is also suggested by the quantum yields for appearance of *cis*-$CpM(CO)_2(PPh_3)X$. The values range from 0.23 to 0.64 (λ = 366 nm) and from 0.034 to 0.33 (λ = 436 nm) and are not affected by addition of the radical scavanger 2,6-di-*tert*-butylphenol[65] (Table III). In contrast, the photosubstitution reaction of $CpW(CO)_3H$ and PBu_3, in which the initial step is homolysis of the tungsten–hydrogen bond, is reported[59] to have a quantum yield (λ = 311 nm) of greater than 30.

As mentioned earlier, *cis*- and *trans*-$CpM(CO)_2(PPh_3)X$ (M = Mo, X = Br, I; M = W, X = I) undergo geometric isomerization upon 366- and 436-nm photolysis in benzene solutions (eq 51). The reactions are conveniently followed

$$cis\text{-}CpM(CO)_2(PPh_3)X \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} trans\text{-}CpM(CO)_2(PPh_3)X \tag{51}$$

by ^1H NMR spectroscopy (Table II). The isomerization processes are genuinely photoinduced, since the substituted complexes are inert to isomerization in the absence of light in solution at room temperature.[6,7]

Quantum yields for cis → trans and trans → cis isomerization of $CpMo(CO)_2(PPh_3)X$ are given in Tables VII and VIII. The 366-nm quantum yields are consistently higher than the 436-nm quantum yields, indicating that the reactions are more efficient at the higher energy irradiative wavelength. This is particularly true for the iodo complexes. *cis*-$CpMo(CO)_2(PPh_3)Cl$ does *not* undergo photochemical isomerization in benzene solutions to produce the presently unknown *trans*-$CpMo(CO)_2(PPh_3)Cl$ complex.

Table VII. Quantum Yields for Isomerization of *cis*- and *trans*-$CpMo(CO)_2(PPh_3)X$ Complexes at 366-nm Irradiation Wavelength[a,b]

complex	solvent/added reagent	Φ ($\pm 0.20\Phi$)
cis-$CpMo(CO)_2(PPh_3)Br$	C_6H_6	0.036
	C_6H_6/CO[c]	0.034
	C_6H_6/PPh_3[d]	0.016[f]
	$C_6H_6/C_{12}H_{22}O$[e]	0.029
	CH_2Cl_2	0.068
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	0.075
trans-$CpMo(CO)_2(PPh_3)Br$	C_6H_6	0.40
	C_6H_6/CO[c]	0.35
	C_6H_6/PPh_3[d]	0.32
	$C_6H_6/C_{12}H_{22}O$[e]	0.29
	CH_2Cl_2	0.27
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	0.27
cis-$CpMo(CO)_2(PPh_3)I$	C_6H_6	0.16
	C_6H_6	0.18[h]
	C_6H_6/CO[c]	0.23
	C_6H_6/CO[c]	0.20[h]
	C_6H_6/PPh_3[d]	0.081
	C_6H_6/PPh_3[g]	0.086[h]
	$C_6H_6/C_{12}H_{22}O$[e]	0.15
	CH_2Cl_2	0.23
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	0.23
trans-$CpMo(CO)_2(PPh_3)I$	C_6H_6	0.12
	C_6H_6	0.14[h]
	C_6H_6/CO[c]	0.086
	C_6H_6/CO[c]	0.11[h]
	C_6H_6/PPh_3[d]	0.11
	C_6H_6/PPh_3[g]	0.11[h]
	$C_6H_6/C_{12}H_{22}O$[e]	0.12
	CH_2Cl_2	0.13
	$CH_2Cl_2/(n\text{-}Bu)_4NBPh_4$	0.10

[a] Determined by integration of the cyclopentadienyl region in the proton NMR spectra. [b] $[CpMo(CO)_2(PPh_3)X] = 1.00 \times 10^{-3}$ M unless noted otherwise. [c] One atmosphere of CO pressure. [d] $[PPh_3] = 1.00 \times 10^{-3}$ M. [e] $C_{12}H_{22}O$ = 2,6-di-*tert*-butylphenol. [f] Error considerably greater than $\pm 0.20\Phi$. Reported value corresponds to 3% conversion to *trans*-$CpMo(CO)_2(PPh_3)Br$. Formation of $CpMo(CO)(PPh_3)_2Br$ prevents quantum yield measurements at higher cis → trans conversions. [g] $[PPh_3] = 2.00 \times 10^{-3}$ M. [h] $[CpMo(CO)_2(PPh_3)X] = 2.00 \times 10^{-3}$ M.

In addition to geometric isomerization, 366- and 436-nm irradiation of either *cis*- or *trans*-$CpM(CO)_2(PPh_3)X$ for extended periods of time (i.e., 1 h or more) leads to formation of the "disproportionation" products $CpM(CO)_3X$ and $CpM(CO)(PPh_3)_2X$ (eq 52). These complexes are produced in

$$2CpM(CO)_2(PPh_3)X \xrightarrow{h\nu} CpM(CO)_3X + CpM(CO)(PPh_3)_2X \tag{52}$$

equimolar amounts, as measured by integration of the relative intensities of the cyclopentadienyl proton resonances in the NMR spectra of photolyzed samples. They are each present in about 10% of the total complex concentration after irradiation of $CpM(CO)_2(PPh_3)X$ for 2 h at 366 nm. The disproportionation products apparently arise from loss of carbon monoxide and PPh_3 from $CpM(CO)_2(PPh_3)X$ to afford the coordinatively unsaturated intermediates $CpM(CO)(PPh_3)X$ and $CpM(CO)_2X$, respectively (eq 53 and 54). Reactions

$$CpM(CO)_2(PPh_3)X \xrightarrow{h\nu} CpM(CO)(PPh_3)X + CO \tag{53}$$

$$CpM(CO)_2(PPh_3)X \xrightarrow{h\nu} CpM(CO)_2X + PPh_3 \tag{54}$$

of these intermediates with a ligand other than that which

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(64) H. B. Abrahamson and M. S. Wrighton, *Inorg. Chem.*, **17**, 1003 (1978).

(65) J. K. Kochi, "Free Radicals", Vol. 1, Wiley, New York, 1973.

Table VIII. Quantum Yields for Isomerization of *cis*- and *trans*-$\mathrm{CpMo(CO)_2(PPh_3)X}$ Complexes at 436-nm Irradiation Wavelength[a],[b]

complex	added ligand	Φ ($\pm 0.20\Phi$)
cis-$\mathrm{CpMo(CO)_2(PPh_3)Br}$		0.018
cis-$\mathrm{CpMo(CO)_2(PPh_3)Br}$	CO[c]	0.021
cis-$\mathrm{CpMo(CO)_2(PPh_3)Br}$	$\mathrm{PPh_3}$[d]	0.009[e]
trans-$\mathrm{CpMo(CO)_2(PPh_3)Br}$		0.12
trans-$\mathrm{CpMo(CO)_2(PPh_3)Br}$	CO[c]	>0.07[f]
trans-$\mathrm{CpMo(CO)_2(PPh_3)Br}$	$\mathrm{PPh_3}$[d]	0.14
cis-$\mathrm{CpMo(CO)_2(PPh_3)I}$		0.025
cis-$\mathrm{CpMo(CO)_2(PPh_3)I}$	CO[c]	0.049
cis-$\mathrm{CpMo(CO)_2(PPh_3)I}$	$\mathrm{PPh_3}$[d]	0.025
trans-$\mathrm{CpMo(CO)_2(PPh_3)I}$		0.024
trans-$\mathrm{CpMo(CO)_2(PPh_3)I}$		0.021[g]
trans-$\mathrm{CpMo(CO)_2(PPh_3)I}$	CO[c]	0.017
trans-$\mathrm{CpMo(CO)_2(PPh_3)I}$	$\mathrm{PPh_3}$[d]	0.019

[a] Irradiation in benzene solution at 25 °C. [$\mathrm{CpMo(CO)_2(PPh_3)X}$] = 1.00×10^{-3} M unless noted otherwise. [b] Determined by integration of the cyclopentadienyl region in the proton NMR spectra. [c] One atmosphere of CO pressure. [d] [$\mathrm{PPh_3}$] = 1.00×10^{-3} M. [e] Error considerably greater than $\pm 0.20\Phi$. Reported value corresponds to 2% conversion to *trans*-$\mathrm{CpMo(CO)_2(PPh_3)Br}$. Formation of $\mathrm{CpMo(CO)(PPh_3)_2Br}$ prevents quantum yield measurements at higher cis → trans conversions. [f] Lower limit quantum yield. Reaction of *cis*-$\mathrm{CpMo(CO)_2(PPh_3)Br}$ with CO is significant. [g] [$\mathrm{CpMo(CO)_2(PPh_3)X}$] = 2.00×10^{-3} M.

Table IX. Quantum Yields for the Reactions $\mathrm{CpMo(CO)_2(PPh_3)X + CO \rightarrow CpMo(CO)_3X + PPh_3}$[a],[b]

complex	irradn λ, nm	Φ ($\pm 0.20\Phi$)
cis-$\mathrm{CpMo(CO)_2(PPh_3)Cl}$	366	>0.11[c]
cis-$\mathrm{CpMo(CO)_2(PPh_3)Br}$	366	0.14
trans-$\mathrm{CpMo(CO)_2(PPh_3)Br}$	366	0.25
cis-$\mathrm{CpMo(CO)_2(PPh_3)I}$	366	0.10
trans-$\mathrm{CpMo(CO)_2(PPh_3)I}$	366	0.12
cis-$\mathrm{CpMo(CO)_2(PPh_3)Cl}$	436	>0.10[c]
cis-$\mathrm{CpMo(CO)_2(PPh_3)Br}$	436	0.14
trans-$\mathrm{CpMo(CO)_2(PPh_3)Br}$	436	0.10
cis-$\mathrm{CpMo(CO)_2(PPh_3)I}$	436	0.10
trans-$\mathrm{CpMo(CO)_2(PPh_3)I}$	436	0.034

[a] Irradiation in benzene solutions at 25 °C. [$\mathrm{CpMo(CO)_2(PPh_3)X}$] = 1.00×10^{-3} M. [b] Determined by integration of the cyclopentadienyl region in the proton NMR spectra. [c] Lower limit quantum yield. Back-reaction of $\mathrm{CpMo(CO)_3Cl}$ with $\mathrm{PPh_3}$ is significant.

Table X. Quantum Yields for the Reactions $\mathrm{CpMo(CO)_2(PPh_3)X + PPh_3 \rightarrow CpMo(CO)(PPh_3)_2X + CO}$[a],[b]

complex	irradn λ, nm	Φ ($\pm 0.20\Phi$)
cis-$\mathrm{CpMo(CO)_2(PPh_3)Cl}$	366	>0.07[c]
cis-$\mathrm{CpMo(CO)_2(PPh_3)Br}$	366	0.11
trans-$\mathrm{CpMo(CO)_2(PPh_3)Br}$	366	0.38
cis-$\mathrm{CpMo(CO)_2(PPh_3)I}$	366	0.14
trans-$\mathrm{CpMo(CO)_2(PPh_3)I}$	366	0.15
cis-$\mathrm{CpMo(CO)_2(PPh_3)Br}$	436	0.048
trans-$\mathrm{CpMo(CO)_2(PPh_3)Br}$	436	0.11
cis-$\mathrm{CpMo(CO)_2(PPh_3)I}$	436	0.031
trans-$\mathrm{CpMo(CO)_2(PPh_3)I}$	436	0.015

[a] Irradiation in benzene solutions at 25 °C. [$\mathrm{CpMo(CO)_2(PPh_3)X}$] = 1.00×10^{-3} M. [b] Determined by integration of the cyclopentadienyl region in the proton NMR spectra. [c] Lower limit quantum yield. Back-reaction of $\mathrm{CpMo(CO)(PPh_3)_2Cl}$ with CO is significant.

dissociated from the starting complex would give the observed products (eq 55 and 56). The dissociative nature of the

$$\mathrm{CpM(CO)(PPh_3)X + PPh_3 \rightarrow CpM(CO)(PPh_3)_2X} \qquad (55)$$

$$\mathrm{CpM(CO)_2X + CO \rightarrow CpM(CO)_3X} \qquad (56)$$

photoprocesses is strongly suggested by the observation that formation of $\mathrm{CpM(CO)(PPh_3)_2X}$ is totally quenched by irradiation of $\mathrm{CpM(CO)_2(PPh_3)X}$ in benzene solutions saturated with carbon monoxide (eq 57). Similarly, $\mathrm{CpM(CO)_3X}$

$$\mathrm{CpM(CO)_2(PPh_3)X + CO \xrightarrow{h\nu} CpM(CO)_3X + PPh_3} \qquad (57)$$

complexes are *not* produced upon irradiation of $\mathrm{CpM(CO)_2(PPh_3)X}$ in the presence of excess $\mathrm{PPh_3}$ (eq 58).

$$\mathrm{CpM(CO)_2(PPh_3)X + PPh_3 \xrightarrow{h\nu} CpM(CO)(PPh_3)_2X + CO} \qquad (58)$$

Quantum yields for reactions 57 and 58 are given in Tables IX and X, respectively. Lower limit values are given for the reactions of *cis*-$\mathrm{CpMo(CO)_2(PPh_3)Cl}$ with carbon monoxide and $\mathrm{PPh_3}$, since control experiments reveal that the products (vide supra) undergo thermal back-reactions (eq 59 and 60)

$$\mathrm{CpMo(CO)_3Cl + PPh_3 \rightarrow \textit{cis}\text{-}CpMo(CO)_2(PPh_3)Cl} \qquad (59)$$

$$\mathrm{CpMo(CO)(PPh_3)_2Cl + CO \rightarrow \textit{cis}\text{-}CpMo(CO)_2(PPh_3)Cl} \qquad (60)$$

to a significant extent during the time required for ^{1}H NMR analysis of photolyzed samples. Quantum yields for the reactions of *cis*-$\mathrm{CpMo(CO)_2(PPh_3)X}$ with carbon monoxide (eq 57) are invariant to the wavelength of irradiation (366 or 436 nm). Reactions for which quantum yields are independent of irradiation wavelengths are usually assumed to originate from the lowest energy vibrationally relaxed excited states.[10,34,57,66,67] A similar interpretation is tentatively made for these reactions. Quantum yields for the reactions of *trans*-$\mathrm{CpMo(CO)_2(PPh_3)X}$ complexes with carbon monoxide (eq 57) and for $\mathrm{PPh_3}$ substitution of *cis*- and *trans*-$\mathrm{CpMo(CO)_2(PPh_3)X}$ (eq 58) are wavelength dependent ($\Phi_{366} > \Phi_{436}$). The variation in quantum yields with energy of excitation is more pronounced for the iodo than for the bromo complexes, paralleling the observations made for $\mathrm{PPh_3}$ substitution of $\mathrm{CpMo(CO)_3X}$. Wavelength-dependent quantum yields are generally attributed to at least two different reactive electronic excited states or to a single reactive electronic excited state in which vibrational equilibration has not been achieved.[10,34,35] The latter possibility is not likely in this case, since the reactions were carried out in the liquid phase. In solution, vibrational relaxation of excited-state molecules is known to be exceedingly rapid due to the high rate of collisions with solvent molecules.[10,11,34]

A major point of concern in this study is elucidation of the pathway by which *cis*- and *trans*-$\mathrm{CpM(CO)_2(PPh_3)X}$ complexes isomerize photochemically. A number of metal carbonyl complexes undergo photochemical geometric rearrangements in which ligand dissociation is the initial step in the reaction sequence.[67–71] Thermal cis ⇌ trans rearrangements of $\mathrm{CpMo(CO)_2(L)X}$ and structurally related complexes are intramolecular in nature.[5,72–75] Mechanistic models proposed

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(66) D. L. Morse and M. S. Wrighton, *J. Am. Chem. Soc.*, **98**, 3931 (1976).
(67) P. J. Giordano and M. S. Wrighton, *Inorg. Chem.*, **16**, 160 (1977).
(68) D. J. Darensbourg and M. A. Murphy, *J. Am. Chem. Soc.*, **100**, 463 (1978).
(69) C. F. J. Barnard, J. A. Daniels, J. Jeffery, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 953 (1976).
(70) C. F. J. Barnard, J. A. Daniels, J. Jeffery, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1861 (1976).
(71) J. D. Black and P. S. Braterman, *J. Organomet. Chem.*, **63**, C19 (1973).
(72) J. W. Faller, A. S. Anderson, and C. C. Chen, *Chem. Commun.*, 719 (1969).
(73) J. W. Faller, A. S. Anderson, and A. Jakulbowski, *J. Organomet. Chem.*, **27**, C47 (1971).
(74) J. W. Faller, D. A. Haitko, R. D. Adams, and D. F. Chodosh, *J. Am. Chem. Soc.*, **99**, 1654 (1977).

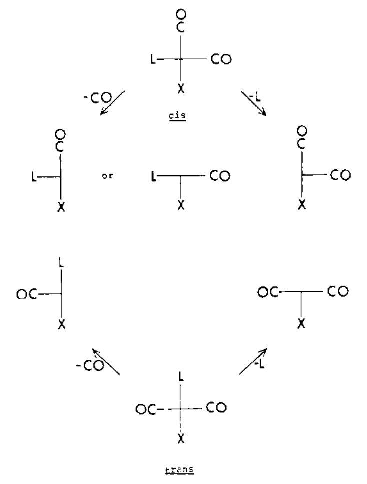

Figure 5. Intermediates formed by loss of CO or L from *cis*- and *trans*-$CpM(CO)_2LX$ complexes. The metal and the cyclopentadienyl ring have been omitted for clarity.

for interconversion of the square-pyramidal complexes involve trigonal-bipyramidal intermediates, with the cyclopentadienyl ligand occupying one of the axial positions of the trigonal bipyramid.[5,75] Both dissociative and intramolecular pathways were considered for the photochemical isomerization reactions of *cis*- and *trans*-$CpM(CO)_2(PPh_3)X$ complexes.

Loss of carbon monoxide or PPh_3 from excited-state $CpM(CO)_2(PPh_3)X$ complexes would lead to formation of one of the coordinatively unsaturated intermediates shown in Figure 5. The particular intermediate produced depends upon the geometry of the starting complex and the coordination site vacated. Rearrangement of these possible intermediates prior to metal–ligand recombination could in principle account for the observed cis ⇌ trans isomerizaiton reactions. If formation of the coordinatively unsaturated complexes is a prerequisite for geometric isomerization, then reactions leading to destruction of the intermediates would be competitive with the isomerization processes. Enhanced production of $CpM(CO)_3X$ (eq 56) or $CpM(CO)(PPh_3)_2X$ (eq 55) via irradiation of *cis*- or *trans*-$CpM(CO)_2(PPh_3)X$ in the presence of free carbon monoxide or PPh_3, respectively, would therefore inhibit geometric isomerization of the complexes.

Quantum yields (λ = 366 and 436 nm) for isomerization of *cis*- and *trans*-$CpMo(CO)_2(PPh_3)X$ complexes in benzene solutions containing added carbon monoxide or PPh_3 are given in Tables VII and VIII. The isomerization quantum yields are not significantly affected by addition of either of the free ligands. These results suggest that dissociation of either carbon monoxide or PPh_3 from excited-state $CpMo(CO)_2(PPh_3)X$ complexes is not required for cis ⇌ trans isomerization to occur.

Ligand-dissociation pathways may make a minor contribution to the isomerization reactions. Photolysis of *trans*-$CpMo(CO)_2(PPh_3)X$ in the presence of PPh_3 yields the disubstituted complexes $CpMo(CO)(PPh_3)_2X$ (eq 58) in which the phosphine ligands are trans to each other[2,12] (Figure 1). The geometries of the reacting complexes and the products dictate either that *cis*-$CpMo(CO)(PPh_3)_2X$ complexes rapidly isomerize to *trans*-$CpMo(CO)(PPh_3)_2X$ or that, following loss of carbon monoxide from *trans*-$CpMo(CO)_2(PPh_3)X$, the $CpMo(CO)(PPh_3)X$ intermediates rearrange before reacting with PPh_3. Rearrangement of the intermediates prior to recombination with carbon monoxide would yield *cis*-$CpMo(CO)_2(PPh_3)X$ (Figure 6). In contrast, irradiation of *trans*-$CpMo(CO)(PPh_3)_2X$ (X = Cl, I) in benzene solutions

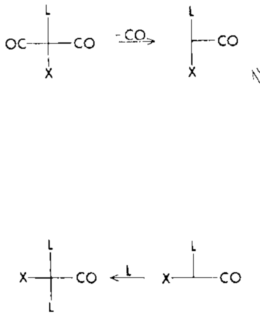

Figure 6. Dissociative pathway involving rearrangement of intermediates for the reaction *trans*-$CpMo(CO)_2(PPh_3)X + PPh_3 \xrightarrow{h\nu}$ *trans*-$CpMo(CO)(PPh_3)_2X + CO$. The metal and the cyclopentadienyl ligand have been omitted for clarity. L = PPh_3.

saturated with carbon monoxide stereospecifically yields *cis*-$CpMo(CO)_2(PPh_3)X$ (eq 61), suggesting that capture of coordinatively unsaturated $CpMo(CO)(PPh_3)X$ by carbon monoxide occurs at the expense of possible structural rearrangements of this intermediate.

$$CpMo(CO)(PPh_3)_2X + CO \xrightarrow{h\nu} cis\text{-}CpMo(CO)_2(PPh_3)X + PPh_3 \quad (61)$$

It is conceivable that loss of the halogen and structural rearrangement of the metal-containing fragment prior to recombination with the halogen could account for the cis ⇌ trans isomerizations. However, consistent with the observations made for $CpMo(CO)_3X$, all evidence is negative with respect to heterolytic or homolytic cleavage of the metal–halogen bond of $CpMo(CO)_2(PPh_3)X$ complexes.

Photoinduced heterolysis of the metal–halogen bond would yield the coordinatively unsaturated complex $CpMo(CO)_2(PPh_3)^+$ and a halide anion (eq 62). The 16-electron cationic complex is expected to react with carbon monoxide or PPh_3 to yield the 18-electron complexes $CpMo(CO)_3(PPh_3)^+$ [31] or $CpMo(CO)_2(PPh_3)_2{}^+$,[25] respectively. These cations should precipitate out of benzene solutions as the halide salts.[12] However, no precipitates are observed upon 366- or 436-nm irradiation of *cis*- or *trans*-$CpMo(CO)_2(PPh_3)X$ complexes in benzene solutions containing free carbon monoxide or PPh_3. Furthermore, the cationic derivatives are not observed in the infrared or ^1H NMR spectra of the photolyzed samples (Table II). Addition of the inert electrolyte $(n\text{-}Bu)_4N^+BPh_4{}^-$ to methylene chloride solutions containing *cis*- or *trans*-$CpMo(CO)_2(PPh_3)X$ does not affect the isomerization quantum yields (Table VII), indicating that ionic photoprocesses are not involved.

$$CpMo(CO)_2(PPh_3)X \xrightarrow{h\nu} CpMo(CO)_2(PPh_3)^+ + X^- \quad (62)$$

Homolysis of the metal–halogen bond of $CpM(CO)_2(PPh_3)X$ complexes would lead to formation of $CpMo(CO)_2(PPh_3)\cdot$ and halogen radicals (eq 63). The substituted metal-based radicals are expected to abstract halogens from CCl_4 and CBr_4, as do $CpMo(CO)_3\cdot$ and $CpW(CO)_3\cdot$ radicals.[18,19,64] Irradiation of cis/trans mixtures of $CpMo(CO)_2(PPh_3)X$ in benzene solutions containing CX'_4 (X = Cl, X′ = Br; X = Br or I, X′ = Cl) does *not* afford $CpMo(CO)_2(PPh_3)X'$, as evidenced by analysis of the parent regions of the mass spectra of photolyzed samples. Furthermore, quantum yields for isomerization of *cis*- and *trans*-$CpMo(CO)_2(PPh_3)X$ are not affected by addition of 2,6-di-*tert*-butylphenol[65] to benzene solutions of the complexes (Table VII). These observations parallel those made for $CpM(CO)_3X$ complexes and demonstrate that photolysis of $CpMo(CO)_2$-

$$CpMo(CO)_2(PPh_3)X \xrightarrow{h\nu} CpMo(CO)_2(PPh_3)\cdot + X\cdot \quad (63)$$

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(75) T. C. Flood, E. Rosenberg, and A. Sarhangi, *J. Am. Chem. Soc.*, **99**, 4334 (1977).

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(PPh$_3$)X does not generate radical intermediates.

On the basis of these results, we conclude that photoinduced geometric isomerization reactions of *cis*- and *trans*-CpM(CO)$_2$(PPh$_3$)X occur via intramolecular rearrangements of the excited-state complexes. There are apparently three chemically distinct excited-state deactivation pathways available to these complexes, i.e., intramolecular isomerization, dissociation of carbon monoxide, and dissociation of PPh$_3$. However, knowledge concerning the electronic structures of the ground-state complexes and the character of the low-lying excited states and their conversion pathways to other electronic states is severely lacking. Hopefully, relationships between electronic structure and photochemical reactivity patterns for these complexes will be elucidated in the near future.

Acknowledgment. Portions of this work were carried out during the term of a University of Missouri Graduate Research Fellowship (to D.G.A.). We are indebted to Professor T. L. Brown for valuable discussions.

Registry No. CpMo(CO)$_3$Cl, 12128-23-3; *cis*-CpMo(CO)$_2$(PPh$_3$)Cl, 32011-69-1; CpMo(CO)(PPh$_3$)$_2$Cl, 33152-14-6; CpMo(CO)$_3$Br, 12079-79-7; *cis*-CpMo(CO)$_2$(PPh$_3$)Br, 31851-05-5; *trans*-CpMo(CO)$_2$(PPh$_3$)Br, 31851-06-6; CpMo(CO)$_3$I, 12287-61-5; *cis*-CpMo(CO)$_2$(PPh$_3$)I, 57606-00-5; *trans*-CpMo(CO)$_2$(PPh$_3$)I, 32011-70-4; CpMo(CO)(PPh$_3$)$_2$I, 73104-92-4; CpW(CO)$_3$Cl, 12128-24-4; CpW(CO)$_3$Br, 37131-50-3; CpW(CO)$_3$I, 31870-69-6; CpMo(CO)(PPh$_3$)$_2$Br, 73208-29-4; [CpMo(CO)$_3$]$_2$, 12091-64-4; *cis*-CpW(CO)$_2$(PPh$_3$)Cl, 71425-48-4; *cis*-CpW(CO)$_2$(PPh$_3$)Br, 73173-84-9; *cis*-CpW(CO)$_2$(PPh$_3$)I, 53110-41-1; *trans*-CpW(CO)$_2$(PPh$_3$)I, 53110-40-0; [CpW(CO)$_3$]$_2$, 12566-66-4; [CpW(CO)$_4$]BF$_4$, 68868-84-8; *cis*-CpMo(CO)$_2$(^{13}CO)Br, 73104-93-5; *trans*-CpMo(CO)$_2$(^{13}CO)Br, 73175-01-6.

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Chemistry via Metal Atom Cocondensation: Isomerization and Complexation Reactions of Organocyclopropanes and Spirocycles

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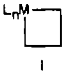
Received August 30, 1979

Reactions of metal atoms with structurally diverse organocyclopropanes have been studied. Quadricyclane (**4**) is isomerized to norbornadiene (**5**) upon cocondensation with a variety of metals, but control experiments suggest this reaction is heterogeneously catalyzed by metal aggregates which form upon warming the matrix. Norcarane (**6**), 2-norcarene (**7**), 3-carene (**8**), and 3-norcarene (**9**) give no reaction when cocondensed with a broad spectrum of metal atoms, despite the presence of an olefinic group in the latter three. When cyclopropylbenzene (**11**) is cocondensed with chromium, only bis(cyclopropylbenzene)chromium(0) (**12**) is formed. However, reaction of iron atoms with spiro[2.4]hepta-4,6-diene (**14**) yields a 14:64:6:17 ratio of 1,1′-diethylferrocene (**15**), 1-ethyl-1′-vinylferrocene (**16**), 1,1′-divinylferrocene (**17**), and [4]ferrocenophane (**18**) in 44% yield based upon iron. Cocondensations of iron with spiro[2.4]heptane (**20**; no reaction) and spiro[4.4]nona-1,3-diene (**23**; formation of bis(tetrahydroindenyl)iron (**24**) and 1,2-tetramethylene-1′-butylferrocene (**25**)) are also reported. Possible mechanisms of spirocycle (**14**, **23**) ring opening and product formation are discussed. No volatile bis(arene)chromium(0) complexes are formed when benzocyclopropene (**27**) and dispiro[2.2.2.2]deca-4,9-diene (**28**) are cocondensed with chromium, although the former is polymerized. The preparation of **18** from 1,1′-dilithioferrocene (**19**) and 1,4-dibromobutane is also described.

Introduction

The catalytic and stoichiometric interaction of inorganic and organometallic compounds with organocyclopropanes has been of substantial recent interest.[1,2] Strained cyclopropanes such as bicyclobutanes have been isomerized to more stable valence isomers with a variety of catalysts.[2,3] Numerous stoichiometric ring opening reactions have been observed. The involvement of metallocyclobutanes such as **1** has been suggested in many of these transformations. Metallocyclobutanes are also believed to be pivotal olefin metathesis intermediates,[4] and their involvement in Ziegler–Natta olefin polymerization has recently been proposed.[5]

General preparative routes to metallocyclobutanes have not yet been developed. A few metallocyclobutanes have been obtained by the oxidative addition of cyclopropanes to platinum complexes,[6] and the tungsten metallocyclobutane **2** has been prepared from a cationic π-allyl precursor.[7] Since improved accessibility of metallocyclobutanes would facilitate the study of their properties, we considered the possibility that the parent ring system **3** might result from the insertion of a transition-metal *atom* into a cyclopropane carbon–carbon bond.



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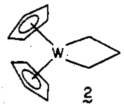

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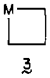

3

Transition-metal atoms are highly reactive species by virtue of the 70–200 kcal/mol required for their formation.[8a] Hence they can be utilized for the preparation of organometallic compounds whose synthesis would be difficult or impossible

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(1) Recent leading references: (a) Sarel, S. *Acc. Chem. Res.* **1978**, *11*, 204; (b) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201; (c) Hogeveen, H.; Nusse, B. J. *Ibid.* **1978**, *100*, 3110; (d) Rajaram, J.; Ibers, J. A. *Ibid.* **1978**, *100*, 829; (e) Salomon, R. G.; Salomon, M. F.; Kachinski, J. L. C. *Ibid.* **1977**, *99*, 1043.

(2) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461.

(3) (a) Gassman, P. G.; Reitz, R. R. *J. Am. Chem. Soc.* **1973**, *95*, 3057. (b) Dauben, W. G.; Kielbania, A. J.; Raymond, K. N. *Ibid.* **1973**, *95*, 7166. (c) Paquette, L. A.; Zon, G. *Ibid.* **1974**, *96*, 203, 215, 224.

(4) (a) Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16*, 283. (b) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (c) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.

(5) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604.

(6) (a) McQuillin, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123. (b) Lenarda, M.; Ros, R.; Graziani, M.; Belluco, U. *J. Organomet. Chem.* **1974**, *65*, 407. (c) Binns, S. E.; Cragg, R. H.; Gillard, R. D.; Heaton, B. T.; Pilbrow, M. F. *J. Chem. Soc. A* **1969**, 1227. (d) Al-Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Organomet. Chem.* **1978**, *150*, 295.

(7) (a) Ephritikhine, M.; Green, M. L. H.; MacKenzie, R. E. *J. Chem. Soc., Chem. Commun.* **1976**, 619. (b) Ephritikhine, M.; Green, M. L. H. *Ibid.* **1976**, 926.

(8) (a) Timms, P. L. *Adv. Inorg. Chem. Radiochem.* **1972**, *14*, 121. (b) Timms, P. L.; Turney, T. W. *Adv. Organomet. Chem.* **1977**, *15*, 53.

0020-1669/80/1319-1543$01.00/0