no trace of H–Fe–I is observed in the infrared spectrum. The Mössbauer spectrum of Fe in pure HI shows the formation of FeI_2.

From these considerations, the products obtained from the reaction of iron atoms with the hydrogen halides as a function of HX (X = F, Cl, Br, I) concentration in inert matrices can be summarized as follows:

$$\mathrm{Fe + HX\ (<1\%) \rightarrow Fe_1} \qquad (4)$$

$$\mathrm{Fe + HX\ (1\text{–}10\%) \rightarrow H\text{–}Fe\text{–}X\ (X \neq F)\ or\ Fe(FH)\ (X = F)} \qquad (5)$$

$$\mathrm{Fe + HX\ (>7\%) \rightarrow FeX_2} \qquad (6)$$

Thus, as the HX concentration is progressively raised, (4), then (5), then (6) becomes the predominant reaction.

Acknowledgment. This work was supported by a grant from the Deparment of Energy (Contract DE AS03-76SF00034). We thank the University of California for assistance in purchasing the infrared spectrometer. We thank Dr. M. Doeff for the HCl–DCl experiment.

Registry No. Fe, 7439-89-6; HCl, 7647-01-0; HBr, 10035-10-6; HI, 10034-85-2; HF, 7664-39-3; Ar, 7440-37-1; H-Fe-Cl, 88610-39-3; H-Fe-Br, 88610-40-6; H-Fe-I, 88610-41-7; FeF_2, 7789-28-8; FeF_3, 7783-50-8; Kr, 7439-90-9.

Mechanism of Halogenation of Dimanganese, Manganese–Rhenium, and Dirhenium Decacarbonyls

Steven P. Schmidt, William C. Trogler,*[‡] and Fred Basolo*

Contribution from the Chemistry Department, Northwestern University, Evanston, Illinois 60201.

Received July 11, 1983

Abstract: The reactions between halogens ($X_2 = Cl_2, Br_2, I_2$, and ICl) and $M_2(CO)_{10}$ ($M_2 = Mn_2$, MnRe, and Re_2) in CH_3CN solvent yield equal amounts of $M(CO)_5X$ and $[M(CO)_5(CH_3CN)]^+$. For $X_2 = I_2$ the rate law was shown to obey second-order kinetics, $k[M_2(CO)_{10}][I_2]$. For $M_2 = Re_2$ the activation parameters were $\Delta H^\ddagger = 5.8 \pm 0.2$ kcal/mol and $\Delta S^\ddagger = -34.9 \pm 0.9$ cal/(mol K), for M_2 = MnRe $\Delta H^\ddagger = 6.3 \pm 1.5$ kcal/mol and $\Delta S^\ddagger = -41 \pm 6$ cal/(mol K), and for $M_2 = Mn_2$ $\Delta H^\ddagger = 8.5 \pm 1.4$ kcal/mol and $\Delta S^\ddagger = -39 \pm 5$ cal/(mol K). The relative rates of halogenation follow the order $Re_2(CO)_{10} > MnRe(CO)_{10} > Mn_2(CO)_{10}$, which opposes the order expected based upon homolysis of the metal–metal bond. The rate of iodination varies by more than a millionfold depending on the solvent. In nonpolar solvents such as decalin or toluene the oxidation proceeds slowly to yield $M(CO)_5I$, whereas in CH_3CN or CH_3NO_2 the reaction proceeds rapidly to produce both $M(CO)_5I$ and $[M(CO)_5(\text{solvent})]^+$. The evidence suggests that halogen attacks the metal–metal bond via one end of the dihalogen molecule and that heterolytic cleavage of the halogen–halogen bond takes place to yield free halide ion and a halogenium-bridged metal dimer. In many respects this resembles the mechanism for the bromination of alkenes.

The reaction between metal–metal bonded carbonyls and halogens frequently yields monomeric metal carbonyl halides.[1] For example, the standard preparation of $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I) proceeds from the action of X_2 on $M_2(CO)_{10}$.[2-7] Few mechanistic studies concerning this reaction type have been reported. Haines, Hopgood, and Poë described[8] the reaction between iodine and $Mn_2(CO)_{10}$ according to the rate law $k_1[Mn_2(CO)_{10}] + k_2[Mn_2(CO)_{10}][I_2]$. Here k_1 is a first-order rate constant similar to the rate of decomposition in an oxygenated solvent at the same temperature, and the second term results from a bimolecular reaction between I_2 and $Mn_2(CO)_{10}$. A similar rate law was obtained[9a] with $Re_2(CO)_{10}$ and I_2; however, the activation parameters differ greatly from those of $Mn_2(CO)_{10}$. The two iodination reactions were postulated[9a] to proceed by different mechanisms.

Candlin and Cooper[10] reported formation of a cluster–halogen charge-transfer complex in the reaction between $Os_3(CO)_{12}$ and Cl_2 or Br_2. The ultimate product is the linear molecule $[X\{Os(CO)_3\}_3X]$. A series of product studies for halogenation of $[\{M'(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$[11-14] (M′ = Fe or Ru) and $[\{M(\eta^5\text{-}C_5H_5)(CO)_2L\}]$ (M = Mo or W, L = CO; M = Mo, L = $P(OCH_3)_3$)[15,16] have suggested that these reactions proceed via a halogen-bridged intermediate. The general mechanism that was proposed involves initial electrophilic attack of the dihalogen molecule on the metal complex, followed by heterolytic cleavage of the halogen–halogen bond and formation of a halide-bridged cationic intermediate. This intermediate, which could be isolated in certain instances, then undergoes nucleophilic attack by the halide ion to afford the neutral halide complex. No kinetic studies were reported in support of this mechanism.

In other kinetic studies, Cullen and Hou[17] proposed a bimolecular pathway for the reaction of iodine and some $[M_2(CO)_8$-

---

[‡] Alfred P. Sloan Research Fellow (1983–1985). Address correspondence to the Department of Chemistry, D-006, University of California, San Diego, La Jolla, CA 92093.

(1) Candlin, J. P.; Taylor, K. A.; Thompson, D. T. "Reactions of Transition-Metal Complexes"; Elsevier: Amsterdam, 1968; pp 408–411.

(2) Brimm, E. O.; Lynch, M. A. *J. Am. Chem. Soc.* **1954**, *76*, 3831–3835.

(3) Abel, E. W.; Wilkinson, G. *J. Chem. Soc.* **1959**, 1501–1505.

(4) Hileman, J. C.; Huggins, D. K.; Kaesz, H. D. *J. Am. Chem. Soc.* **1961**, *53*, 2953–2954.

(5) King, R. B. "Organometallic Syntheses"; Eisch, J. J., King, R. B., Eds.; Academic Press: New York, 1965; Vol. 1, p 174.

(6) Reimer, R. J.; Shaver, A.; Quick, M. H.; Angelici, R. J. *Inorg. Synth.* **1979**, *19*, 158–163.

(7) Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorg. Synth.*, submitted for publication.

(8) Haines, L. I. B.; Hopgood, D.; Poë, A. J. *J. Chem. Soc. A.* **1968**, 421–428.

(9) (a) Haines, L. I. B.; Poë, A. J. *J. Chem. Soc. A* **1969**, 2826–2833. (b) Poë, A. J. *Inorg. Chem.* **1981**, *20*, 4029–4031.

(10) Candlin, J. P.; Cooper, J. *J. Organomet. Chem.* **1968**, *15*, 230–232.

(11) Brown, D. A.; Manning, A. R.; Thornhill, D. J. *J. Chem. Soc., Chem. Commun.* **1969**, 338.

(12) Haines, R. J.; Du Preez, A. L. *J. Am. Chem. Soc.* **1969**, *91*, 769–770.

(13) Haines, R. J.; Du Preez, A. L. *J. Chem. Soc. A.* **1970**, 2341–2346.

(14) Haines, R. J.; Du Preez, A. L. *J. Chem. Soc., Dalton Trans.* **1972**, 944–948.

(15) Burckett-St. Laurent, J. C. T. R.; Field, J. S.; Haines, R. J.; McMahon, M. *J. Organomet. Chem.* **1978**, *153*, C19–C22.

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

(17) Cullen, W. R.; Hou, F. L. *Inorg. Chem.* **1975**, *14*, 3121–3124.

0002-7863/84/1506-1308$01.50/0

(L–L)] complexes (M_2 = Mn_2, MnRe, or Re_2; L = a chelating group 5 ligand coordinated at the equatorial position of each metal atom). These reactions are faster than for the unsubstituted carbonyls, and the metal atoms remain connected through the chelating ligand. Poë and co-workers have also reported a series of kinetic studies on the oxidation of $[M_2(CO)_{10-n}L_n]$ (M_2 = Mn_2, MnRe, or Re_2; n = 1 or 2; L = phosphorus donor ligand) with Br_2[18] and I_2,[19] in addition to studies on $[Ru_3(CO)_9L_3]$[20] (L = PPh_3, $P(n\text{-}Bu)_3$, or $P(OPh)_3$) and $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$[21] with I_2, ICl, and Br_2. In all cases the kinetics data suggest the rapid formation of adducts (in a preequilibrium step) between the complex and one or more halogen molecules. It was postulated that the halogen molecules in the adducts are connected to the oxygen atoms of the CO ligands. Subsequent slow reactions involve weakening of the metal–metal bonds through intramolecular electron transfer and fission to form mononuclear halogeno complexes.

In view of the pivotal role that the $M_2(CO)_{10}$ complexes (M_2 = Mn_2, Re_2, and MnRe) have played in our understanding of substitution reaction mechanisms,[22-26] photochemistry,[27] spectroscopy, and bonding[28,29] in metal carbonyl clusters, we have embarked upon a study of their redox mechanisms. This paper reports a study of the products, solvent effects, and rates resulting from reactions between $M_2(CO)_{10}$ and I_2, Br_2, Cl_2, and ICl.

Experimental Section

Materials. Acetonitrile (Burdick and Jackson, 0.01% H_2O) was purified by three successive distillations under nitrogen, the first from CaH_2 and those subsequent from P_2O_5 (~5 g/L). All other solvents (reagent grade) were distilled before use. Decahydronaphthalene (decalin) and toluene were distilled from Na, and the decalin was bubbled with N_2 for 1 h after distillation. Dichloromethane and nitromethane were distilled from P_2O_5. The distilled nitromethane was also passed through a column of activated alumina. Hexane, after storage over H_2SO_4, and tetrahydrofuran were dried over sodium benzophenone ketyl and distilled prior to use. Iodine (Mallinckrodt) was sublimed twice, bromine (Baker) was vacuum distilled twice, and iodine monochloride (Baker) and chlorine (Matheson, High Purity) were used as received. Dimanganese carbonyl, purified by sublimation, and dirhenium carbonyl, used as received, were obtained from Strem Chemicals. Nitrosyl tetrafluoroborate (Alfa) was stored under N_2 at −35 °C.

Preparations. All of the preparations were performed at room temperature under an atmosphere of dry nitrogen. When necessary, solids were handled and stored in a Vacuum Atmospheres glovebox equipped with an HE-493 dri train. The glassware was dried at 110 °C and assembled immediately for use. The following compounds were prepared by literature methods or a slight modification thereof: $Mn(CO)_5Cl$,[3] $Mn(CO)_5Br$,[5] $Mn(CO)_5I$,[2] $Re(CO)_5X$ (X = Cl, Br, and I),[7] $KMn(CO)_5$,[30] $[Mn(CO)_5(NCCH_3)]BF_4$,[31] and CsI_3.[32] The infrared spectra of the carbonyl compounds in CH_3CN solvent appear in Table I in the supplementary material.

$MnRe(CO)_{10}$. A modified version of the method of Michels and Svec[33] was used. Manganese carbonyl (0.62 g, 1.6 mmol) was reduced to $KMn(CO)_5$ (0.70 g, 3.0 mmol) by action of an alkyl borohydride reagent.[30] The $KMn(CO)_5$ was transferred into 20 mL of THF in a 100-mL three-necked flask equipped with a reflux condenser and 50-mL addition funnel. A solution of $Re(CO)_5Br$ (1.2 g, 3.0 mmol) in 35 mL of THF was prepared in the addition funnel and was added dropwise to the clear, green solution. The resulting orange-yellow solution was stirred under N_2 for 12 h and refluxed for 2 h until the infrared bands of $Re(CO)_5Br$ and $KMn(CO)_5$ disappeared. The solution was concentrated to 25 mL under reduced pressure and filtered into a Schlenk flask equipped with a removable cold finger. After removal of the solvent by vacuum distillation at room temperature, sublimation of 60 °C at 0.1 mm static vacuum affords lemon-yellow needles of $MnRe(CO)_{10}$ (1.2 g, 70% yield, based on $Mn_2(CO)_{10}$). Infrared analysis showed no detectable amounts of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$.

Spectral Studies and Stoichiometry Experiments. Infrared spectra were recorded with a Perkin-Elmer 283 or a Nicolet 7199 FT-IR spectrophotometer using variable pathlength (0.1–0.5 mm) CaF_2 cells. Electronic absorption spectra were recorded with a Perkin-Elmer 330 or Hitachi 320 UV–vis spectrophotometer, and the samples were contained in 1.00-cm quartz cells specially adapted for use with air-sensitive compounds. Concentrations were determined by using the molar extinction coefficients measured for solutions of the pure compounds by IR and UV–vis spectrometry (Tables I and II, supplementary material). Details of the stoichiometry experiments for $Re(CO)_{10}$ are given below. The same procedures or slight modifications thereof apply to $Mn_2(CO)_{10}$ and $MnRe(CO)_{10}$.

$Re_2(CO)_{10}$ + Cl_2. $Re_2(CO)_{10}$ (0.10 mmol) in 15 mL of CH_3CN was bubbled with Cl_2 for 1 min with stirring at room temperature. The resulting green solution was evacuated to remove excess Cl_2, and an infrared spectrum revealed equimolar formation of $Re(CO)_5Cl$ and $[Re(CO)_5(NCCH_3)]^+$. To further confirm the identity of products, the solvent was removed under reduced pressure and the volatile $Re(CO)_5Cl$ was sublimed from the crude reaction residue at 80 °C (0.1 mm). Sublimation was continued (2 h) until all of the $Re(CO)_5Cl$ collects on the coldfinger. Analysis of the oily residue by infrared spectroscopy showed only $[Re(CO)_5(NCCH_3)]^+$. The identity of the anion could not be discerned by UV–vis spectrometry; however, since the stability of Cl_3^- is much lower than the I_3^- and Br_3^- counterparts,[34,35] it is reasonable to assume the anion is Cl^-.

$Re_2(CO)_{10}$ + Br_2. $Re_2(CO)_{10}$ (0.1 mmol) in 15 mL of CH_3CN was mixed with a Br_2 solution (0.4 mmol) in CH_3CN. After the solution was stirred, the infrared spectrum revealed the presence of $Re(CO)_5Br$ and $[Re(CO)_5(NCCH_3)]^+$ in a 1:1 ratio. As before, sublimation and infrared analysis established this product mixture, and the UV absorption spectrum showed the presence of Br_3^- (267 nm)[34] as the counterion.

$Re_2(CO)_{10}$ + I_2. $Re_2(CO)_{10}$ (0.1 mmol) in 15 mL of CH_3CN was mixed with freshly sublimed I_2 (0.4 mmol) dissolved in CH_3CN. An infrared spectrum (before and after separation by sublimation) showed the presence of $Re(CO)_5I$ and $[Re(CO)_5(NCCH_3)]^+$ in a 1:1 ratio, where the identity of the anion was determined to be I_3^- by UV analysis (362 and 294 nm).[34]

$Re_2(CO)_{10}$ + ICl. $Re_2(CO)_{10}$ (0.2 mmol) in 12 mL of CH_3CN was freeze–pump–thaw degassed several times and ICl (27 mmHg vapor pressure at 25 °C)[36] was vacuum transferred into the reaction mixture at −196 °C. The solution warmed to 25 °C, and infrared analysis revealed the 1:1 production of $Re(CO)_5I$ and $[Re(CO)_5(NCCH_3)]^+$. The identity of the anion could not be determined by UV–vis spectrometry. The initial $Re(CO)_5I$ product slowly reacts with excess ICl to yield $Re(CO)_5Cl$.

Kinetics Procedures. The rates of iodination of $Mn_2(CO)_{10}$ (M_2 = Mn_2, MnRe, Re_2) were determined by measuring changes in the electronic or infrared absorption spectra as a function of time. Care was taken to exclude room light during these experiments in order to avoid photochemical reactions. Rapid reactions were monitored with an Applied Photophysics Model 1705 stopped-flow instrument which was modified for work with air-sensitive solutions. In UV–vis experiments for slower reactions, a specially equipped 1.00-cm quartz cell was thermostated in the cell holder of the Perkin-Elmer 330 and Hitachi 320 spectrophotometers (±0.2 °C). For the infrared experiments a sealed flask was thermostated in a Polyscience Model 90 constant-temperature bath (±0.1 °C). For UV–vis experiments in CH_3CN, a solution of I_2

---

[18] Kramer, G.; Patterson, J.; Poë, A. *J. Chem. Soc., Dalton Trans.* **1979**, 1165–1171.

[19] Kramer, G.; Patterson, J.; Poë, A. J.; Ng, L. *Inorg. Chem.* **1980**, *19*, 1161–1169.

[20] Kramer, G.; Poë, A.; Amer, S. *Inorg. Chem.* **1981**, 20, 1362–1367.

[21] Amer, S.; Poë, A.; Kramer, G. *J. Organomet. Chem.* **1981**, *220*, 75–85.

[22] Basolo, F.; Wawersik, H. *Inorg. Chim. Acta* **1969**, *3*, 113–120.

[23] Sonnenberger, D.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 3484–3489.

[24] Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorg. Chem.* **1982**, *21*, 1698–1699.

[25] Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 822–827.

[26] Coville, N. J.; Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 2499–2500.

[27] Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

[28] Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 6042–6047.

[29] Martin, M.; Rees, B.; Mitschler, A. *Acta Crystallogr. Sect. B* **1982**, *B38*, 6–15.

[30] Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553–558.

[31] Drew, D.; Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1975**, *14*, 1579–1584.

[32] Briggs, T. R.; Greenawald, J. A.; Leonard, J. W. *J. Phys. Chem.* **1930**, *34*, 1950–1960.

[33] Michels, G. D.; Svec, H. J. *Inorg. Chem.* **1981**, *20*, 3445–3447.

[34] Popov, A. I. "Halogen Chemistry"; Gutmann, V., Ed.; Academic Press: New York, 1967; Vol. 1 p 256.

[35] Giordano, M. C.; Macagno, V. A.; Sereno, L. E. *Anal. Chem.* **1973**, *45*, 205–207.

[36] Shriver, D. F. "Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969; pp 275–276.

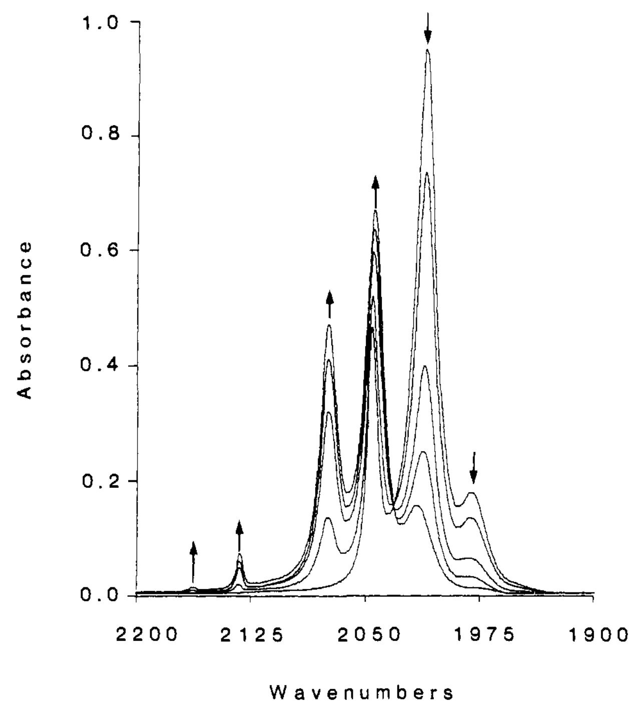


Figure 1. Infrared spectral changes for the reaction between 1.78 × 10^{-3} M $Mn_2(CO)_{10}$ and 2.59 × 10^{-2} M I_2 in CH_3CN at 25.0 °C.

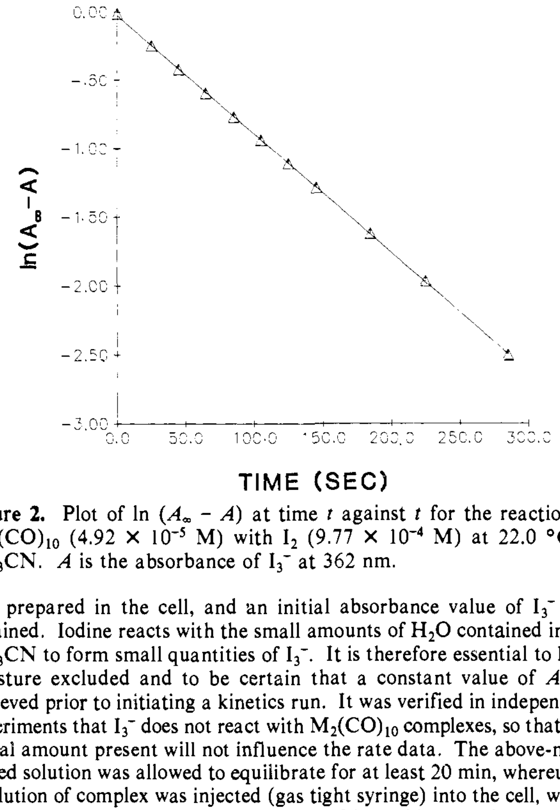


Figure 2. Plot of ln (A_∞ - A) at time t against t for the reaction of $Re_2(CO)_{10}$ (4.92 × 10^{-5} M) with I_2 (9.77 × 10^{-4} M) at 22.0 °C in CH_3CN. A is the absorbance of I_3^- at 362 nm.

was prepared in the cell, and an initial absorbance value of I_3^- was obtained. Iodine reacts with the small amounts of H_2O contained in the CH_3CN to form small quantities of I_3^-. It is therefore essential to keep moisture excluded and to be certain that a constant value of A_0 be achieved prior to initiating a kinetics run. It was verified in independent experiments that I_3^- does not react with $M_2(CO)_{10}$ complexes, so that any initial amount present will not influence the rate data. The above-mentioned solution was allowed to equilibrate for at least 20 min, whereupon a solution of complex was injected (gas tight syringe) into the cell, which was vigorously shaken. The appearance of I_3^- at 291 or 362 nm can be followed for at least 3 half-lives. In addition, for every such experiment the absorbance at 291 or 362 nm showed 1 equiv of I_3^- was produced per equiv of $M_2(CO)_{10}$.

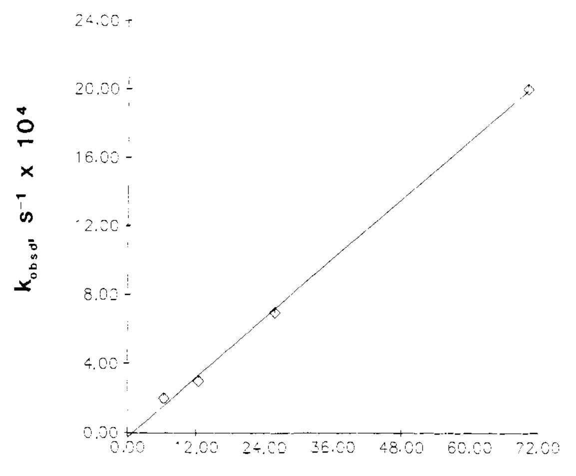


Figure 3. Plot of k_{obsd} (s^{-1}) vs. I_2 concentration for the reaction of $Mn_2(CO)_{10}$ and I_2 at 25.0 °C in CH_3CN.

Table I. Rate Constants at 25.0 °C and Activation Parameters[a] for Reactions 1 and 2, Where $X_2 = I_2$

complex	k_2, s^{-1} M^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal mol^{-1} K^{-1}
$Mn_2(CO)_{10}$	2.87 ± 0.24 × 10^{-2}	8.5 ± 1.4	−39 ± 5
$MnRe(CO)_{10}$	1.69 ± 0.41 × 10^{-1}	6.3 ± 1.5	−41 ± 6
$Re_2(CO)_{10}$	8.76 ± 0.21	5.8 ± 0.2	−34.9 ± 0.9

[a] Errors represent 95% confidence limits from a least-squares analysis.

An infrared sampling technique was employed for slower reactions. In each case solutions of reactants were mixed in the appropriate solvent and samples were removed by syringe. At least six readings were taken over a period of three half-lives. The absorbance of the most isolated IR band was monitored, and in some cases the absorbances of several bands were included to check the agreement of calculated rate constants. A sample experiment for the infrared spectrophotometric monitoring of the reaction between $Mn_2(CO)_{10}$ and I_2 in CH_3CN is shown in Figure 1. When the order of I_2 was determined in the high-temperature decalin reactions, a sample was removed by syringe and placed in a 1.00-cm cuvette where the visible absorbance (518 nm) due to unreacted I_2 could be monitored.

All rate constants were measured under pseudo-first-order conditions with the concentration of halogen about 10 times that of the complex (or vice versa). The initial concentration of halogen and complex could be determined either by weighing the cell and calculating the appropriate dilution or by measuring the initial absorbance due to halogen and the absorbance change after complete reaction (1 equiv of $M_2(CO)_{10}$ produces 1 equiv of X_3^-). Plots of ln (A_∞-A) or ln (A - A_∞) vs. time were linear ($r^2 > 0.995$) for 2-3 half-lives for all reactions investigated. A typical plot is shown in Figure 2. Observed pseudo-first-order rate constants were calculated from the slope of the line by a least-squares program. Individual reproducibility of rate constants was generally within 5%. Least-squares error analyses for the I_2 concentration dependence plots and Arrhenius plots were performed and are provided in the data tables (errors reported are three standard deviations).

Results

The IR and UV-vis spectral studies show (e.g., Figure 1) that the stoichiometry of the halogenations (X = Cl, Br, I) of $M_2(CO)_{10}$ (M_2 = Mn_2, MnRe, Re_2) can be described by reactions 1 and 2.

$$M_2(CO)_{10} + X_2 \xrightarrow[k_{obsd}]{CH_3CN} M(CO)_5X + [M(CO)_5(NCCH_3)]^+ + X^- \text{ (or } X_3^-\text{)} \quad (1)$$

$$M_2 = Mn_2, Re_2$$

$$MnRe(CO)_{10} + X_2 \xrightarrow[k_{obsd}]{CH_3CN} Mn(CO)_5X + [Re(CO)_5(NCCH_3)]^+ + X^- \text{ (or } X_3^-\text{)} \quad (2)$$

In the case of Cl_2, it is believed that Cl^- is the counterion. For Br_2 and I_2, the counterion was shown to be Br_3^- or I_3^-, respectively. All pseudo-first-order reactions with excess I_2 gave linear plots of ln (A_∞ - A) vs. t or ln (A - A_∞) vs. t (Figure 2). Subsequent experiments were performed to determine the rate law for these reactions by establishing the dependence of rate upon I_2 concentration. A sample plot of k_{obsd} vs. $[I_2]$ is shown in Figure 3 for the oxidation of $Mn_2(CO)_{10}$. A similar dependence of $[I_2]$ was found for $MnRe(CO)_{10}$ and $Re_2(CO)_{10}$. The second-order rate constants and the activation parameters are collected in Table

Table II, Rate Constants for the Reaction of $Re_2(CO)_{10}$ and I_2 in Decalin

$[Re_2(CO)_{10}]$, M	$[I_2]$, M	k_{obsd}, s^{-1} [a]	T, °C
4×10^{-4}	4.82×10^{-3}	5.9×10^{-5}	130[b]
2.11×10^{-4}	1.76×10^{-3}	1.74×10^{-4}	130
3.62×10^{-3}	3.28×10^{-2}	9.32×10^{-6}	25
	3.28×10^{-2}	4.93×10^{-6}	25[d]
9.49×10^{-3}	1.62×10^{-3} [c]	6.59×10^{-5}	120
3.21×10^{-3}	2.87×10^{-2}	3.77×10^{-4}	129,2
3.21×10^{-3}	2.87×10^{-2}	2.13×10^{-4}	119.3
3.21×10^{-3}	2.87×10^{-2}	1.35×10^{-4}	109.6

[a] Monitoring rate of disappearance of $Re_2(CO)_{10}$ at 2074 cm^{-1}, pseudo first order in I_2. [b] Reference 9. [c] Pseudo first order in $Re_2(CO)_{10}$. [d] Calculated from the activation parameters.

Table III, Activation Parameters[a] for the Iodination of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ in Decalin

complex	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
$Mn_2(CO)_{10}$[b]	28.0 ± 0.3[c] (31)	+4.7 ± 0.9 (+10)
$Re_2(CO)_{10}$	15 ± 3 (16.9 ± 1.2)	−30 ± 6 (−26.1 ± 1.8)

[a] Values in parentheses are from ref 8 and 9a. [b] Decomposition of product posed a problem in this case. [c] Errors represent three standard deviations.

I (CH_3CN solvent). Complete tables of the observed rate constants as a function of concentration and temperature are available as supplementary material.

The case of iodine monochloride is more complicated, and FT-IR studies reveal the following series of reactions (3–5).

$$M_2(CO)_{10} + ICl \xrightarrow{CH_3CN} M(CO)_5I + [M(CO)_5(NCCH_3)]^+ + Cl^- \quad (3)$$

$$M_2 = Mn_2, Re_2$$

$$MnRe(CO)_{10} + ICl \xrightarrow{CH_3CN} Mn(CO)_5I + [Re(CO)_5(NCCH_3)]^+ + Cl^- \quad (4)$$

$$M(CO)_5I + ICl \rightarrow M(CO)_5Cl + I_2 \quad (5)$$

No attempt was made to measure rates with ICl due to the complications from halogen exchange and the fact that the initial reactions are complete upon warming the frozen sample. The reaction between $Mn_2(CO)_{10}$ and Br_2 was the only bromination that we were able to monitor with the stopped-flow spectrophotometer. A reaction with 6.08×10^{-5} M $Mn_2(CO)_{10}$ and 1.52×10^{-3} M Br_2 gave a k_{obsd} of 1.26×10^{-2} s^{-1}, In addition, several competition experiments were performed. For example, 1.17×10^{-2} M $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ solutions in CH_3CN were combined with a 1.26×10^{-2} M Br_2 solution. Analysis by FT-IR revealed no detectable trace of oxidized manganese product. Therefore, as we found for the I_2 oxidations, $Re_2(CO)_{10}$ must react much faster than does $Mn_2(CO)_{10}$.

In decalin solvent, reactions 6 and 7 were observed. Both

$$Mn_2(CO)_{10} + I_2 \xrightarrow[k_{obsd}]{decalin} 2Mn(CO)_5I \quad (6)$$

$$Re_2(CO)_{10} + I_2 \xrightarrow[k_{obsd}]{decalin} 2Re(CO)_5I \quad (7)$$

reactions exhibited excellent pseudo-first-order behavior for the disappearance of $M_2(CO)_{10}$ in the presence of excess I_2 as well as for the disappearance of I_2 in the presence of excess $M_2(CO)_{10}$ (Table II). These experiments establish the rate law (eq 8).

$$-d[M_2(CO)_{10}]/dt = k_2[M_2(CO)_{10}][I_2] \quad (8)$$

Decomposition of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ did not complicate our kinetic experiments; however, we did observe a thermal instability and/or decomposition of the $Mn(CO)_5I$ to form a precipitate. Activation parameters for the decalin reactions are given in Table III, along with those reported in the literature.[8,9a] Tables of observed rate constants as a function of concentration and temperature are available as supplementary material.

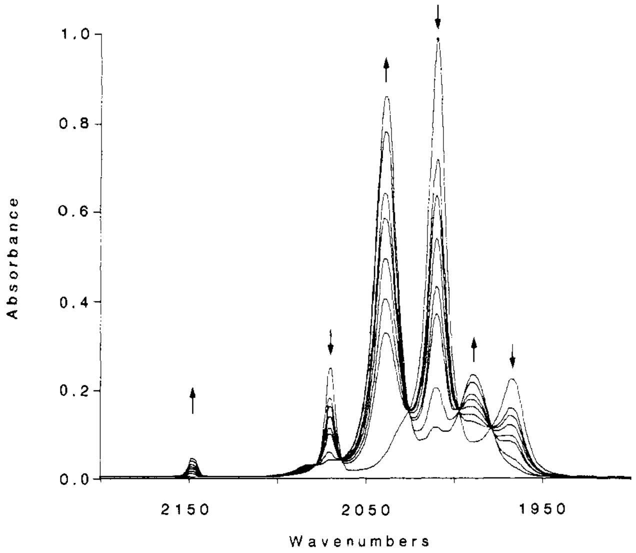


Figure 4. Infrared spectral changes for the reaction between 5.45×10^{-3} M $Re_2(CO)_{10}$ and 5.45×10^{-2} M I_2 in THF at 25 °C.

Table IV, Rate Constants for the Iodination of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ in Various Solvents at 25 °C[a]

solvent	position of I_2 absorption, nm	ϵ (25 °C)[b]	solvent acceptor number[c]	k_2, s^{-1} M^{-1}	
				$Mn_2(CO)_{10}$	$Re_2(CO)_{10}$
NO_2CH_3		38.6	24.5	5.91×10^{-2}	
CH_3CN	460	36.2	19.3	2.87×10^{-2}	1.02×10^{1} [d]
CH_2Cl_2	502	8.9	20.4	1.39×10^{-3}	5.69×10^{-2} [e]
THF	454	7.32	8.0	4.17×10^{-5}	5.06×10^{-2}
toluene	496	2.38	8.2	[f]	1.05×10^{-4} [e]
decalin	518	2.2	0	ca. 10^{-11} [g]	2.84×10^{-4}

[a] Rates were determined by monitoring the most separated product or reactant peak. [b] Reference 37. [c] From ref 39; the value for benzene is used for toluene. [d] 22 °C. [e] 30 °C. [f] Too slow to measure at 50 °C. [g] Extrapolated from the activation parameters in Table III.

To span intermediate ranges of solvent polarity, four other solvents were used in the iodinations: toluene, CH_2Cl_2, THF, and CH_3NO_2. In each case the reactions were followed by IR or UV-vis spectroscopy, and, in toluene, CH_2Cl_2, and THF, the sole products were the metal pentacarbonyl iodides. The IR spectral changes for the reaction between I_2 and $Re_2(CO)_{10}$ in THF are shown in Figure 4. For the CH_3NO_2 solvent, a small amount (13%) of the product exists as $[Re(CO)_5(CH_3NO_2)]I_3$ (ν_{CO} = 2163 (w), 2076 (s), and 2046 cm^{-1} (m)), with the remainder present as $Re(CO)_5I$. The dielectric constants[37] of the solvents studied and the second-order rate constants for the iodinations of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ are provided in Table IV.

Discussion

Previous studies of the rates of iodine oxidation of $M_2(CO)_{10}$ (M = Mn and Re) in decalin solvent suggested the rate law[8,9a]

$$\text{rate} = k_1[M_2(CO)_{10}] + k_2[M_2(CO)_{10}][I_2] \quad (9)$$

These experiments[8,9a] were conducted at several higher temperatures than in our investigation. Attention was devoted primarily to the I_2 independent term in the rate law and to its similarity with the ligand substitution mechanism. The mechanism for the I_2-dependent pathway was not considered in detail. It should be noted that the ligand substitution mechanism proposed in the early studies[8,9a,b] has been disproven.[23-26] In contrast to the previous studies, our concern was the mechanism of the second-order process, and the experiments were conducted at conditions where this is the exclusive pathway. However, we did investigate the

---

(37) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; pp 3–13.

reaction of $Mn_2(CO)_{10}$ in decalin solution at 110 °C and obtained results in agreement with the previously reported[8,9a] two-term rate law (eq 9).

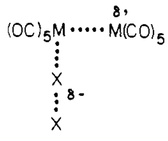
The rates of oxidation and the activation parameters (Table III) do differ significantly from those reported[8,9a] for CO substitution (Mn_2,[8] $\Delta H^\ddagger = 36.2 \pm 0{,}3$ kcal mol^{-1}, $\Delta S^\ddagger = 16.8 \pm 0.7$ cal mol^{-1} K^{-1}; Re_2,[9a] $\Delta H^\ddagger = 38{,}6 \pm 0{,}4$ kcal mol^{-1}, $\Delta S^\ddagger = 13{,}7 \pm 1.0$ cal mol^{-1} K^{-1}). The CO substitution process obeys a purely first-order rate law, $k[M_2(CO)_{10}]$,[22-26] in contrast to that observed for iodination. The substitution and halogenation mechanisms, therefore, appear to be unrelated. This conclusion has to be qualified for $Mn_2(CO)_{10}$. The observed activation parameters were sufficiently different from the dirhenium case (Table III) to cause concern. One problem with the $Mn_2(CO)_{10}$ kinetics experiments was the decomposition of $Mn(CO)_5I$ to an unidentified insoluble precipitate during the latter stages of the oxidation reaction. Consequently, we view the kinetic parameters for the dimanganese system (in decalin solvent) with caution and do not believe that a partial contribution from CO dissociation can be ruled out.

One question concerning reaction 10 is whether both M–X

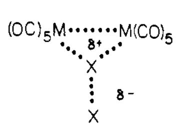
$$M_2(CO)_{10} + X_2 \rightarrow 2\ M(CO)_5X \qquad (10)$$

bonds form simultaneously or whether cationic metal complex intermediates are involved. In order to gain insight into this problem, we examined redox reactions in coordinating solvents.

Acetonitrile seemed a good choice for a solvent, because the $[Mn(CO)_5(CH_3CN)]^+$ and $[Re(CO)_5(CH_3CN)]^+$ complexes are known and substitute acetonitrile relatively slowly.[31] *In this solvent* $Mn_2(CO)_{10}$ *and* $Re_2(CO)_{10}$ *react cleanly with* I_2, Br_2, *and* Cl_2 *to yield 1 equiv of the appropriate metal pentacarbonyl halide and 1 equiv of the metal pentacarbonyl acetonitrile cation* (*eq 1*). The product distributions, second-order rate law for the I_2 oxidations, and relatively negative $\Delta S^\ddagger$ (Table I) are consistent with an end-on attack of halogen on the metal–metal bond either at one or both metal centers;



a

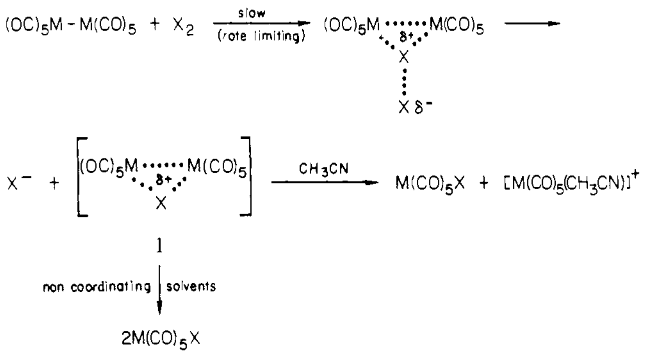


b

This also conforms with the observation that ICl attacks the metal via the iodine atom to yield $M(CO)_5I$ and $[M(CO)_5(CH_3CN)]Cl$. In this way the δ– charge develops on the highly electronegative chlorine atom. The ascending order of the rate constants parallels the increase in the dielectric constants of the solvents (Table IV) and spans 10^5–10^9 orders of magnitude. This dramatic solvent effect would be expected for a reaction proceeding via a polar transition state. In poorer coordinating solvents, the amount of $M(CO)_5X$ product increases along with a decrease in rate. The smooth transition in rates upon changing solvent (Table IV) and similar activation parameters (a negative $\Delta S^\ddagger$ in all but one case) measured in acetonitrile and decalin (Tables I and III) could mean that the mechanism is fundamentally the same in all of the solvents or that a smooth change in mechanism takes place. For example, in nonpolar solvents the species a and b could fragment to produce neutral intermediates such as $M(CO)_5I$ and $\{M(CO)_5,I\}$ in a radical cage. In order to further probe the mechanism in nonpolar media, we analyzed the affect of added CH_3CN on the rate and product distribution in toluene solutions.

For the iodination of $Re_2(CO)_{10}$, when $[CH_3CN] = 1.97 \times 10^{-1}$ M and 5.52×10^{-1} M, the respective rate constants are $k_2 = 6.00 \times 10^{-4}$ and 4.81×10^{-3} s^{-1} M^{-1} at 30 °C. These values are significantly greater than that of the reaction in pure toluene (Table IV). We attribute this smooth rate increase to the concomitant increase in solvent polarity upon increasing the acetonitrile concentration. Interestingly, $[Re(CO)_5(CH_3CN)]^+$ or I_3^- could not be detected until $[CH_3CN]$ reached 1.90 M, whereupon a small (~5%) amount of the cation is produced. Since halide ion will be produced in the second coordination sphere when intermediate a or b fragments, it is not surprising that significant concentrations of CH_3CN are necessary to alter the product distribution.

Scheme I. Mechanism for Halogen Oxidation of Dimetal Decacarbonyls



An alternative explanation for the solvent effects on the rate would be the involvement of halogen-solvent charge-transfer complexes as oxidants. It is well-known that I_2 forms donor–acceptor complexes with numerous solvents. This interaction is characterized by a blue shift in the normal $\sigma \rightarrow \sigma^*$ transition (at 518 nm in decalin and at 517 nm in the vapor phase[38]) of the I_2 molecule.[39,40] From the data in Table IV, it is clear that the rate acceleration does not correlate well with the position of the I_2 absorption. It is believed that the transfer of charge from solvent to I_2 and the increase in the I–I bond length parallel the blue shift in the I_2 absorption.[39,40] The rate constants also do not correlate with the solvent donor numbers of Gutmann,[39] and there is a marginal dependence on solvent acceptor numbers (Table IV). It has been noted[39] that anionic members of a redox couple become stabilized in "acceptor" solvents due to favorable solvation of the anion. In a sense, this is equivalent to our rationale that the more polar solvents stabilize the ionic transition states depicted in a and b.

One surprising aspect of the results concerns the relative ordering for the ease of oxidation $Re_2(CO)_{10} > MnRe(CO)_{10} > Mn_2(CO)_{10}$. From Table I it can be seen that the ordering arises primarily from the differences in $\Delta H^\ddagger$. Regardless of the mechanism, the metal–metal bond must be broken, yet the enthalpy of activation is greatest for the complex that contains the weakest metal-metal bond.[41-46] A rationale based upon redox potentials[18,19] is, on the one hand, questionable because $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ exhibit identical anodic peaks at 1.56 V (vs. SCE) in CH_3CN solvent.[47a] Another investigation[47b] of the oxidation behavior of $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$, and $Re_2(CO)_{10}$ in DMF solvent places their respective anodic waves at +1.8, +1.7, and +1.65 V vs. SCE. These latter data indicate that the greater ease of halogenation of $Re_2(CO)_{10}$ could be attributed to a more favorable potential for oxidation. Differences in the steric environment of the metal-metal bond could also contribute to the observed variation in k_2 (Table I). The metal-metal bond lengths of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ are 3.0413 (11) and 2.9038 (6) Å,

---

(38) Herzberg, G. "Molecular Spectra and Molecular Structure", 2nd ed.; Van Nostrand Reinhold: New York, 1950.

(39) Gutmann, V. "The Donor-Acceptor Approach to Molecular Interactions"; Plenum Press: New York, 1978.

(40) Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York, 1969.

(41) Quicksall, C. O.; Spiro, T. G. *Inorg. Chem.* **1969**, *8*, 2363–2367.

(42) Spiro, T. G. *Prog. Inorg. Chem.* **1970**, *11*, 1–51.

(43) Good, W. D.; Fairbrother, D. M.; Waddington, G. *J. Phys. Chem.* **1958**, *62*, 853–857.

(44) Connor, J. A.; Skinner, H. A.; Virami, Y. *J. Chem. Soc., Faraday Trans. I* **1972**, *68*, 1754–1763.

(45) Connor, J. A.; Skinner, H. A.; Virmani, Y. *Symp. Faraday Soc.* **1973**, *8*, 18–28.

(46) Connor, J. A.; Skinner, H. A. In "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, pp 197–205.

(47) (a) Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1975**, 879–886. (b) Lemoine, P.; Gross, M. *J. Organomet. Chem.* **1977**, *133*, 193–199. We thank an alert referee for pointing out the alternative redox potentials in this reference.

respectively.[48] Furthermore, the M–C equatorial distances are 1.853 (2) for $Mn_2(CO)_{10}$ and 1.973 (6) for $Re_2(CO)_{10}$. For these reasons, it is reasonable to assume that I_2 may approach the metal–metal bond most readily in the case of $Re_2(CO)_{10}$.

In the context of these results, consider the reactivity of $MnRe(CO)_{10}$. As expected the rate of halogenation lies between those of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. The product distribution of $Mn(CO)_5I$ and $Re(CO)_5(CH_3CN)^+$ does not follow directly from the greater ease of halogen attack at $Re_2(CO)_{10}$ compared to $Mn_2(CO)_{10}$. If intermediate a were involved, then $Re(CO)_5I$ and $Mn(CO)_5(CH_3CN)^+$ would be the expected products (i.e., halogen attack would occur at the larger metal atom). Therefore, a mechanism involving species b (as outlined in Scheme I) is preferred. A symmetrically bridged intermediate (**1** in Scheme I) could cleave to form the most stable products. Apparently these are $Mn(CO)_5X$ and $[Re(CO)_5(CH_3CN)]^+$ when $MnRe(CO)_{10}$ is the reactant. Although we made several attempts to directly measure the equilibrium (eq 11) from both directions, these efforts

$$Mn(CO)_5(CH_3CN)^+ + Re(CO)_5I \rightleftarrows Mn(CO)_5I + Re(CO)_5(CH_3CN)^+ \quad (11)$$

were not successful. Alternatively, an intermediate such as **1** (Scheme I) may fragment due to attack by the CH_3CN nucleophile. Since steric access is more facile at Re, then this could also account for the product distribution.

Conclusions

The associative pathway for the halogenation of $M_2(CO)_{10}$ seems to involve a halogenium intermediate (Scheme I) that bears a resemblance to the bromonium ion which has been invoked in the mechanism of bromination of alkenes.[49,50] There is precedent for similar species in the inorganic literature. For example, the intermediate proposed in reactions of $[\{M'(C_5H_5)(CO)_2\}_2]$ (M' = Fe or Ru)[11-14] and of $[\{M(C_5H_5)(CO)_2L\}_2]$ (M = Mo or W, L = CO; M = Mo, L = $P(OCH_3)_3$)[15,16] with halogens. For the case of the Mo or W dimers the species $[\{M(C_5H_5)(CO)_3\}_2(\mu\text{-}I)][B(C_6H_5)_4]$ has been isolated. It was suggested that nucleophilic attack on the bridged intermediate by the free halide ion (generated in the reaction) results in formation of the monomeric halides. We do no favor a mechanism for halogenation of $M_2(CO)_{10}$ complexes similar to that proposed for $M_2(CO)_8(PPh_3)_2$ (M = Mn_2, MnRe, Re_2).[18,19] With the substituted complexes, evidence for prior complex formation was indicated by initial fast spectral changes and the complexation of I_2 to carbonyl oxygen was suggested.[18,19] For the systems $M_2(CO)_{10}$ in the various solvents used, we find no evidence for significant quantities of a $[M_2(CO)_{10}]\cdot X_2$ adduct.[51] Oxidation in CH_3CN and other solvents appears to involve a bimolecular attack by X_2 according to an inner-sphere mechanism[52] depicted in Scheme I.

Acknowledgment. This paper is based upon work supported by the National Science Foundation Grant No. CHE-8210514 and -8402168.

Registry No. Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2; ICl, 7790-99-0; $Mn_2(CO)_{10}$, 10170-69-1; $MnRe(CO)_{10}$, 14693-30-2; $Re_2(CO)_{10}$, 14285-68-8.

Supplementary Material Available: Tables of infrared and electronic absorption spectral data used in the kinetics analyses and tables of rate constants for the reaction between $Mn_2(CO)_{10}$ and I_2 in CH_3CN, $MnRe(CO)_{10}$ and I_2 in CH_3CN, $Re_2(CO)_{10}$ and I_2 in CH_3CN, and $Mn_2(CO)_{10}$ and I_2 in decalin (6 pages). Ordering information is given on any current masthead page.

---

(48) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609–1611.

(49) March, J. "Advanced Organic Chemistry—Reactions, Mechanisms, and Structure"; McGraw-Hill: New York, 1977; p 281.

(50) Alder, R. W.; Baker, R.; Brown, J. M. "Mechanism in Organic Chemistry"; Wiley-Interscience: London, 1971; pp 295–305.

(51) It should be noted that the phosphine-substituted clusters are significantly more reducing than the parent complexes. The formation of a charge-transfer complex with iodine in the substituted clusters may be rationalized on the basis of this difference.

(52) Taube, H. "Electron Transfer Reactions of Complex Ions in Solution"; Academic Press: New York, 1970.