Contribution from the Department of Chemistry,
University of Oregon, Eugene, Oregon 97403

Photochemistry of Organometallic Halide Complexes. Mechanisms for the Formation of Ionic Products

Xiong Pan, Cecelia E. Philbin, Michael P. Castellani, and David R. Tyler*

Received July 16, 1987

The photochemical reactions of the $Mn(CO)_5X$ (X = Cl, Br, I), $CpMo(CO)_3X$ (X = Cl, I), and $CpFe(CO)_2I$ complexes with various ligands were investigated with an emphasis on determining how ionic products form in these reactions. Two pathways account for the formation of ionic products: (1) M–X heterolysis and (2) metal–metal-bonded dimer formation followed by subsequent disproportionation. The metal–metal-bonded dimer may form via a secondary photolysis of a M–CO-loss photoproduct, via M–X heterolysis, or via a minor M–X homolysis pathway, followed by coupling of two metal radicals. $CpMo(CO)_3X$ reacts photochemically with a variety of ligands to give substitution products, but ionic products form only with pyridine and DMSO. With pyridine, the following sequence of reactions was found to yield ionic products: (1) $CpMo(CO)_3Cl \xrightarrow{h\nu} CpMo(CO)_3 + Cl$; (2) $2CpMo(CO)_3 \rightarrow Cp_2Mo_2(CO)_6$; (3) $Cp_2Mo_2(CO)_6 \xrightarrow{h\nu} CpMo(CO)_3^- + CpMo(CO)_3py^+$. (Reaction 3 is the photochemical disproportionation of $Cp_2Mo_2(CO)_6$ described previously by us.) The $CpMo(CO)_3X$ complexes are the only halides studied for which some M–X homolysis occurs; however, homolysis of the Mo–X bond is very inefficient: $\Phi = 9 \times 10^{-4}$. For $CpMo(CO)_3X$ in DMSO, the only ionic product is $CpMo(CO)_2(DMSO)_2^+$, formed by the following route: $CpMo(CO)_3Cl + DMSO \xrightarrow{h\nu} CpMo(CO)_2(DMSO)Cl \xrightarrow{h\nu} CpMo(CO)_2DMSO^+ + Cl^- \rightarrow CpMo(CO)_2(DMSO)_2^+$. Ionic products form in the photochemical reactions of $Mn(CO)_5X$ complexes via the following route involving initial Mn–CO bond dissociation: $Mn(CO)_5X \xrightarrow{h\nu} Mn_2(CO)_8X_2 \xrightarrow{h\nu} MnX_2 + 3CO + {}^1/_2\, Mn_2(CO)_{10}$. Photochemical disproportionation of the $Mn_2(CO)_{10}$ complex then occurs. Ionic products also form in the photochemical reactions of the $CpFe(CO)_2I$ complex via the intermediate formation of the metal–metal-bonded dimer, followed by disproportionation of this species. In this case, however, the dimer is formed by initial heterolysis of the Fe–I bond ($CpFe(CO)_2I \xrightarrow{h\nu} CpFe(CO)_2^+ + I^-$) followed by the sequence of reactions in Scheme II.

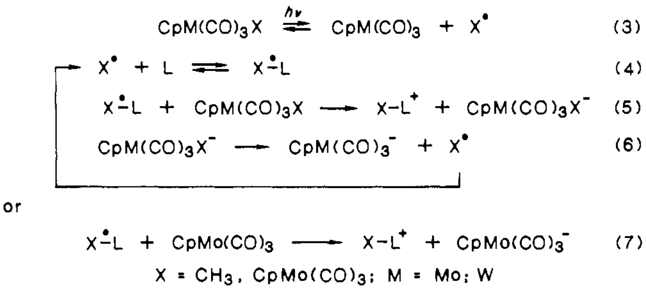
We recently showed that the mechanisms of reactions 1 and 2 are analogous (Scheme I).[1]

$$Cp(CO)_3Mo{-}Mo(CO)_3Cp + PR_3 \rightarrow CpMo(CO)_3^- + CpMo(CO)_3PR_3^+ \quad (1)$$

$$Cp(CO)_3W{-}CH_3 + PR_3 \rightarrow CpW(CO)_3^- + CH_3{-}PR_3^+ \quad (2)$$

In each reaction, photolysis of the M–X bond [eq 3, X = CH_3 or $Mo(CO)_3Cp$] leads to a radical that then combines with a ligand (eq 4) to form an adduct (a 19-electron species[2] in the case of reaction 1 or a phosphoranyl radical[3] in reaction 2).

Scheme I



The adduct then transfers an electron (eq 5 or 7), and the ionic products form. The important sequence of steps in each pathway is thus

$$X + L \rightarrow X\dot{-}L \xrightarrow{-e^-} X{-}L^+ \quad (8)$$

X = CH_3 or $Mo(CO)_3Cp$; L = PR_3 or another ligand

The mechanistic similarity of reactions 1 and 2 (i.e. eq 8) suggests that a general feature of organometallic radical reactions may be the ability of radicals to form electronically supersaturated adducts that undergo electron transfer. To investigate the generality of this concept, we studied the photochemistry of a series of complexes that should yield radicals when irradiated; our goal was to determine whether reactions analogous to eq 1 and 2 occurred and, if so, whether the reaction sequence in eq 8 was involved. The complexes were of the type ML_nX where ML_n = $Mn(CO)_5$, $CpMo(CO)_3$, $CpFe(CO)_2$ and X = Cl, Br, I, $SnCl_3$, $SnPh_3$, $GeMe_3$ and CH_3. Not surprisingly, the reactivity of the complexes depended on the nature of X. Essentially one type of reactivity was observed for X = halide and another reactivity for the remaining X. In this paper, we report the results of our study for the complexes with X = halide.[4]

Experimental Section

All reactions of air-sensitive materials were performed under a nitrogen atmosphere by employing standard Schlenk techniques. $Mn(CO)_5X$,[8] $CpMo(CO)_3X$,[9] and $CpFe(CO)_2I$[10] were prepared by literature methods. Solutions of these complexes (10^{-3}–10^{-2} M) and the appropriate ligand (phosphines were 10^{-1}–10^{-2} M; THF, DMSO, and DMF were used neat; amine concentrations by volume ranged from 1% to neat) were deoxygenated by a nitrogen purge as previously described.[11] Solvents were dried and distilled by standard methods.[12] Photochemical and dark reactions were monitored by infrared spectroscopy on a Nicolet 5DXB FT-IR or Beckman 4240 spectrophotometer and by electronic absorption spectroscopy with a Beckman DU-7 spectrophotometer. A 200-W Oriel Co. high-pressure Hg arc lamp was used for all irradiations. The following Corning cutoff filters were used for wavelength selection: CS 0-56, $\lambda > 250$ nm; CS 0-52, $\lambda > 345$ nm; CS 3-74, $\lambda > 400$ nm; CS 3-73, $\lambda > 420$ nm; CS 3-70, $\lambda > 490$ nm. NMR spectra were obtained with a GE QE-300 NMR spectrometer. Quantum yields were measured by infrared spectroscopy as previously described.[11] Lamp intensities were measured by using ferrioxalate actinometry[13] or Aberchrome 540.[14]

Results

The results of irradiating solutions of ML_nX (X = Cl, Br, I)

---

(1) Goldman, A. S.; Tyler, D. R. *J. Am. Chem. Soc.* **1986**, *108*, 89–94.

(2) The phrase "19-electron complex" is used to describe the adducts that form when 17-electron radicals react with 2-electron ligands. For a thorough discussion of these complexes see Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* **1986**, *5*, 215–245.

(3) (a) Roberts, B. P. *Adv. Free-Radical Chem.* **1980**, *6*, 225–285. (b) Bentrude, W. G. *Phosphorus Sulfur* **1977**, *3*, 109–130.

(4) Previous workers have investigated the photochemical substitution reactions of the $CpMo(CO)_3X$,[5] $CpFe(CO)_2X$,[6] and $Mn(CO)_5X$[7] complexes for various X. Our emphasis was on the photochemical reactions of these complexes that yield ionic products.

(5) Alway, D. G.; Barnett, K. W. *Inorg. Chem.* **1980**, *19*, 1533–1543.

(6) Alway, D. G.; Barnett, K. W. *Inorg. Chem.* **1978**, *17*, 2826–2831.

(7) A summary is found in: Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979; p 128.

(8) *Inorganic Synthesis*; D. F. Shriver, Ed.; Wiley-Interscience: New York, 1979; Vol. 19, p 158.

(9) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104–124.

(10) King, R. B. *Organometallic Syntheses*; Academic: New York, 1965; Vol. 1.

(11) Tyler, D. R. *Inorg. Chem.* **1980**, *20*, 2257–2261.

(12) Perrin, D. D.; Armarego, W. L.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, England, 1966.

(13) (a) Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966. (b) Bowman, W. D.; Demas, J. N. *J. Phys. Chem.* **1976**, *80*, 2434.

(14) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 341–343.

0020-1669/88/1327-0671$01.50/0

Table I. Organometallic Products from the Irradiation of the Halide Complexes and Selected Ligands

	ligand or reagent					
complex	py	THF, DMSO, or DMF	PR_3[b]	CCl_4	benzene or hexane (control irradiation)	$NH_2C_6H_{11}$
$Mn(CO)_5Cl$	$Mn(CO)_3(py)_2Cl$	$Mn_2(CO)_{10}$ $Mn(CO)_5^-$[a]	$Mn(CO)_4PR_3Cl$ $Mn(CO)_3(PR_3)_2Cl$		$Mn_2(CO)_{10}$	*cis*-$Mn(CO)_4(NH_2C_6H_{11})$-$(CONHC_6H_{11})$
$Mn(CO)_5Br$	$Mn(CO)_3(py)_2Br$ $Mn(CO)_5^-$				$Mn_2(CO)_{10}$ $Mn_2(CO)_8Br_2$	
$Mn(CO)_5I$	$Mn(CO)_3py_2I$ $Mn_2(CO)_{10}$ $Mn(CO)_5^-$ $Mn(CO)_3py_3^+$		$Mn(CO)_4PR_3I$ $Mn(CO)_3(PR_3)_2I$		$Mn_2(CO)_{10}$ $Mn_2(CO)_8I_2$	*cis*-$Mn(CO)_4(NH_2C_6H_{11})$-$(CONHC_6H_{11})$
$CpMo(CO)_3Cl$	$CpMo(CO)_2(py)Cl$[c,d] $CpMo(CO)(py)_2Cl$ $Cp_2Mo_2(CO)_5py$ $CpMo(CO)_3py^+$ $CpMo(CO)_3^-$ $Mo(CO)_3(py)_3$ $Mo(CO)_4(py)_2$	$CpMo(CO)_2LCl$ $CpMo(CO)L_2Cl$ $CpMo(CO)_2$-$(DMSO)_2^+$	$CpMo(CO)_2PR_3Cl$[e]	$CpMo(CO)_2Cl_3$	no $Cp_2Mo_2(CO)_6$	
$CpMo(CO)_3I$	$CpMo(CO)_2(py)I$ $CpMo(CO)(py)_2I$	$CpMo(CO)_2LI$ $CpMo(CO)_2$-$(DMSO)_2^+$	$CpMo(CO)_2PR_3I$ $CpMo(CO)(PBu_3)_2I$	$CpMo(CO)_3Cl$ $CpMo(CO)_2Cl_3$	no $Cp_2Mo_2(CO)_6$	
$CpFe(CO)_2I$	$CpFe(CO)(py)I$ $Cp_2Fe_2(CO)_4$ (trace)		$CpFe(CO)PR_3I$	no $CpFe(CO)_2Cl$	no $Cp_2Fe_2(CO)_4$	

[a] $Mn(CO)_3(THF)_2Cl$ also forms in THF. [b] PR_3 = PBu_3, $PBuPh_2$, PPh_3, $P(C_6H_{11})_3$, $PMePh_2$, triphos, $P(i\text{-}Pr)_3$, $P(OPh)_3$, $P(p\text{-}Tol)_3$, $P(OBu)_3$, $P(O\text{-}i\text{-}Pr)_3$. [c] Irradiation with $\lambda > 490$ nm only yields $CpMo(CO)_2(py)Cl$. $CpMo(CO)(py)_2Cl$ and the other products form at higher energy ($\lambda > 345$ nm). [d] The $CpMo(CO)_2(py)Cl$ and $CpMo(CO)(py)_2Cl$ products may be $[CpMo(CO)_2Cl]_2$ and $[CpMo(CO)(py)Cl_2]$, respectively. See ref 15 and 59. [e] Some of these reactions also proceed thermally at room temperature. See ref 5.

and various ligands are summarized in Table I. Products were identified by comparison of their infrared spectra to reported literature spectra (with the reference given in Table II). In general, excitation was into the lowest energy absorption band (Table III). However, all complexes were also irradiated with increasing energy up to $\lambda > 250$ nm (see the list of filters given in the Experimental Section); with only one exception [$Cp(Mo(CO)_3Cl$; see footnote *c*, Table I], the products that formed were independent of the wavelength. To some extent the relative amounts of the various products depended on the wavelength. No attempt was made in Table I to differentiate secondary photolysis products from primary products; the discussion below does so, however.

Discussion

$CpFe(CO)_2I$. The reactivity of the $CpFe(CO)_2I$ complex is summarized as follows:

$$CpFe(CO)_2I + L \xrightarrow{h\nu} CpFe(CO)(L)I + CO \qquad (9)$$

$$L = \text{a phosphine or phosphite}$$

$$CpFe(CO)_2P + py \xrightarrow{h\nu} CpFe(CO)(py)I + \text{minor amounts of } Cp_2Fe_2(CO)_4 \qquad (10)$$

Clearly, CO substitution is the dominant photoreaction and Fe–CO bond dissociation is the likely primary photoprocess. The formation of small amounts of $Cp_2Fe_2(CO)_4$ in pyridine suggests concurrent Fe–I homolysis, but two experiments suggest that Fe–I homolysis is not an important process: (1) no $CpFe(CO)_2Cl$ forms when $CpFe(CO)_2I$ is irradiated in neat CCl_4 (eq 11), and (2) $Cp_2Fe_2(CO)_4$ does not form when $CpFe(CO)_2X$ (X = Cl, I) is irradiated in inert solvents (benzene or hexane) (eq 12).

$$CpFe(CO)_2I \overset{h\nu}{\nrightarrow} CpFe(CO)_2 + I \xrightarrow{CCl_4} CpFe(CO)_2Cl + CCl_3 \qquad (11)$$

$$CpFe(CO)_2I \overset{h\nu}{\underset{\text{inert solvent}}{\nrightarrow}} Cp_2Fe_2(CO)_4 \qquad (12)$$

The mechanism of $Cp_2Fe_2(CO)_4$ formation from $CpFe(CO)_2Cl$ in pyridine was studied by Ali, Cox, and Kemp, and the disproportionation pathway in Scheme II was proposed on the basis of a stoichiometric analysis of the products.[15a] A similar mechanism probably yields $Cp_2Fe_2(CO)_4$ from $CpFe(CO)_2I$ in pyridine. Note that the pathway involves the initial heterolysis of the Fe–X bond,

---

(15) The product identified as $CpMo(CO)_2(py)Cl$ (by comparison of its infrared spectrum to that of other $CpMo(CO)_2LCl$ complexes) may actually be $[CpMo(CO)_2Cl]_2$. See: (a) Ali, L. H.; Cox, A.; Kemp, T. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1475–1478. (b) Hart-Davis, A. J.; White, C.; Mawbry, R. J. *Inorg. Chim. Acta* **1970**, *4*, 431–434.

(16) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065–2072.

(17) (a) Smith, F. E.; Butler, I. S. *Can. J. Chem.* **1969**, *47*, 1311–1319. (b) Chiswell, B.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 417–419. (c) Abel, E. W.; Wilkinson, G. *J. Chem. Soc.* **1959**, 1501–1505. (d) Butler, I. S.; Coville, N. J. *J. Organomet. Chem.* **1974**, *66*, 111–118.

(18) Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q.; Pitts, R. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1189–1193.

(19) El-Sayed, M. A.; Kaesz, H. D. *Inorg. Chem.* **1963**, *2*, 158–162.

(20) (a) Drew, D.; Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1975**, *14*, 1579–1584. (b) Stiegman, A. E.; Tyler, D. R. *Inorg. Chem.* **1984**, *23*, 527–529.

(21) Dombek, B. D.; Angelici, R. J. *J. Organomet. Chem.* **1977**, *134*, 203–217.

(22) (a) Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. A* **1967**, 686–688. (b) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1966**, 1606–1607. (c) Goldman, A. S.; Tyler, D. R. *Organometallics* **1984**, *3*, 449–456.

(23) (a) King, R. B.; Houk, L. W.; Pannell, K. H. *Inorg. Chem.* **1969**, *8*, 1042–1048. (b) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1967**, 94–98. (c) Treichel, P. M.; Barnett, K. W.; Shubkin, R. L. *J. Organomet. Chem.* **1967**, *7*, 449–459.

(24) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032–6037.

(25) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263–268.

(26) Burckett-St. Laurent, J.; Field, J. S.; Haines, R. J.; McMahon, M. *J. Organomet. Chem.* **1979**, *181*, 117–130.

(27) This complex was identified by comparison of its infrared spectrum to those of similar $Cp_2Mo_2(CO)_5L$ complexes. See: (a) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 43–46. (b) Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *161*, 23–37.

(28) Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 201–214.

(29) This complex was identified by comparison of its infrared spectrum to those of similar complexes reported in ref 26.

(30) Note that photochemical disproportionation of the $Cp_2Mo_2(CO)_6$ complex occurs in DMSO to yield $CpMo(CO)_2(DMSO)_2^+$ and $CpMo(CO)_3^-$ (and $CpMo(CO)_3DMSO^+$ with short irradiation times). The $CpMo(CO)_2(DMSO)_2^+$ produced in eq 18 was also identified by comparing its infrared spectrum to that of the $CpMo(CO)_2(DMSO)_2^+$ formed in the disproportionation reaction.

(31) This product was identified by comparison of its infrared spectrum to the spectra of related complexes in ref 5 and 15a.

(32) This complex wass identified by comparison of its infrared spectrum to the $CpMo(CO)_2(L)I$ products reported in ref 5.

a step that may be pyridine assisted. Also note that photochemical disproportionation of the $Cp_2Fe_2(CO)_4$ complex does not occur with amine ligands.[33] Thus, no ionic products will form via this route.

Scheme II

$$CpFe(CO)_2Cl \xrightarrow[py]{h\nu} CpFe(CO)_2^+ + Cl^-$$

$$CpFe(CO)_2^+ + CpFe(CO)_5Cl \rightarrow CpFe(CO)_2 + CpFe(CO)_2Cl^+$$

$$2CpFe(CO)_2 \rightarrow Cp_2Fe_2(CO)_4$$

$$CpFe(CO)_2Cl^+ \xrightarrow{H^+} FeCl^{2+} + 2CO + {}^1/_2[C_5H_6]_2$$

In summary, irradiation of $CpFe(CO)_2I$ leads predominantly to Fe–CO bond dissociation and perhaps to a smaller extent some Fe–I heterolysis. Of course, the absence of Fe–X homolysis explains why no reaction analogous to eq 1 and 2 occurs.[36,38,39]

$CpMo(CO)_3X$. Again, no reaction analogous to reactions 1 and 2 occurs with the $CpMo(CO)_3X$ complexes. As Table I shows, the major reaction for all L is substitution:

$$CpMo(CO)_3X + L \xrightarrow{h\nu} CpMo(CO)_2LX + CpMo(CO)L_2X \quad (13)$$

$$X = Cl, I$$

The reactions of $CpMo(CO)_3Cl$ in pyridine are interesting because longer irradiation times yielded $CpMo(CO)_3^-$, $Mo(CO)_3(py)_3$, and $Mo(CO)_4(py)_2$. The series of spectra in Figure 1 clearly show that these species are products of secondary and tertiary photochemical reactions. The sequence of reactions leading to these products is best described as

$$CpMo(CO)_3Cl \xrightarrow{h\nu} Cp_2Mo_2(CO)_6 \xrightarrow{h\nu} Cp_2Mo_2(CO)_5py \xrightarrow{h\nu} CpMo(CO)_3^- + CpMo(CO)_3py^+ \quad (14)$$

These reactions are then followed by

$$CpMo(CO)_3py^+ \xrightarrow[dark]{py} Mo(CO)_3(py)_3\ (+\ Cp\text{–}py^+) \quad (15)$$

$$Mo(CO)_3(py)_3 \xrightarrow[dark]{CO} Mo(CO)_4(py)_2 \quad (16)$$

These reactions require comment and are discussed below.

We propose that $Cp_2Mo_2(CO)_6$ is formed in pyridine solution via photochemical homolysis of the Mo–Cl bond in $CpMo(CO)_3Cl$. Homolysis is an inefficient process compared to M–CO dissociation, and for that reason, $Cp_2Mo_2(CO)_6$ formed via the homolysis route is not observed in the presence of good ligands (PR_3, etc.).[40] [Quantum yields for M–CO dissociation in $CpMo(CO)_3X$ are in the range of 0.2–0.8[5] (depending on X) while the quantum yield for homolysis is about 9×10^{-4}, see below.] In pyridine, however,

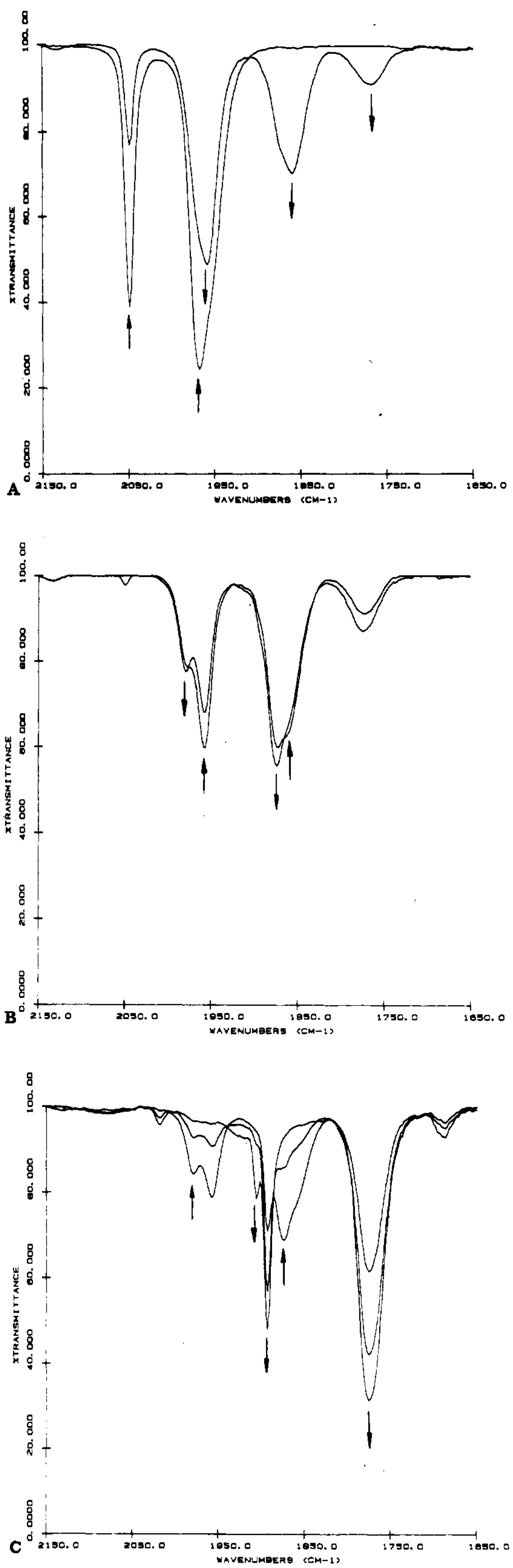


Figure 1. Infrared spectra obtained by irradiating ($\lambda > 345$ nm) $(MeCp)Mo(CO)_3Cl$ (2.0×10^{-3} M) in neat pyridine. (A) Initial spectrum and the spectrum after 5 s of irradiation. The arrows indicate the disappearance of $(MeCp)Mo(CO)_3Cl$ and the appearance of $(MeCp)Mo(CO)_2(py)Cl$ and $(MeCp)Mo(CO)(py)_2Cl$. (B) Spectra of the same solution after 20 and 60 s of irradiation. The arrows show the appearance of $(MeCp)_2Mo_2(CO)_5py$ and the disappearance of $(MeCp)Mo(CO)_2(py)Cl$. (C) Spectra of the same solution after 3.5, 5.0, and 8.0 min of irradiation. The arrows show the appearance of $(MeCp)Mo(CO)_3^-$ and $Mo(CO)_3(py)_3$ and the disappearance of $(MeCp)Mo(CO)_2(py)Cl$ and $(MeCp)_2Mo_2(CO)_5py$.

---

(33) Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1987**, *26*, 253–258.

(34) This complex was identified by comparison of its infrared spectrum to the CpFe(CO)(L)I complexes reported in ref 6.

(35) Labinger, J. A.; Madhaven, S. *J. Organomet. Chem.* **1977**, *134*, 381–389.

(36) Geoffroy and coworkers recently reported[37] that irradiation of $Cp^*Os(CO)_2I$ ($Cp^* = \eta^5\text{-}C_5Me_5$) may result in Os–I homolysis. The following pathway was one of two proposed for formation of $[Cp^*Os(CO)_2PR_3]I$:

$$Cp^*Os(CO)_2I \xrightarrow{h\nu} Cp^*Os(CO)_2 + I^\bullet \xrightarrow{PR_3} Cp^*Os(CO)_2PR_3 \xrightarrow{I^\bullet} [Cp^*Os(CO)_2PR_3]I$$

(37) Pourreau, D. B.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1986**, *5*, 1337–1345.

(38) For related reactions of the CpFe(CO)LBr complexes, see: Allen, D. M.; Cox, A.; Kemp, T. J.; Ali, L. H. *J. Chem. Soc., Dalton Trans.* **1973**, 1899–1901.

(39) For related thermal reactions of the $CpFe(CO)_2Cl$ complexes, see: Haines, R. J.; DuPreez, A. L.; Marais, I. L. *J. Organomet. Chem.* **1971**, *28*, 405–413.

(40) Note that in inert solvents $Cp_2Mo_2(CO)_6$ will back-react with Cl_2 to reform $CpMo(CO)_3Cl$.

Table II. Infrared Data[a]

complex	$\nu(\mathrm{C{\equiv}O})$, cm^{-1}	solvent	ref
$\mathrm{Mn(CO)_5Cl}$	2125, 2048, 2009	DMSO	8, 16
	2140, 2046, 2010	THF	
	2140, 2056, 2009	$\mathrm{CH_2Cl_2}$	
$\mathrm{Mn(CO)_3(py)_2Cl}$	2030 s, 1944 s, 1906 s	py	17, 18
$\mathrm{Mn(CO)_4(PPh_3)Cl}$	2095, 2030, 2006, 1951	$\mathrm{CH_2Cl_2}$	17
$\mathrm{Mn(CO)_3(PPh_3)_2Cl}$	2049, 1954, 1918	$\mathrm{CH_2Cl_2}$	17
cis-$\mathrm{Mn(CO)_4(P(OBu)_3)Cl}$[b]	2100, 2014, 1968	$\mathrm{CH_2Cl_2}$	17
cis-$\mathrm{Mn(CO)_3(P(OBu)_3)_2Cl}$[b]	2032, 1968, 1929	$\mathrm{CH_2Cl_2}$	17
$\mathrm{Mn(CO)_2(P(OBu)_3)_3Cl}$	1970 m, 1904 s, 1884 sh	$\mathrm{CH_2Cl_2}$	17
$\mathrm{Mn(CO)_5Br}$	2139, 2053, 2009	$\mathrm{CH_2Cl_2}$	8, 18
	2140, 2045, 2011	THF	
	2136, 2048, 2005	hexane–py (1:1)	
$\mathrm{Mn(CO)_3(py)_2Br}$	2026, 1946, 1906	hexane–py (1:1)	17
$\mathrm{Mn_2(CO)_8Br_2}$	2099 w, 2042 s, 2011 m, 1975 m	$\mathrm{CCl_4}$	19
$\mathrm{Mn(CO)_4(P(OBu)_3)Br}$[b]	2095, 2009, 1969	THF	17
$\mathrm{Mn(CO)_3(P(OBu)_3)_2Br}$	2028, 1969, 1931	THF	17
$\mathrm{Mn(CO)_2(P(OBu)_3)_3Br}$	1969, 1904, 1890		17b
$\mathrm{Mn(CO)_5I}$	2129 w, 2046 s, 2009 m	$\mathrm{C_8H_6}$	8, 16
	2126, 2045, 2006	hexane	
	2129, 2040, 2010	THF	
$\mathrm{Mn(CO)_3(py)_2I}$	2017 s, 1940 s, 1910 s	hexane–py (1:1)	17
$\mathrm{Mn(CO)_4PPh_3I}$	2080 m, 2017 m, 2002 s, 1964 m	hexane	17
$\mathrm{Mn(CO)_3(PPh_2Me)_2I}$[c]	2028 w, 1955 s, 1911 m	hexane	17
$\mathrm{Mn_2(CO)_{10}}$	2046, 2010, 1981	THF	16
	2046, 2016, 1988	hexane	
$\mathrm{Mn(CO)_5^-}$	1902, 1859	hexane	18, 20
$\mathrm{Mn(CO)_3(py)_3^+}$	2045, 1941	hexane	20
cis-$\mathrm{Mn(CO)_4(NH_2C_6H_{11})(CONHC_6H_{11})}$	2065 w, 1974 s, 1923 m	hexane	21
$\mathrm{Mn_2(CO)_8I_2}$	2089 w, 2036 s, 2015 m, 1982 m	hexane	19
$\mathrm{CpMo(CO)_3Cl}$	2052 s, 1973 s, 1962 sh	$\mathrm{C_6H_6}$	5
$\mathrm{CpMo(CO)_2(py)Cl}$	1962 s, 1867 m	$\mathrm{C_6H_6}$	5, 15a
$\mathrm{CpMo(CO)(py)_2Cl}$	1778 b	$\mathrm{C_6H_6}$	5, 15a
$\mathrm{CpMo(CO)_2Cl_3}$	2104, 2065	THF	22
$\mathrm{CpMo(CO)_2(DMSO)Cl}$	1972, 1890	$\mathrm{C_6H_6}$	23
$\mathrm{CpMo(CO)(DMSO)_2Cl}$	1776 b	$\mathrm{C_6H_6}$	23
$\mathrm{CpMo(CO)_2(PBu_3)Cl}$	1963, 1871	$\mathrm{C_6H_6}$	5, 23
$\mathrm{CpMo(CO)(PBu_3)_2Cl}$	1795	$\mathrm{C_6H_6}$	5, 23
$\mathrm{CpMo(CO)_3^-}$	1894, 1776		15a, 24, 25
$\mathrm{(MeCp)Mo(CO)_3py^{+}}$[d]	2058 s, 1989 m, sh, 1962 s	py	23c, 26
$\mathrm{(MeCp)Mo(CO)_2(py)_2^{+}}$[d]	1986 m, 1874 m	py	23c, 26
$\mathrm{(MeCp)_2Mo_2(CO)_5py}$[d]	1978 m, 1873 s, br	py	27
fac-$\mathrm{Mo(CO)_3(py)_3}$	1905 s, 1778 s	py	28
cis-$\mathrm{Mo(CO)_4(py)_2}$	2012 m, 1891 s, 1878 s, sh, 1832 m	py	28
$\mathrm{(MeCp)Mo(CO)_2(DMSO)_2^+}$	1950, 1841	DMSO	29, 30
$\mathrm{CpMo(CO)_3I}$	2037 s, 1964 s	$\mathrm{C_6H_6}$	5
	2041 s, 1973 s, 1957 m	$\mathrm{CCl_4}$	
$\mathrm{CpMo(CO)_2(py)I}$	1956 s, 1862 s	$\mathrm{C_6H_6}$	31
$\mathrm{CpMo(CO)(py)_2I}$	1780 b	$\mathrm{C_6H_6}$	32
$\mathrm{CpMo(CO)_2(DMSO)I}$	1966 s, 1884 s	$\mathrm{C_6H_6}$	31
$\mathrm{CpMo(CO)_2(PPh_3)I}$	1972 s, 1877 s	$\mathrm{C_6H_6}$	5, 23
$\mathrm{CpMo(CO)(PPh_3)_2I}$	1803	$\mathrm{C_6H_6}$	5, 23
$\mathrm{CpMo(CO)_2(PBu_3)I}$	1962, 1872	$\mathrm{C_6H_6}$	5, 23
$\mathrm{CpMo(CO)(PBu_3)_2I}$	1795	$\mathrm{C_6H_6}$	5, 23
$\mathrm{Cp_2Mo_2(CO)_6}$	2018 w, 1961 s, 1916 s	$\mathrm{C_6H_6}$	24
$\mathrm{Cp_2Fe_2(CO)_4}$	1998, 1956, 1769	$\mathrm{CH_2Cl_2}$	33
$\mathrm{CpFe(CO)_2I}$	2037 s, 1990 s	$\mathrm{CH_2Cl_2}$	10
	2039 s, 1995 s	hexane	
$\mathrm{CpFe(CO)(py)I}$	1957	hexane	34
$\mathrm{CpFe(CO)_2Cl}$	2056, 2004	hexane	6
$\mathrm{CpFe(CO)(PPh_3)I}$	1948	hexane	10
$\mathrm{CpFe(CO)(P(OMe)_3)I}$	1967	hexane	34
$\mathrm{Cp_2Fe_2(CO)_3py}$	1957 s, 1718 m	hexane	35

[a] Stereoisomers not indicated unless shown. [b] The $\mathrm{P(OBu)_3}$-substituted complex values are typical of other phosphine- and phosphite-substituted complexes. [c] The $\mathrm{PPh_2Me}$-substituted complex values are typical of other phosphine- and phosphite-substituted complexes. [d] (MeCp) = η^5-$\mathrm{CH_3C_5H_4}$. The $\mathrm{(MeCp)Mo(CO)_3Cl}$ complex was used for the investigation of eq 14–16.

the $\mathrm{CpMo(CO)_2(py)Cl}$ (or $\mathrm{Cp_2Mo_2(CO)_4Cl_2}$[15]) product can back-react with CO to re-form $\mathrm{CpMo(CO)_3Cl}$.[41] Consequently, the only photoprocess that yields net reactivity in pyridine is Mo–Cl homolysis; $\mathrm{Cp_2Mo_2(CO)_6}$ and $\mathrm{Cp_2Mo_2(CO)_5py}$ are the products of this process. Once formed, these dimer species disproportionate.[24,42]

The disproportionation reactions of the dimers are well understood, and the products are $\mathrm{CpMo(CO)_3^-}$ and $\mathrm{CpMo(CO)_3py^+}$ (eq 14).[24,42] As shown elsewhere, $\mathrm{CpMo(CO)_3py^+}$ is not stable

---

[41] Irradiation ($\lambda > 345$ nm) of $\mathrm{CpMo(CO)_3Cl}$ in pyridine in a sealed IR cell gives quantitative conversion to $\mathrm{CpMo(CO)_2(py)Cl}$ and $\mathrm{CpMo(CO)(py)_2Cl}$. These products disappear after the cell was allowed to stand in the dark for 5 min, and $\mathrm{CpMo(CO)_3Cl}$ reappears. The apparent quantum yield for the disappearance of $\mathrm{CpMo(CO)_3Cl}$ in pyridine (measured after ≈1 min) is $\approx 2.5 \times 10^{-3}$, i.e. only 3 times greater than the quantum yield for homolysis.

[42] Philbin, C. E.; Tyler, D. R., manuscript in preparation.

Table III. Electronic Absorption Spectra of the Halide Complexes at 298 K in CH_2Cl_2

complex	λ_{max}, nm (ϵ)	complex	λ_{max}, nm (ϵ)
$Mn(CO)_5Cl^a$	374 (510) 277 (1670)	$CpMo(CO)_3Cl$	477 (440) 318 sh (1700)
$Mn(CO)_5Br^a$	384 (420) 270	$CpMo(CO)_3I$	485 (595) 310 (3780)
$Mn(CO)_5I^a$	405 (210) 300 (3200)	$CpFe(CO)_2I$	391 sh (≈1500) 337 (3010)

[a] For higher energy bands, see ref 54b.

in pyridine and it reacts as shown in eq 15.[42,43] This reaction and reaction 16 are the source of $Mo(CO)_3(py)_3$ and $Mo(CO)_4(py)_2$. Control experiments confirm that the latter product forms from $Mo(CO)_3(py)_3$ in the presence of CO.[42,44]

Although the predominant primary photoprocess in the $CpMo(CO)_3X$ complexes is M–CO dissociation, evidence for Mo–X homolysis comes from the photochemical reaction of $CpMo(CO)_3I$ with CCl_4. The reaction proceeds as follows:

$$CpMo(CO)_3I \xrightarrow[CCl_4]{h\nu} CpMo(CO)_3Cl \xrightarrow{h\nu} CpMo(CO)_2Cl_3 \quad (17)$$

The first reaction in this sequence probably occurs by Mo–I homolysis followed by the known reaction of $CpMo(CO)_3$ with CCl_4 to give $CpMo(CO)_3Cl$.[45] [The secondary photochemical reaction of $CpMo(CO)_3Cl$ with CCl_4 to give $CpMo(CO)_2Cl_3$ is expected; we recently reported on the mechanism of this reaction.][22c] The quantum yield (366 nm) for disappearance of $CpMo(CO)_3I$ in eq 17 is 9×10^{-4}. Recall that the quantum yield for Mo–CO bond dissociation is 0.2–0.8. Clearly, homolysis is much less efficient than Mo–CO bond dissociation, if it is assumed that Mo–Cl homolysis occurs with an efficiency similar to that of Mo–I homolysis.

Finally, heterolysis of the Mo–X bond may occur in some substituted derivatives of $CpMo(CO)_3Cl$. Thus, for example, irradiation in DMSO initially yields $CpMo(CO)_{3-n}(DMSO)_nX$. Continued irradiation then yields $CpMo(CO)_2(DMSO)_2^+$ but no $CpMo(CO)_3^-$. The absence of $CpMo(CO)_3^-$ indicates that disproportionation of a dimer formed via Mo–X homolysis (eq 14) is not occurring. The suggested pathway is Mo–X heterolysis:[46]

$$\begin{tikzcd} CpMo(CO)_2(DMSO)Cl \arrow[r, "h\nu"] & CpMo(CO)_2DMSO^+ \arrow[d, "DMSO"] & + \; Cl^- \\ & CpMo(CO)_2(DMSO)_2^+ & (18) \end{tikzcd}$$

In summary of the $CpMo(CO)_3X$ complexes, we find that Mo–CO bond dissociation is the dominant photoprocess but Mo–X homolysis also occurs as a very minor route. Mo–X heterolysis occurs in some substituted derivatives of these complexes.

$Mn(CO)_5X$. As Table I shows, substitution products form in the reactions of the $Mn(CO)_5X$ complexes with all potential ligands. In addition, ionic products also form in py, THF, DMSO, or DMF, while $Mn_2(CO)_{10}$ and $Mn_2(CO)_8X_2$ are the products in hexane or benzene. As with the other metal halide complexes, it is quite clear that M–CO dissociation is the dominant photoprocess. The quantum yield (λ = 405 nm) for substitution of CO by PPh_3 in $Mn(CO)_5I$ is 0.10. Note that M–CO bond dissociation yields not only the substitution products $Mn(CO)_{5-n}L_nX$ but also the $Mn_2(CO)_8X_2$ dimers.[47]

The formation of $Mn_2(CO)_{10}$ in inert solvents could be indicative of Mn–X homolysis in $Mn(CO)_5X$. However, Bamford, Burley, and Coldbeck showed that irradiation (λ = 436 nm) of $Mn_2(CO)_8Br_2$ in benzene gave $Mn_2(CO)_{10}$:[48]

$$Mn_2(CO)_8Br_2 \xrightarrow{h\nu} MnBr_2 + 3CO + {}^1/_2Mn_2(CO)_{10} \quad (19)$$

Thus, $Mn_2(CO)_{10}$ is a secondary photolysis product in the irradiation of $Mn(CO)_5X$. Consistent with this interpretation is our observation that no $Mn_2(CO)_{10}$ forms during irradiation of the $Mn(CO)_5X$ complexes in the presence of phosphines; only substitution products of $Mn(CO)_5X$ form. The phosphines probably prevent the formation of $Mn_2(CO)_8X_2$ [by coordinating to the primary photoproduct $Mn(CO)_4X$], and consequently reaction 19 cannot occur. The observation that irradiation (λ > 250 nm) of $Mn(CO)_5I$ in benzene under 1 atm CO did not lead to $Mn_2(CO)_{10}$ is also consistent with the conclusion that Mn–X homolysis does not occur.

Although ionic products form in several of the reactions of the $Mn(CO)_5X$ complexes,[49] the data clearly indicate that these products form via the disproportionation of $Mn_2(CO)_{10}$:[20b]

$$Mn_2(CO)_{10} \xrightarrow{h\nu} Mn(CO)_5^- + Mn(CO)_3L_3^+ \quad (20)$$

Consistent with this interpretation are the observations that $Mn(CO)_3L_3^+$ is the counterion formed along with $Mn(CO)_5^-$ and that $Mn(CO)_5^-$ forms only with ligands that disproportionate $Mn_2(CO)_{10}$. Thus, for example, no ionic products form when L = a phosphine; it is well-established that $Mn_2(CO)_{10}$ does not disproportionate with monodentate phosphines.[20b] Also, note that no $I(py)_2^+$ could be detected by ^1H NMR in the reaction of $Mn(CO)_5I$ in pyridine giving $Mn(CO)_5^-$.[50] This iodopyridinium complex would be the expected cationic product from the analogue of reaction 1 or 2.

In summary of $Mn(CO)_5X$ reactivity, M–CO bond dissociation is the dominant photoprocess and no evidence for M–X homolysis was found.[51] The reactivity can be summarized by Scheme III.

---

(43) The following reactions have also been reported:

$$CpMo(CO)_3X + 4PR_3 \rightarrow CpL^+ + Mo(CO)_3L_3 + X^-$$

See: Mawbry, R. J.; White, C. *Inorg. Chim. Acta* **1970**, *4*, 261–266.

(44) Other control experiments are consistent with the above interpretation of reactions leading to $CpMo(CO)_3^-$ and $Mo(CO)_3(py)_3/Mo(CO)_4(py)_2$. Thus, $CpMo(CO)_2(py)Cl$ and $CpMo(CO)(py)_2Cl$ do not react with py in the dark (2 h) to yield $Mo(CO)_3(py)_3$ or $Mo(CO)_4(CO)_2$. From this experiment we conclude that $Cp_2Mo_2(CO)_5py$ (and consequently $CpMo(CO)_3py^+$) is a necessary intermediate on the pathway to $Mo(CO)_3(py)_3$. In addition, $CpMo(CO)_3^-$ does not react thermally or photochemically with py to yield $Mo(CO)_3(py)_3$ or $Mo(CO)_4(py)_2$.

(45) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246–4251.

(46) In early work,[23a] King et al. suggested that the photochemical substitution reactions of the $CpMo(CO)_3X$ complexes may proceed via M–X heterolysis. This suggestion was based on the observation that bidentate phosphine ligands reacted thermally with $CpMo(CO)_3X$ to give $[CpMo(CO)_2L_2]X$, which then reacted upon UV irradiation to give $CpMo(CO)L_2X$. However, our work and that of others[5] could find no evidence for M–X heterolysis in unsubstituted $CpMo(CO)_3X$ complexes. Also, control experiments showed that low-energy irradiation (λ > 490 nm) of $CpMo(CO)_3(PPh_3)^+$ and Cl^- did not yield $CpMo(CO)_2PPh_3Cl$. (λ > 345 nm did however.)

(47) The most reasonable mechanisms for formation of the $[Mn(CO)_4X]_2$ dimers are as follows:

mechanism 1

$$Mn(CO)_5X \xrightarrow{h\nu} Mn(CO)_4X + CO$$

$$2Mn(CO)_4X \rightarrow [Mn(CO)_4X]_2$$

See: Wrighton, M. S.; Morse, D. L.; Gray, H. B.; Ottesen, D. K. *J. Am. Chem. Soc.* **1976**, *98*, 1111–1119.

mechanism 2

$$Mn(CO)_5X \xrightarrow{h\nu} Mn(CO)_4X + CO$$

$$Mn(CO)_4X + Mn(CO)_5X \rightarrow Mn_2(CO)_9X_2$$

$$Mn_2(CO)_9X_2 \rightarrow Mn_2(CO)_8X_2 + CO$$

See: Tyler, D. R., manuscript in preparation.

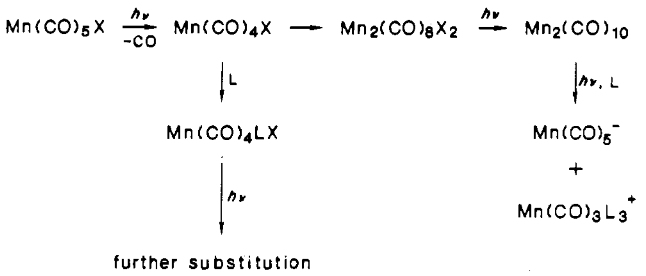
(48) Bamford, C. H.; Burley, J. W.; Coldbeck, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1846–1852.

(49) See also ref 18.

(50) Schuster, I. I.; Roberts, J. D. *J. Org. Chem.* **1979**, *44*, 2658–2662.

(51) Our earlier study also showed that Re–Br homolysis does not occur in the $Re(CO)_5Br$ complex. See: Tyler, D. R.; Petrylak, D. P. *Inorg. Chim. Acta* **1981**, *53*, L185–L187.

Scheme III



Note that Mn–X homolysis could be occurring to a small extent but that thermodynamics may prevent a reaction according to the mechanism in Scheme I. Wrighton and Faltynek showed that PPh_4^+ reacted with $Mn(CO)_5^-$ as follows:[52]

$$\mathrm{Mn(CO)_5^- + PPh_4^+ \rightarrow Mn(CO)_4(PPh_3)Ph + CO} \quad (21)$$

This reaction is essentially the back-reaction of eq 1 or 2. If the back-reaction is general, the conclusion is that $L{\cdot}X$ in Scheme I does not have the potential to reduce $Mn(CO)_5$ or, more likely, $Mn(CO)_5X$.

Electronic Structures. The electronic spectra of the $CpFe(CO)_2X$, $CpMo(CO)_3X$, and $Mn(CO)_5X$ complexes have been reported and discussed previously.[5,6,53,54] Briefly summarized, the low-energy absorption bands of the complexes are thought to be ligand field bands. Higher energy (near-UV) bands in the $CpFe(CO)_2X$ and $CpMo(CO)_3X$ complexes are assigned to M → CO(π^*) charge transfer while those in $Mn(CO)_5X$ are assigned to Mn → CO(π^*) with some admixture of I(π^*) → CO(π^*) charge transfer in the $Mn(CO)_5I$ complex. Of most importance to this study is the fact that no photochemically relevant bands in any of the complexes have been assigned as X(π^*) → M(σ^*) or X(σ^*) → M(σ^*) transitions. Efficient M–X homolysis generally requires these latter transitions;[55] we suggest their absence accounts for the lack of M–X homolysis.

Conclusions. The organometallic halide complexes in this study do not react analogously to the disproportionation reactions of metal–metal-bonded dimers (eqs 1 and 2). The lack of reactivity can be attributed to the absence of low-energy X → M charge-transfer bands, excitation into which would yield M–X homolysis. Despite the fact that analogous reactivity is not observed, ionic products do form in the photoreactions of these neutral halide complexes. Two pathways account for the formation of the ionic products: (1) M–X heterolysis (e.g. eq 18) and (2) dimer formation followed by subsequent disproportionation. The dimer may form via a secondary photolysis of a M–CO loss photoproduct (e.g. Scheme III), via M–X heterolysis (e.g. Scheme II), or via a minor M–X homolysis pathway, followed by coupling of two metal radicals (eq 14). This latter pathway occurs only with $CpMo(CO)_3X$ and only for the special case where the Mo–CO bond dissociation pathway is highly reversible, as in pyridine. Under these conditions, the Mo–X homolysis photoprocess becomes reasonably efficient relative to the Mo–CO dissociation pathway, allowing dimer formation to occur.

The reactivity of the halide complexes is in contrast to that of the related ML_nX (X = $SnCl_3$, $GeMe_3$, etc.) complexes.[56] Reactions analogous to eq 1 and 2 occur with these complexes, e.g.[57,58]

$$\mathrm{Co(CO)_4SnCl_3 \xrightarrow[h\nu]{L} Co(CO)_4L^+ + SnCl_3^-} \quad (22)$$

The next paper in this series will discuss the reactivity and mechanisms of these reactions.[56]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Air Force Office of Scientific Research for the support of this research. D.R.T. acknowledges the Alfred P. Sloan Foundation for a research fellowship.

Registry No. py, 110-86-1; $Mn(CO)_5Cl$, 14100-30-2; $Mn(CO)_5Br$, 14516-54-2; $Mn(CO)_5I$, 14879-42-6; $CpMo(CO)_3Cl$, 12128-23-3; $CpMo(CO)_3I$, 12287-61-5; $CpFe(CO)_2I$, 12078-28-3; Me_2SO, 67-68-5; $NH_2C_6H_{11}$, 108-91-8; $P(OBu)_3$, 102-85-2; PPh_3, 603-35-0; PPh_2Me, 1486-28-8; PBu_3, 998-40-3; $P(OMe)_3$, 121-45-9.

---

(52) Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 2701–2705.

(53) See ref 7, Chapter 2.

(54) (a) Vogler, A. In *Concepts in Inorganic Chemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; p 285. (b) Blakney, G. B.; Allen, W. F. *Inorg. Chem.* **1971**, *10*, 2763–2770.

(55) See: Endicott, J. F. In ref 54a, p 81.

(56) Philbin, C. E.; Pan, X.; Tyler, D. R., manuscript in preparation.

(57) In these latter complexes, electronic absorption bands analogous to the $\sigma \rightarrow \sigma^*$ absorption bands in the metal carbonyl dimers are observed. Homolysis of the M–X bond thus results.

(58) (a) Absi-Halabi, M.; Brown, T. C. *J. Am. Chem. Soc.* **1977**, *99*, 2982–2988. (b) Berry, A. D.; MacDiarmid, A. G. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 601–605. (c) Bald, Jr., J. F.; MacDiarmid, A. G. *J. Organomet. Chem.* **1970**, *22*, C22–C24.

(59) Dimerization of solvent-substituted metal carbonyl halide complexes is quite common. In addition to ref 15, see: Zingales, F.; Graziani, M.; Faraone, F.; Belluco, U. *Inorg. Chim. Acta* **1967**, *1*, 172–176.