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Electrophilic Attack at Metal Carbonyls. Kinetics of Reactions of Halogens with Some Substituted Dimetal Carbonyls^{1,2}

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The kinetics have been studied of reactions (in cyclohexane or decalin) of iodine with a number of dimetal carbonyls $M_2(CO)_{10-x}L_x$ (for $x = 1$, $M = Re$, $L = PPh_3$; for $x = 2$, $M_2 = Mn_2$, $MnRe$, and Re_2 , $L = PPh_3$; for $x = 2$, $M = Mn$, $L = P(OPh)_3$, $P(OMe)_3$, PPh_3 , $P(p-MeOC_6H_4)_3$, PPh_2Et , $PPhEt_2$, PEt_3 , $P(n-Bu)_3$, and $P(C_6H_{11})_3$). The reactions are first order in the concentration of the reacting complex. The predominant term in most of the rate equations is $k_3[I_2]^2$, but a term as high as $k_5[I_2]^4$ is observed in one case, and for $Mn_2(CO)_8[P(OPh)_3]_2$ the rate equation is $k_{obsd} = \{k_3[I_2]^2 + k_4[I_2]^3\}/\{1 + \beta_1[I_2] + \beta_2[I_2]^2 + \beta_3[I_2]^3\}$. Some reactions were also followed in CCl_4 , CH_2Cl_2 , $MeOH$, $EtOAc$, and $n-Bu_2O$. The reactions are concluded to involve rapid preformation of a series of adducts, complex- nI_2 , where n can be as high as 4. This is followed by electron transfer and fission of the metal-metal bond with formation of mononuclear iodo complexes. The effects of the nature of L on the rate constants for reactions with I_2 or Br_2 can best be interpreted in terms of initial electrophilic attack at the O atoms of the CO ligands, the surface of the complex providing an extended area of suitably high electron density which can bind several halogen molecules. The electronic effect appears to operate mainly through the σ -donor ability of the substituents and not their π -acid character. Some comparisons are drawn with reactions of halogens with other metal-carbonyl complexes and with some aryl-Sn compounds.

Introduction

Reactions of halogens with polynuclear metal carbonyls have received little kinetic study²⁻⁷ although they proceed with partial or complete breaking of the metal cluster framework.⁸⁻¹⁰ They could therefore provide a quantitative measure of the susceptibility of such clusters to fragmentation. We have recently reported kinetic studies of the reactions of bromine with a number of group 7 dinuclear carbonyls that were axially substituted with phosphorus-donor ligands.⁷ These studies showed that reaction proceeded via initial formation of complex- nBr_2 adducts in a labile preequilibrium, the number of Br_2 molecules in the eventual transition state being as high as three in one case. There was a strong dependence of the rates on the basicity of the substituents, but this was offset, in some cases, by steric effects. It was concluded that the major factor determining these relative rates was the electron density at the O atoms of the CO ligands and that electrophilic attack by the Br_2 occurred at or near these atoms. We report here a series of analogous studies of the reactions of I_2 with such complexes.

Experimental Section

The axially substituted complexes and solvents used were exactly as described before¹¹ apart from the complex $Mn_2(CO)_8[P(p-MeOC_6H_4)_3]_2$ which was a gift from Dr. R. A. Jackson. Stock solutions of I_2 (Baker Analyzed reagents) were prepared by weighing, and their stability was checked spectroscopically. Carbon tetrachloride, dichloromethane, and methanol were dried over molecular sieves.

Unless otherwise specified, the reactions were followed in cyclohexane at 25.0 °C. $Mn_2(CO)_8[P(p-MeOC_6H_4)_3]_2$ was slow to dissolve

in cyclohexane and was therefore dissolved initially in a few drops of CH_2Cl_2 . This was removed under reduced pressure after addition of cyclohexane. Other solutions were prepared, and all the kinetic runs were performed, exactly as described previously.⁷ Reactions were followed by monitoring the decrease in intensity of the absorption maximum in the near-UV that is characteristic of all these complexes.^{11,12}

Analysis of Data. The first-order nature of the reactions with respect to the initial concentrations, C_0 , of the reactant complexes was generally established from the constancy of observed values of pseudo-first-order rate constants, k_{obsd} , over a range of values of C_0 . The dependence of values of k_{obsd} on $[I_2]$ was usually more or less complex, and graphical analysis was used initially to establish the probable form of the relationship. Where possible, the presumed rate equations were rearranged into linear form so that a linear least-squares analysis could be performed by using standard types of computer programs. Values of k_{obsd} for a particular set of runs were assumed to have a constant percent uncertainty and were weighted appropriately. Standard deviations obtained from such analyses were adjusted according to the number of degrees of freedom involved so that 95% confidence levels could be obtained by doubling them, and it is these adjusted values that are quoted. In some cases the rate equations took the form of a simple power series and were analyzed by an appropriate nonlinear program while in other, more complicated, cases where fractions were involved a nonlinear optimization technique was adopted that involved the subroutine VAO4A.¹³ This required initial estimates of the parameters to be chosen, and these were available from the graphical analyses. The program varies the initial estimates systematically until $\sum(\Delta\%)^2$ is minimized. $\Delta\% = 100(k_{obsd} - k_{calcd})/k_{calcd}$, where k_{calcd} is the value expected for the pseudo-first-order rate constant according to the particular rate equation and to the set of values being considered for the parameters. When there was doubt as to the importance of a parameter widely divergent, initial estimates were used to ensure that the minimum in $\sum(\Delta\%)^2$ was not a misleading "local" one. When small negative (and, therefore, unreal) values for parameters were obtained, they were fixed at zero and the analysis was repeated. This nonlinear analysis did not lead to standard deviations for the parameters although estimated values of $\sigma(k_{obsd})$ were given by $\{\sum(\Delta\%)^2/(N - M)\}^{1/2}$. (N = number of independent determinations of k_{obsd} and M = number of parameters being determined.) Values of $\Delta\%$ were inspected to detect any systematic variations with $[I_2]$.

Results

Products. The reactions were accompanied by complete disappearance of the electronic and IR absorptions characteristic of the metal-metal-bonded complexes.^{11,12} The IR

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spectra of the products of reaction with 10^{-2} M I_2 were measured immediately after mixing and repeatedly at intervals of several minutes to confirm stability of the products. The spectra were characteristic¹⁴ of the formation of *cis*-Mn(CO)₄LI in high yields. In most cases bands attributable¹⁴ to formation of some of the corresponding *trans* isomers were also observed, but overlap of the strongest bands due to the two isomers made precise measurement of isomer ratios difficult, and no detailed investigation was attempted. It generally appeared, however, that the *cis* isomer was formed in 50–75% yield.

Reaction of I_2 with $Mn_2(CO)_8[P(C_6H_{11})_3]_2$. First-order rate plots based on the decreasing absorbance of the reactant complex at 366 nm were linear for at least 50% of reaction. The first-order nature was confirmed by five measurements of the first-order rate constant, k_{obsd} , over a range of values of C_0 from 4.33×10^{-6} to 3.03×10^{-5} M and with $[I_2] = 5.79 \times 10^{-3}$ M. The average value, \bar{k}_{obsd} , was $3.91 \times 10^{-2} s^{-1}$ with a mean deviation of 5.6%.

The dependence of k_{obsd} on $[I_2]$ was determined by 11 runs over the range $10^3[I_2] = 1.22$ –6.40 M. A plot of $\log k_{obsd}$ against $\log [I_2]$ had a gradient of 0.93 ± 0.05 and a weighted linear least-squares analysis of the data according to eq 1 led

$$k_{obsd} = k_1 + k_2[I_2] \quad (1)$$

to values of k_1 , k_2 , and $\sigma(k_{obsd})$ as shown in Table V. An upper estimate of $\leq 10^2 M^{-2} s^{-1}$ can be obtained for k_3 in the possible additional term $k_3[I_2]^2$ in eq 1.

Reaction of I_2 with $Mn_2(CO)_8[P(p\text{-MeOC}_6\text{H}_4)_3]_2$. The low solubility of this complex prevented a study of its reactions over a wide range of values of C_0 , but six determinations of k_{obsd} at $10^4[I_2] = 4.08$ M and $10^6 C_0 = 3.0$ –10.0 M gave $\bar{k}_{obsd} = 4.13 \times 10^{-3} s^{-1}$ with a mean deviation of 2.0%. The dependence of k_{obsd} on $[I_2]$ was determined from 15 runs over the range $10^4[I_2] = 2.33$ –9.32 M. Even in the absence of I_2 slow decrease of absorbance due to the complex occurred, but the rate was $\leq 10\%$ of any of the rates with I_2 . This could probably be ascribed to aerial oxidation.¹⁵ The dependence of k_{obsd} on $[I_2]$ was describable by eq 2 with $k_1 = ca. 1 \times 10^{-4}$

$$k_{obsd} = k_1 + k_2[I_2] + k_3[I_2]^2 \quad (2)$$

s^{-1} . The parameters from a weighted linear least-squares analysis of the dependence of $(k_{obsd} - k_1)/[I_2]$ on $[I_2]$ ($k_1 = 1 \times 10^{-4} s^{-1}$) are shown in Table V.

Reaction of I_2 with $Mn_2(CO)_8(PEt_3)_2$ and $Mn_2(CO)_8(PPhEt)_2$. Reaction with $Mn_2(CO)_8(PEt_3)_2$ was studied at $C_0 = 2 \times 10^{-5}$ M and $10^4[I_2] = 0.8$ –25 M. The dependence on C_0 was not investigated, but good first-order rate plots were usually obtained at lower values of $[I_2]$. Reactions became steadily less reproducible as $[I_2]$ increased, but quite good reproducibility was obtained with $[I_2] \leq 15 \times 10^{-4}$ M. These data showed agreement with eq 3, 31 measurements of k_{obsd}

$$k_{obsd} = k_1 + k_3[I_2]^2 \quad (3)$$

leading to $10^5 k_1 = -1.2 \pm 1.1 s^{-1}$, $10^{-4} k_3 = 2.50 \pm 0.05 M^{-2} s^{-1}$, and $\sigma(k_{obsd}) = 8.9\%$. Data below $[I_2] = 5 \times 10^{-4}$ M were even more reproducible, and the average of seventeen values of $10^{-4} k_{obsd}/[I_2]^2$ was $2.48 \pm 0.04 M^{-2} s^{-1}$ with $\sigma(k_{obsd}) = 5.8\%$. Sixteen values of $k_{obsd}/[I_2]^2$ obtained at temperatures in the range 24.7–38.6 °C were used to estimate the activation parameters shown in Table VI.

This reaction was also used to check the absence of any dependence of k_{obsd} on the slit width of the monochromator of the stopped-flow apparatus. Six measurements at $[I_2] = 8.0 \times 10^{-4}$ M and slit widths 0.5–5.0 mm were constant with a mean deviation of 4.5%.

An investigation of the effect of using different solvents was also undertaken. Nineteen values of k_{obsd} for reaction in CH_2Cl_2 ($10^4[I_2] = 2.20$ –24.5 M) were well represented by eq 1. Reaction in MeOH showed an initial fast reaction followed by a much slower one. Seven values of k_{obsd} for the fast reaction ($10^4[I_2] = 9.0$ –30.0 M) also followed eq 1. Reaction in CCl_4 showed a different dependence on $[I_2]$. A plot of $k_{obsd}/[I_2]$ against $[I_2]$ (11 measurements with $10^4[I_2] = 3.0$ –26 M) showed a rise toward a limiting value, and a plot of $[I_2]/k_{obsd}$ against $1/[I_2]$ was linear. This suggested that the rate equation (4) was being followed, and this was confirmed

$$k_{obsd} = k_3[I_2]^2 / \{1 + \beta_1[I_2]\} \quad (4)$$

by the small value of $\sigma(k_{obsd})$ found by least-squares analysis. Rate parameters for these reactions are given in Table V.

Reaction of I_2 with $Mn_2(CO)_8(PPhEt)_2$ was studied at $C_0 = ca. 10^{-5}$ M and $10^4[I_2] = 0.7$ –20 M. Excellent first-order rate plots were obtained with lower values of $[I_2]$, but for $[I_2] \geq 15 \times 10^{-4}$ M the rate plots were somewhat curved. A plot of 17 values of k_{obsd} against $[I_2]^2$ ($[I_2] \leq 5 \times 10^{-4}$ M at 23.3 °C) gave an excellent straight line through the origin in accordance with eq 3 and a negligible value of k_1 . The average value of $10^{-5} k_3$ (obtained from the values of $k_{obsd}/[I_2]^2$) is shown in Table V. Thirty-five measurements of $k_{obsd}/[I_2]^2$ over the temperature range 23.0–40.1 °C were used to estimate the activation parameters shown in Table VI.

Reaction of I_2 with $Mn_2(CO)_8(PPh_3)_2$, $MnRe(CO)_8(PPh_3)_2$, and $Re_2(CO)_8(PPh_3)_2$. Reaction with $Mn_2(CO)_8(PPh_3)_2$ was studied at $C_0 = ca. 10^{-5}$ M and $10^4[I_2] = 0.7$ –26.5 M. Good first-order rate plots were obtained, and the best analysis of the $[I_2]$ dependence, based on 33 values of k_{obsd} , was provided by eq 3. Introduction of terms $k_2[I_2]$ and $k_4[I_2]^3$ did not decrease $\sigma(k_{obsd})$ and gave values of k_2 and k_4 not significantly different from zero.

Reaction with $MnRe(CO)_8(PPh_3)_2$ was followed at 25.0, 29.9, 35.1, and 45.0 °C with $C_0 = 1 \times 10^{-5}$ M and $10^4[I_2]$ in the range 7–30 M. Plots of k_{obsd} against $[I_2]^2$ at each temperature were linear with very small or insignificant intercepts so that eq 3 was followed. The parameters obtained from the data at 25 °C are given in Table V, and 16 values of $k_{obsd}/[I_2]^2$ at the various temperatures and with $[I_2] \geq 10^{-3}$ M combined to give the activation parameters in Table VI.

Reaction with $Re_2(CO)_8(PPh_3)_2$ in decalin showed first-order dependence on [complex]. Thirteen values of k_{obsd} at $10^3[I_2] = 2.13$ M and over the wide range $10^6 C_0 = 2.8$ –83 M had $\sigma(k_{obsd}) = 20.6\%$. There was no systematic trend with C_0 of the deviations from the mean. Seven values of k_{obsd} with $10^4[I_2] = 2.8$ –60.5 M gave a good linear plot of k_{obsd} against $[I_2]^2$ with a negligible intercept. The value of k_3 given in Table V is the average of the values of $k_{obsd}/[I_2]^2$. Twenty-five values of k_3 over the temperature range 25.0–48.1 °C gave the activation parameters in Table VI.

Reaction of I_2 with $Re_2(CO)_8PPh_3$ in Decalin. The mean of seven values of k_{obsd} at $[I_2] = 75 \times 10^{-4}$ M and $10^5 C_0 = 5.35$ –53.5 M had a mean deviation of 6.6%, and the reaction is therefore first order in [complex]. Graphical analysis of the dependence of k_{obsd} on $[I_2]$ (25 measurements over the range $(7$ –140) $\times 10^{-4}$ M) suggested that the rate equation (5)

$$k_{obsd} = k_3[I_2]^2 + k_4[I_2]^3 + k_5[I_2]^4 \quad (5)$$

was followed with $k_3 = 35 M^{-2} s^{-1}$, $k_5 = 4.9 \times 10^5 M^{-4} s^{-1}$, and k_4 relatively small and ill-defined. A nonlinear, weighted, least-squares analysis gave $k_3 = 35.5 \pm 2.1 M^{-2} s^{-1}$, $k_4 = 651 \pm 1034 M^{-3} s^{-1}$, $k_5 = (4.10 \pm 0.91) \times 10^5 M^{-4} s^{-1}$, and $\sigma(k_{obsd}) = 9.6\%$. It is, therefore, quite possible that k_4 is finite, but its value is not well established. Measurements of k_{obsd} with $10^4[I_2] = 7$ –15 M (where more than ca. 90% of the reaction is proceeding by the path second order in $[I_2]$) over the temperature range 21.5–44.3 °C allowed the values in Table VI

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Table I. Kinetic and Thermodynamic Parameters for the Reaction of I_2 with $Mn_2(CO)_8(PBu_3)_2$ in Cyclohexane

temp, °C	$10^{-4}k_3, M^{-2} s^{-1}$	β_1, M^{-1}	$\sigma(k_{obsd}), \%$
24.8	9.35 ± 0.81	372 ± 63	9.8
34.1	12.8 ± 1.0	354 ± 56	7.9
39.8	13.0 ± 0.8	276 ± 35	7.2
46.3	14.8 ± 0.9	254 ± 32	7.4

$$\Delta H_1^\ddagger = -3.6 \pm 2.5 \text{ kcal mol}^{-1}$$

$$\Delta S_1^\ddagger = -0.3 \pm 8.2 \text{ cal K}^{-1} \text{ mol}^{-1}$$

for ΔH_3^\ddagger and ΔS_3^\ddagger to be obtained, the values of k_3 calculated from these parameters having a mean deviation of ca. 7% from the measured values.

Reaction of I_2 with $Mn_2(CO)_8(P-n-Bu_3)_2$. This reaction was studied with $C_0 = \text{ca. } 5 \times 10^{-5} \text{ M}$ and $10^4[I_2] = 10\text{--}90 \text{ M}$ and over the temperature range 24.8–46.3 °C. Rate plots were linear for over 75% of reaction. The dependence of k_{obsd} on $[I_2]$ followed eq 4 at each temperature as shown by the linearity of the plots of $[I_2]/k_{obsd}$ vs. $1/[I_2]$ and the low values found for $\sigma(k_{obsd})$ from least-squares analyses of the data. Values of the parameters are given in Table I, and the activation parameters found from the temperature dependence of k_3 are in Table VI.

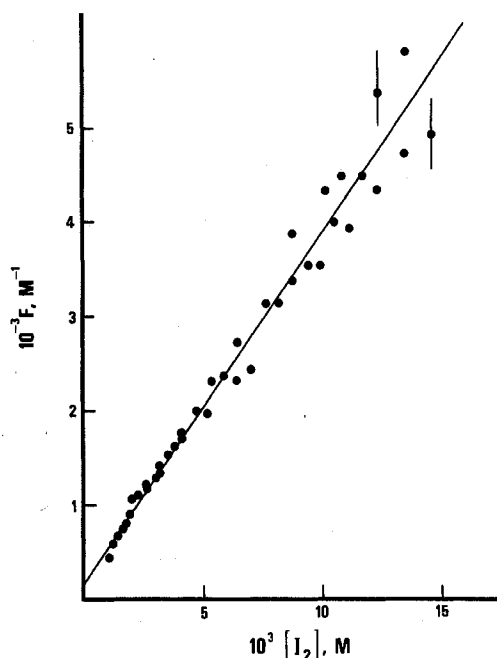
Reaction of I_2 with $Mn_2(CO)_8[P(OMe)_3]_2$. This reaction showed a complicated dependence on $[I_2]$ and was studied in some detail. Rate plots were linear to at least 85% of reaction and the mean deviation of four values of k_{obsd} at $[I_2] = 3.2 \times 10^{-3} \text{ M}$ and $10^5 C_0 = 0.6\text{--}3.6 \text{ M}$ was 3.0%. Measurements of k_{obsd} for 65 values of $10^4[I_2]$ over the range 0.96–146 M were in excellent agreement with (6). Thus, with $[I_2] \leq 5$

$$k_{obsd} = k_3[I_2]^2 / (1 + \beta_1[I_2] + \beta_2[I_2]^2) \quad (6)$$

$\times 10^{-4} \text{ M}$ a plot of $k_{obsd}/[I_2]$ against $[I_2]$ was an excellent straight line through the origin. Sixteen values of $k_3 = k_{obsd}/[I_2]^2$ had a mean of $(1.39 \pm 0.04) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ with $\sigma(k_{obsd}) = 6.2\%$. When $10^4[I_2] = \text{ca. } 10$ and 15 M , $10^{-4}k_3$ had dropped to 1.1 and $0.8 \text{ M}^{-2} \text{ s}^{-1}$, respectively. Equation 6 can be rearranged to (7) so that when k_{obsd} is appreciably smaller

$$F = (k_3[I_2]^2 - k_{obsd}) / k_{obsd}[I_2] = \beta_1 + \beta_2[I_2] \quad (7)$$

than $k_3[I_2]^2$, a plot of F against $[I_2]$ should be linear and should provide values for β_1 and β_2 . Such a plot is indeed linear, and a weighted least-squares analysis led to $\beta_1 = 220 \pm 40 \text{ M}^{-1}$

**Figure 1.** Dependence of $F = (k_3[I_2]^2 - k_{obsd})/k_{obsd}[I_2]$ on $[I_2]$ for $Mn_2(CO)_8[P(OMe)_3]_2$. $k_3 = 1.52 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$. Error bars shown correspond to $\pm\sigma(k_{obsd}) = 7.3\%$.

and $\beta_2 = (320 \pm 9) \times 10^3 \text{ M}^{-2}$. The use of these values of k_3 , β_1 , and β_2 to calculate values expected for k_{obsd} led to $\sigma(k_{obsd}) = 10.4\%$. When these graphical values were used as initial input with the subroutine VA04A, the values $k_3 = 1.52 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$, $\beta_1 = 145 \text{ M}^{-1}$, $\beta_2 = 3.76 \times 10^5 \text{ M}^{-2}$, and $\sigma(k_{obsd}) = 7.3\%$ were obtained. A plot of F vs. $[I_2]$ is shown in Figure 1 where k_3 was taken to be $1.52 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$. The fit is excellent especially in view of the fact that errors in k_{obsd} are amplified in the function plotted; e.g., a high value of k_{obsd} will decrease the numerator and increase the denominator. The errors indicated in Figure 1 correspond to the uncertainty in k_{obsd} derived from the VA04A analysis. The values of k_{obsd} are shown in Table II.

A brief study was made of the effects on this reaction of using two other solvents. In di-*n*-butyl ether at $[I_2] = 6.42 \times 10^{-4} \text{ M}$, four values of k_{obsd} at $10^5 C_0 = 0.5\text{--}2.0 \text{ M}$ had a

Table II. Kinetic Data for the Reaction of I_2 with $Mn_2(CO)_8[P(OMe)_3]_2$ in Cyclohexane at 25.0 °C ($[Complex]_0 = \text{ca. } 1 \times 10^{-5} \text{ M}$)

$10^4[I_2], M$	$10^3 k_{obsd}, s^{-1}$	$\Delta, \%$	$10^4[I_2], M$	$10^3 k_{obsd}, s^{-1}$	$\Delta, \%$	$10^4[I_2], M$	$10^3 k_{obsd}, s^{-1}$	$\Delta, \%$
0.960	0.128	-7.1	9.60	10.1	6.7	52.5	31.8	-8.0
1.17	0.172	-15.5	9.91	9.29	-5.9	58.3	34.9	-1.2
1.46	0.301	-4.4	11.2	12.8	9.7	64.0	39.2	9.1
1.47	0.307	-3.8	11.7	12.6	1.6	64.1	33.6	-6.5
1.98	0.602	5.4	12.8	14.3	3.4	69.9	41.2	13.1
1.98	0.607	6.3	14.6	16.2	0.6	75.7	35.2	-4.5
2.50	0.820	-8.5	16.0	17.8	0.4	81.6	37.9	1.9
2.50	0.883	-1.4	18.1	20.5	2.7	87.0	33.1	-11.6
3.01	1.24	-3.0	19.2	20.1	-4.4	87.4	38.1	1.7
3.03	1.23	-5.0	20.4	20.1	-9.1	93.2	38.7	2.6
3.50	1.65	-2.8	22.6	22.1	-7.6	99.1	41.3	8.9
3.52	1.68	-2.1	25.6	24.1	-7.2	100.8	34.6	-8.9
4.03	2.24	1.6	26.2	25.7	-2.5	104.9	39.0	2.3
4.08	2.33	3.3	29.1	26.8	-4.1	107.5	35.6	-6.8
4.80	3.37	11.2	31.0	26.8	-7.1	110.7	41.9	9.5
4.95	3.13	-2.2	31.4	28.4	-2.2	116.5	38.6	0.5
5.50	3.78	-1.9	35.0	28.8	-5.5	122.4	41.9	8.7
5.83	4.19	-1.7	37.9	30.3	-3.6	122.9	34.1	-11.5
6.40	5.93	18.7	40.8	30.5	-5.4	133.1	34.4	-11.2
6.99	5.76	-0.4	41.6	32.2	-0.8	134.0	42.0	9.4
8.00	8.18	14.0	46.6	31.9	-4.9	145.7	44.3	13.8
8.16	7.23	-2.3	51.2	36.0	4.8			

^a $\Delta = 100(k_{obsd} - k_{calcd})/k_{calcd}$ where values of k_{calcd} were obtained by using the parameters given in Table V.

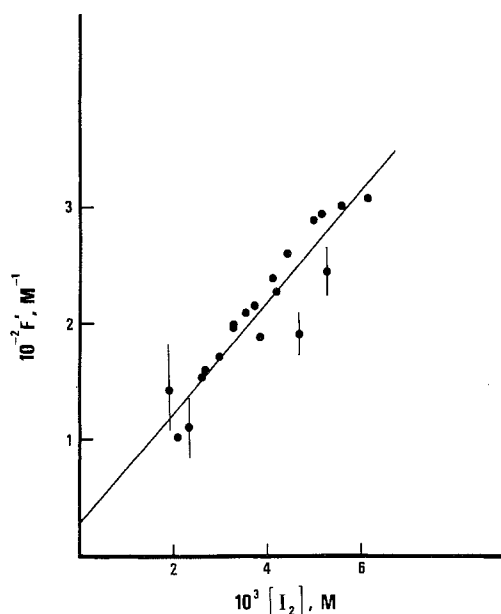


Figure 2. Dependence of $F' = (k_2[I_2] + k_3[I_2]^2 - k_{\text{obsd}})/k_{\text{obsd}}[I_2]$ on $[I_2]$ for $\text{Mn}_2(\text{CO})_8(\text{PPh}_2\text{Et})_2$. $k_2 = 0.19 \text{ M}^{-1} \text{ s}^{-1}$ and $k_3 = 3.8 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$. Error bars shown correspond to $\pm \sigma(k_{\text{obsd}}) = 4.9\%$.

mean deviation of 2.2%. Variation of $10^4[I_2]$ from 1.06 to 6.45 M showed that eq 3 was followed, with k_1 being quite small (Table V).

Reaction in ethyl acetate showed behavior in accord with eq 4. Thus, a plot of k_{obsd} against $[I_2]^2$ ($10^4[I_2] = 1.24\text{--}6.82 \text{ M}$) was a smooth curve, and a plot of $[I_2]/k_{\text{obsd}}$ against $1/[I_2]$ was linear. A weighted least-squares analysis led to the parameters shown in Table V.

Reaction of I_2 with $\text{Mn}_2(\text{CO})_8(\text{PPh}_2\text{Et})_2$. Linear first-order rate plots were obtained for up to 80% of reaction. Five values of k_{obsd} at $[I_2] = 1.46 \times 10^{-3} \text{ M}$ and $10^5 C_0 = 0.95\text{--}2.99 \text{ M}$ had a mean deviation of 2.3%, and the reaction is, therefore, closely first order in [complex]. The dependence of k_{obsd} on $[I_2]$ was determined at $C_0 = 9.5 \times 10^{-6} \text{ M}$ by 31 measurements over the range $10^4[I_2] = 1.92\text{--}60.8 \text{ M}$. The data conformed closely to eq 8. A plot of $k_{\text{obsd}}/[I_2]$ against $[I_2]$ at $[I_2] < 20$

$$k_{\text{obsd}} = (k_2[I_2] + k_3[I_2]^2)/(1 + \beta_1[I_2] + \beta_2[I_2]^2) \quad (8)$$

$\times 10^{-4} \text{ M}$ was linear with an intercept, and a least-squares analysis gave $k_2 = 0.29 \pm 0.03 \text{ M}^{-1} \text{ s}^{-1}$ and $10^{-4}k_3 = 0.337 \pm 0.008 \text{ M}^{-2} \text{ s}^{-1}$. These values were then used to calculate F' in eq 9 so that a plot could be made of this function against

$$F' = (k_2[I_2] + k_3[I_2]^2 - k_{\text{obsd}})/k_{\text{obsd}}[I_2] = \beta_1 + \beta_2[I_2] \quad (9)$$

$[I_2]$ for $[I_2] > 30 \times 10^{-4} \text{ M}$. This plot is reasonably linear, and least-squares analysis gives $\beta_1 = 25 \pm 28 \text{ M}^{-1}$ and $10^{-3}\beta_2 = 37 \pm 7 \text{ M}^{-2}$. The high uncertainty of β_1 reflects the rather long extrapolation to $[I_2] = 0$, but the use of these parameters to calculate values expected for k_{obsd} led to $\sigma(k_{\text{obsd}}) = 6.4\%$. These parameters were used as initial values in the VA04A program. This further reduced $\sigma(k_{\text{obsd}})$ to a minimum of 4.9% when $k_2 = 0.19 \text{ M}^{-1} \text{ s}^{-1}$, $k_3 = 0.38 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$, $\beta_1 = 26 \text{ M}^{-1}$, and $\beta_2 = 4.8 \times 10^4 \text{ M}^{-2}$. A plot of F' (calculated by using the above values of k_2 and k_3) against $[I_2]$ is shown in Figure 2. The uncertainties shown correspond to $\sigma(k_{\text{obsd}}) = 4.9\%$. Values of F' for $[I_2] \lesssim 1.5 \times 10^{-3} \text{ M}$ become very imprecise. If β_1 is fixed at zero, then the VA04A analysis leads to $k_2 = 0.22 \text{ M}^{-1} \text{ s}^{-1}$, $k_3 = 0.36 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$, $\beta_2 = 5.0 \times 10^4 \text{ M}^{-2}$, and $\sigma(k_{\text{obsd}}) = 5.0\%$, so a finite value of β_1 , although allowed by the data, is not required by them. An upper limit of ca. 50 M^{-1} seems to be a reasonable estimate. Values of k_{obsd} etc. are shown in Table III. If the values of k_{obsd} at $10^3[I_2] = 5.24$

Table III. Kinetic Data for Reaction of I_2 with $\text{Mn}_2(\text{CO})_8(\text{PPh}_2\text{Et})_2$ in Cyclohexane at 25.0°C ($[\text{Complex}]_0 = 9.5 \times 10^{-6} \text{ M}$)

$10^4[I_2]$, M	$10^4 k_{\text{obsd}}$, s^{-1}	$\Delta, ^a \%$	$10^4[I_2]$, M	$10^4 \times$ k_{obsd} , s^{-1}	$\Delta, ^a \%$
1.92	1.82	3.5	29.1	217	-1.0
2.88	3.57	-2.1	32.0	241	-3.0
3.84	5.82	-6.1	32.0	240	-3.4
4.80	9.57	1.8	35.0	271	-2.3
6.40	15.6	-3.2	36.7	288	-1.8
8.00	25.1	2.6	37.9	320	5.3
9.60	33.6	-2.2	40.8	322	-2.2
11.2	46.7	2.4	41.6	339	1.0
12.8	56.8	-2.2	43.7	341	-3.3
14.6	74.9	2.0	46.6	438	(16.8) ^b
17.5	108	7.7	49.5	384	-2.8
19.2	112	-4.3	51.2	398	-2.1
20.4	133	3.0	52.4	457	(10.6) ^b
23.3	167	5.0	55.4	437	1.1
25.6	181	-1.1	60.8	490	6.2
26.2	186	-1.7			

^a See footnote to Table II. ^b Not included in computation.

Table IV. Kinetic Data for the Reaction of I_2 with $\text{Mn}_2(\text{CO})_8[\text{P}(\text{O}^i\text{Pr})_3]_2$ in Cyclohexane at 25.0°C ($[\text{Complex}]_0 = 1 \times 10^{-5} \text{ M}$)

$10^4[I_2]$, M	$10^4 k_{\text{obsd}}$, s^{-1}	$\Delta, ^a \%$	$10^4 \times$ $[I_2]$, M	$10^4 \times$ k_{obsd} , s^{-1}	$\Delta, ^a \%$
11.7	0.136	3.60	157	18.3	0.70
14.6	0.219	0.84	166	18.0	-6.72
17.5	0.324	-1.42	182	20.5	-3.48
20.4	0.469	0.46	197	21.0	-8.70
23.3	0.606	-4.15	212	23.3	-5.71
29.1	1.01	-3.62	227	26.4	0.10
35.0	1.55	-1.06	242	26.8	-4.26
40.8	2.03	-6.50	257	28.1	-4.98
52.4	3.57	-0.54	272	31.2	0.28
58.3	4.53	3.26	287	33.4	2.39
69.9	6.37	5.46	303	32.0	-6.41
81.6	8.06	3.89	318	36.4	2.14
93.2	9.63	1.76	333	36.5	-1.48
105	12.0	6.97	348	39.4	2.51
121	14.2	5.80	378	43.3	5.27
122	14.3	5.47	387	44.4	5.91
140	16.1	0.74	402	43.1	-0.28
151	16.6	-4.65			

^a See footnote to Table II.

and 4.66 M are omitted from the computations (see Figure 2), the values of the parameters are barely changed but $\sigma(k_{\text{obsd}})$ drops to 3.8%. It is the parameters obtained in this way that were used to obtain values of k_{calcd} and $\Delta\%$ in Table III, and these parameters are quoted in Table V.

Reaction of I_2 with $\text{Mn}_2(\text{CO})_8[\text{P}(\text{O}^i\text{Pr})_3]_2$. This reaction showed excellent pseudo-first-order rate plots, and the mean deviation of five values of k_{obsd} with $10^5 C_0 = 1.05\text{--}6.30 \text{ M}$ was 3.4% at $[I_2] = 2.42 \times 10^{-2} \text{ M}$. Previous studies² had shown there to be a major dependence of k_{obsd} on $[I_2]^2$ with a rather imprecisely determined additional dependence on $[I_2]^3$. The dependence on $[I_2]$ was therefore studied in greater detail and up to a much higher concentration. The data are shown in Table IV and can be shown to be in excellent agreement with the rate equation (10). Thus, a plot of $k_{\text{obsd}}/[I_2]$

$$k_{\text{obsd}} = \{k_3[I_2]^2 + k_4[I_2]^3\}/\{1 + \beta_1[I_2] + \beta_2[I_2]^2 + \beta_3[I_2]^3\} \quad (10)$$

at low $[I_2]$ shows an upward curvature with increasing $[I_2]$ and extrapolates back to the origin at $[I_2] = 0$. This shows the importance of terms in $[I_2]^2$ and $[I_2]^3$ but that a term in $[I_2]$ is not significant. A good linear plot of $k_{\text{obsd}}/[I_2]^2$ against

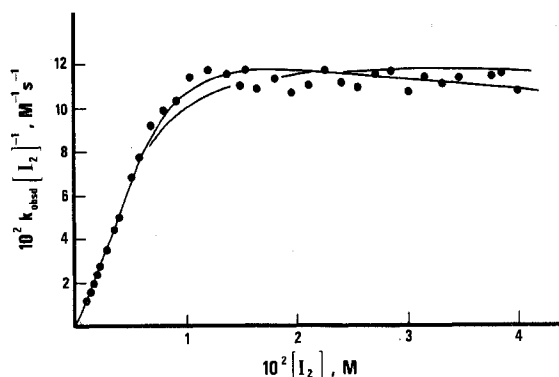


Figure 3. Dependence of $k_{\text{obsd}}/[I_2]$ on $[I_2]$ for $\text{Mn}_2(\text{CO})_8[\text{P}(\text{OPh})_3]_2$. The continuous line is the theoretical one calculated according to eq 10 with β_1 set to zero, and the discontinuous line is calculated with both β_1 and β_3 set to zero.

$[I_2]$ is obtained up to $[I_2] = \text{ca. } 4 \times 10^{-3} \text{ M}$, and the intercept and gradient provide values of $8.6 \pm 0.16 \text{ M}^{-2} \text{ s}^{-1}$ and $(1.14 \pm 0.08) \times 10^3 \text{ M}^{-3} \text{ s}^{-1}$ for k_3 and k_4 , respectively. An extension of this plot to higher values of $[I_2]$, however, shows that $k_{\text{obsd}}/[I_2]^2$ passes through a maximum at $[I_2] = \text{ca. } 6 \times 10^{-3} \text{ M}$ and then decreases steadily toward zero. This shows that a term at least second order in $[I_2]$ must be present in the denominator of the rate equation. At alternative indication of this is the fact that a plot of $k_{\text{obsd}}/[I_2]$ against $[I_2]$, given in Figure 3, shows a rise to a maximum followed by a very gradual decline. The rise to the maximum is gently sigmoid in nature and quite different from that characteristic of the rate equation (4).

Rearrangement of eq 10 provides (11). The values of k_3

$$F'' = (k_3[I_2]^2 + k_4[I_2]^3 - k_{\text{obsd}})/k_{\text{obsd}}[I_2] = \frac{\beta_1 + \beta_2[I_2] + \beta_3[I_2]^2}{\beta_1 + \beta_2[I_2] + \beta_3[I_2]^2} \quad (11)$$

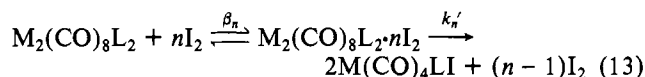
and k_4 found above can be used to calculate F'' . The plot of F'' against $[I_2]$ is reasonably linear and passes close to the origin, showing that terms in β_1 and β_3 are less important than that in β_2 . Analysis using the VA04A routine was therefore undertaken. When all five parameters were included, the value of β_1 decreased steadily and eventually became zero and then negative and, therefore, unreal. Setting β_1 to zero led to the parameters $k_3 = 6.73 \text{ M}^{-2} \text{ s}^{-1}$, $k_4 = 2.69 \times 10^3 \text{ M}^{-3} \text{ s}^{-1}$, $\beta_2 = 2.09 \times 10^4 \text{ M}^{-2}$, $\beta_3 = 1.25 \times 10^5 \text{ M}^{-3}$, and $\sigma(k_{\text{obsd}}) = 4.6\%$. The same values were obtained when, for instance, input values of β_3 were as different as 10^3 and 10^6 M^{-3} . When the value of β_3 was fixed at zero, the values of k_3 , k_4 , and β_2 were not greatly affected, being $6.43 \text{ M}^{-2} \text{ s}^{-1}$, $3.11 \times 10^3 \text{ M}^{-3} \text{ s}^{-1}$, and $2.74 \times 10^4 \text{ M}^{-2}$, respectively. However, the value of $\sigma(k_{\text{obsd}})$ had increased to 5.9%, and, as shown in Figure 3, the theoretical curve through the data did not rise sharply enough to the maximum and did not decrease sufficiently after the maximum was reached. It seems probable, therefore, that the term in β_3 is quite real. The value of β_1 is almost certainly less than ca. 10 M^{-1} , and no term in k_2 contributes significantly to the rate equation.

Discussion

The Stoichiometric Mechanism. The rate equations for these reactions are well established by the data which are generally of good precision. Fortunately the most complicated rate equations are found for reactions which are slower and which show a high degree of precision. Some of the analyses may indeed oversimplify the rate equations in the way observed for the reaction of Br_2 with $\text{Mn}_2(\text{CO})_8(\text{PPhEt}_2)_2$.⁷ In that case a preliminary analysis showed a good fit ($\sigma(k_{\text{obsd}}) = 5.4\%$) to the simple equation $k_{\text{obsd}} = k_1 + k_2[\text{Br}_2]$. More detailed analysis showed an even better fit ($\sigma(k_{\text{obsd}}) = 3.2\%$) to eq 12.

$$k_{\text{obsd}} = \{k_2[\text{Br}_2] + k_3[\text{Br}_2]^2\}/\{1 + \beta_1[\text{Br}_2]\} \quad (12)$$

although the values of k_3 and β_1 were not very precisely defined. This illustrates the point that a small higher order term in the numerator can be concealed by a compensating term in the denominator. Fortunately the analysis in terms of the more complicated equation changed the value of k_2 by less than 50%. We can therefore conclude that the values of the rate constants in Table IV are unlikely to be in error to an extent that would offset the ensuing discussion. On the other hand, the data for several reactions do define unambiguously some very complicated rate equations. The form of these equations provides excellent evidence for a stoichiometric mechanism exactly analogous to that proposed⁷ for reactions of these complexes with Br_2 . This is described in eq 13 for the di-substituted complexes. The mononuclear products are formed in good yield.



The mechanism involves a succession of preequilibria in which rapid formation occurs of a series of adducts between one or more I_2 molecules and the complex. Any or all of these adducts can then undergo further reaction by a process first order in [adduct] and governed by k_n' . The kinetic behavior of all the complexes studied can be described by eq 14. This

$$k_{\text{obsd}} = \frac{\beta_1 k_1' [I_2] + \beta_2 k_2' [I_2]^2 + \beta_3 k_3' [I_2]^3 + \beta_4 k_4' [I_2]^4}{1 + \beta_1 [I_2] + \beta_2 [I_2]^2 + \beta_3 [I_2]^3} \quad (14)$$

is a particular form of the general rate equation appropriate to the mechanism described by (13). Thus, the maximum order 4 with respect to $[I_2]$ was observed for the reaction of $\text{Re}_2(\text{CO})_9\text{PPh}_3$ while a term in $[I_2]^3$ in the denominator was found for reaction of $\text{Mn}_2(\text{CO})_8[\text{P}(\text{OPh})_3]_2$. Equation 13 implies that all the $n\text{I}_2$ molecules that are involved in the transition states are assembled rapidly together with the complex during the preequilibrium process rather than that $n-1$ of them are assembled rapidly into $\text{M}_2(\text{CO})_8\text{L}_2 \cdot (n-1)\text{I}_2$ before this is attacked in a relatively slow bimolecular process by the n th I_2 molecule. The reaction of $\text{Mn}_2(\text{CO})_8[\text{P}(\text{OPh})_3]_2$ provides evidence of a term $\beta_3 [I_2]^3$ in the denominator when the highest dependence on $[I_2]$ in the numerator is also third order. In this case, at least, it appears likely that an adduct containing three molecules of I_2 can be formed rapidly and that this adduct subsequently reacts by a first-order process to form the products. The terms k_2 , k_3 , k_4 , and k_5 in the observed rate equations can generally, therefore, be taken as corresponding respectively to the terms $\beta_1 k_1'$, $\beta_2 k_2'$, $\beta_3 k_3'$, and $\beta_4 k_4'$ in (14).

The absence, in most of the rate equations, of any significant terms independent of $[I_2]$ is also important. It implies that there are generally no reactions where $\beta_1 [I_2] \gg 1$ for all values of $[I_2]$; i.e., the case where $k_1 = k_1'$, $k_2 = \beta_2 k_2'/\beta_1$, etc. does not usually have to be considered. An exception is the reaction of $\text{Mn}_2(\text{CO})_8(\text{PET}_3)_2$ in CH_2Cl_2 and probably also its reaction in MeOH . These will be considered below. Significant values of k_1 could, of course, be caused by straightforward thermal homolytic fission reactions¹¹ followed by rapid reaction of I_2 with the radicals produced. This is almost certainly the case with $\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_{11})_3]_2$ and $\text{Mn}_2(\text{CO})_8[\text{P}(p\text{-MeOC}_6\text{H}_4)_3]_2$ for which the first-order rate constants for homolytic fission at 25 °C are 5×10^{-4} and $1 \times 10^{-4} \text{ s}^{-1}$, respectively.^{11,15} The value of k_1 predicted from the data¹⁶ for the reaction of $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$ with O_2 is also identical

Table V. Kinetic Parameters for Reactions of I_2 with $M_2(CO)_8L_2$ in Cyclohexane at 25 °C

M_2	L	$10^3 k_1, s^{-1}$	$k_2, M^{-1} s^{-1}$	$10^{-4} k_3, M^{-2} s^{-1}$	$10^{-2} \beta_1, M^{-1}$	$\sigma(k_{obsd}), \%$	$\nu_{CO},^a cm^{-1}$
Mn ₂	CO ^b		2×10^{-8}				
Mn ₂	P(C ₆ H ₁₁) ₃	1.2 ± 0.9	6.67 ± 0.39	≤ 0.01		8.8	1946
Mn ₂	P(<i>p</i> -MeOC ₆ H ₄) ₃	ca. 0.1	3.80 ± 0.73	1.61 ± 0.15		9.5	1955
Mn ₂	PEt ₃	-0.01 ± 0.01		2.48 ± 0.04		5.8	1950
Mn ₂	PEt ₃ ^c			7.36 ± 0.36	14.4 ± 1.2	3.7	
Mn ₂	PEt ₃ ^d	482 ± 9	925 ± 12		≥ 500	2.3	
Mn ₂	PEt ₃ ^e	108 ± 55	386 ± 39		≥ 100	8.5	
Mn ₂	PPhEt ₂ ^f			10.1 ± 0.2		6.4	1952
Mn ₂	PPh ₃ ^f	0.07 ± 0.01		0.120 ± 0.003		12.5	1960
MnRe	PPh ₃	0.06 ± 0.01		0.185 ± 0.003		3.2	1965
Re ₂	CO ^g		5×10^{-6}				
Re ₂	PPh ₃ ^h	-0.8 ± 1.3		11.8 ± 0.7		14.7	1960
Re ₂	PPh ₃ ⁱ			$(3.55 \pm 0.21) \times 10^{-3}$		9.6	
Mn ₂	PBu ₃			9.35 ± 0.81	3.72 ± 0.63	9.8	1950
Mn ₂	P(OMe) ₃ ^j			1.52	1.45	7.3	1967
Mn ₂	P(OMe) ₃ ^k	0.05 ± 0.01		0.81 ± 0.02		7.9	
Mn ₂	P(OMe) ₃ ^l			2.81 ± 0.21	30.6 ± 5.2	7.0	
Mn ₂	PPh ₃ Et ^m		0.21	0.37	≤ 0.5	3.8	1958
Mn ₂	P(OPh) ₃ ⁿ			6.7×10^{-4}	< 0.1	4.6	1985

^a Frequency of most intense IR band in C–O stretching region. ^b In decalin; rate constant obtained by extrapolation of data at higher temperatures. ^c In CCl₄. ^d In CH₂Cl₂. ^e In MeOH. ^f At 23.0–23.5 °C. ^g In decalin; rate constant obtained by extrapolation of data at higher temperatures. ^h In decalin. ⁱ Complex is Re₂(CO)₉PPh₃; reaction is in decalin; $k_4 \lesssim 2 \times 10^3 M^{-3} s^{-1}$; $k_5 = (4.10 \pm 0.91) \times 10^5 M^{-4} s^{-1}$. ^j $\beta_2 = 3.76 \times 10^5 M^{-2}$. ^k In *n*-Bu₂O. ^l In EtOAc. ^m $\beta_2 = 5.4 \times 10^4 M^{-2}$. ⁿ $k_4 = 2.7 \times 10^3 M^{-3} s^{-1}$, $\beta_2 = 2.1 \times 10^4 M^{-2}$, and $\beta_3 = 1.3 \times 10^5 M^{-3}$.

with that reported in Table V. Apparently significant values of k_1 can be observed if the term $\beta_1[I_2]$ attains a small but significant value at higher values of $[I_2]$ without its being explicitly considered in the analysis. This was the case with the reaction of Br₂ with Mn₂(CO)₈(PEt₂Ph)₂ and may be the case with the reactions of $[I_2]$ with MnRe(CO)₈(PPh₃)₂ in cyclohexane and with Mn₂(CO)₈[P(OMe)₃]₂ in *n*-Bu₂O (Table V).

Another conclusion that can be drawn from the general absence of terms independent of $[I_2]$ is that photochemical processes do not play a significant part in these reactions. It is known that photochemical reactions of such complexes as Mn₂(CO)₁₀ with I₂, O₂, CCl₄, etc. proceed with limiting quantum yields of < 1 that are independent of [reactant] down to quite low concentrations.^{17,18} Any significant photochemical processes should therefore lead to detectable values of k_1 in the rate equations. The absence of any slit width dependence of k_{obsd} for reaction of Mn₂(CO)₈(PEt₃)₂ shows that the light in the stopped-flow spectrophotometer does not induce detectable photochemical reactions. Similar evidence was obtained for the reaction of Br₂ with Mn₂(CO)₈(PEt₃)₂ and Mn₂(CO)₈[P(OPh)₃]₂.⁷ A solution of 10^{-5} M Mn₂(CO)₁₀ in CCl₄ was exposed to the light beam centered at 343 nm in the Cary 16K spectrophotometer for 12 h without any diminution of the absorbance at that wavelength being observable. The intensity of the light beam in this spectrophotometer was therefore much too low to cause any photochemical contributions to the observed rates.

Trends in the Rate Parameters. Some of these reactions illustrate clearly the very pronounced labilizing effect of substituents. The smallest value of k_2 for a substituted dimanganese complex is a factor of ca. 10^7 greater than that for Mn₂(CO)₁₀ at 25 °C obtained by extrapolation from higher temperatures.³ No values of k_2 are available for reactions of substituted Re₂ complexes, but rough estimates of upper limits can be obtained by assuming that less than 10% of k_{obsd} at the lowest $[I_2]$ can be ascribed to a term $k_2[I_2]$. Thus, at 25 °C, reaction of Re₂(CO)₈(PPh₃)₂ could be up to six orders of magnitude faster than the extrapolated value for Re₂(CO)₁₀.⁵ The effect on k_3 of the second PPh₃ ligand in Re₂(CO)₈(PPh₃)₂

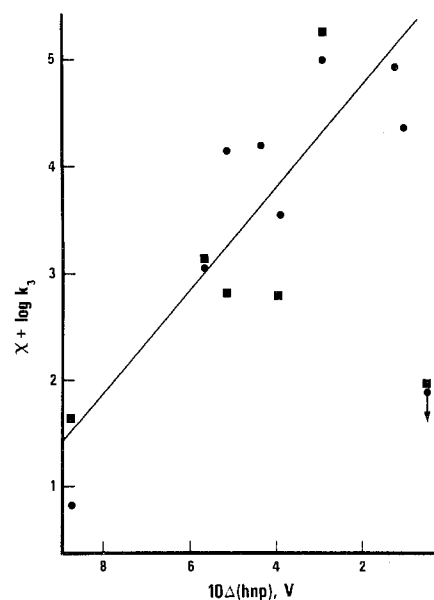


Figure 4. Dependence of $\log k_3$ on $\Delta(hnp)^{20}$ for reaction of Mn₂(CO)₈L₂ with I₂ (●, $x = 0$) and Br₂ (■, $x = -1$). The ligands L are from left to right P(OPh)₃, PPh₃, P(OMe)₃, P(*p*-MeOC₆H₄)₃, PPh₂Et, PPhEt₂, PBu₃, PEt₃, and P(C₆H₁₁)₃.

is to increase it by a factor of 3.4×10^3 compared with k_3 for Re₂(CO)₉(PPh₃), and successive substituents appear therefore to have comparable effects.

As found⁷ for the reactions with Br₂, the rates of reaction of I₂ increase as M₂ in M₂(CO)₈(PPh₃)₂ changes from Mn₂ to MnRe to Re₂. The increase in $\log k_2$ for reaction with Br₂ is linearly related⁷ to the change in reduction potential¹⁹ along the series, the overall change in k_2 being a factor of ca. 10^4 . Only a 10^2 -fold change in k_3 from Mn₂(CO)₈(PPh₃)₂ to Re₂(CO)₈(PPh₃)₂ is observed for reaction with I₂. k_3 for MnRe(CO)₈(PPh₃)₂ is only slightly greater than for Mn₂(CO)₈(PPh₃)₂ for reactions with I₂ or Br₂.

The effect of different σ basicities of the substituents in a series of Mn₂ complexes is quite pronounced for reactions with

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either I_2 or Br_2 . Thus a plot of $\log k_2$ for reaction with Br_2 against the value of $\Delta(\text{hnp})^{20}$ for the substituent is reasonably linear with points for $P(C_6H_{11})_3$ and, to a lesser extent, PPh_3 showing a deviation ascribable to steric effects.⁷ The mean deviation of six values of $\log k_2$ from a least-squares line of gradient -4 V^{-1} is ca. 0.3, and the correlation coefficient, r , is -0.95 . Plots of $\log k_3$ for reactions with I_2 and Br_2 against $\Delta(\text{hnp})$ are very similar, the gradients being almost equal and the line for reaction with Br_2 lying close to 1 log unit above that for reaction with I_2 . The similarity can be seen in Figure 4 where values of $\log k_3$ for reaction with I_2 and of $(\log k_3) - 1$ for reaction with Br_2 are plotted against $\Delta(\text{hnp})$. When the points for $L = P(C_6H_{11})_3$ are ignored, the least-squares line has a gradient of -4.9 V^{-1} , $r = -0.87$, and the mean deviation = 0.53 log unit. The deviations of the points for $P(C_6H_{11})_3$ are substantial and significant, being ≥ 3.7 and 3.7 for reaction with I_2 and Br_2 , respectively. The scatter of the other points around the line is not the same for both reactions. Thus $(\log k_3) - 1$ for reaction of $Mn_2(CO)_8[P(OPh)_3]_2$ with Br_2 lies on the line while $\log k_3$ for its reaction with I_2 lies below it. $(\log k_3) - 1$ for reaction of $Mn_2(CO)_8[P(OMe)_3]_2$ with Br_2 lies below the line while $\log k_3$ for its reaction with I_2 lies well above the line. However, in spite of such differences in detail the broad form of the trends is well established irrespective of whether the reactions are first or second order in [halogen]. Thus the reactions of Br_2 are generally faster than those of I_2 , and the reactions increase systematically in rate with increasing basicity of the substituents. However, when the substituent is $P(C_6H_{11})_3$, its great size²¹ almost completely offsets its high basicity so that $Mn_2(CO)_8[P(C_6H_{11})_3]_2$ reacts only slightly more rapidly than $Mn_2(CO)_8[P(OPh)_3]_2$. It is notable that the values of k_3 for reaction with I_2 cover a range of ca. 10^4 with varying ligand which is much larger than the difference between k_3 values for $Mn_2(CO)_8(PPh_3)_2$ and $Re_2(CO)_8(PPh_3)_2$. The substituents are capable, therefore, of inducing changes in the behavior of a given metal that are considerably greater than when the metal itself is changed. The range of values of ΔG^\ddagger for the disubstituted manganese complexes is ca. 5 kcal mol^{-1} which can be compared with a corresponding range of ca. 1 V or 23 kcal mol^{-1} in the reduction potentials of the closely related complexes $Co_2(CO)_8L_2$.²² In this context, it would be interesting to know whether the reduction potential for $Co_2(CO)_6[P(C_6H_{11})_3]_2$ showed any deviation from the general trend that could be ascribed to the large size of the ligand preventing the complex approaching the electrode as closely as might otherwise be energetically desirable.

It was shown previously⁷ that the reactions with Br_2 increased in rate with decreasing value of ν_{CO} for the complex. This also suggests an enhancement of the rate when the electron density on the CO ligand was increased. The data for reaction with I_2 enable a slightly more detailed analysis to be obtained. Figure 5 shows that a plot of $\log k_3$ against ν_{CO} for complexes containing phosphine ligands (other than $P(C_6H_{11})_3$) is a reasonably good straight line of gradient -0.165 cm , the mean deviation being only ca. 0.2 and $r = -0.91$. The point for $Mn_2(CO)_8[P(C_6H_{11})_3]_2$ lies over 3.5 log units below the line, showing again the pronounced steric effect of $P(C_6H_{11})_3$. The points for $Mn_2(CO)_8[P(OMe)_3]_2$ and $Mn_2(CO)_8[P(OPh)_3]_2$ lie 2 and 2.5 log units, respectively, above this line. Very similar, though somewhat less well-defined, behavior is shown by the values of $\log k_2$ for reactions

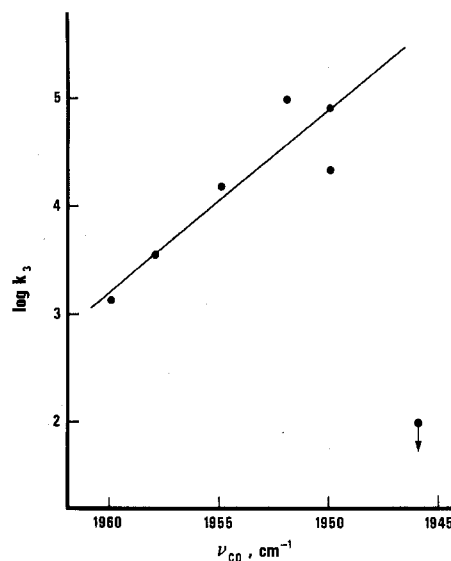


Figure 5. Dependence of $\log k_3$ on ν_{CO} for reaction of $Mn_2(CO)_8L_2$ with I_2 . The ligands L are from left to right PPh_3 , PPh_2Et , $P(p\text{-MeOC}_6\text{H}_4)_3$, $PPhEt_2$, PBu_3 (upper point) and PEt_3 (lower point), and $P(C_6H_{11})_3$.

Table VI. Activation Parameters for Some Reactions of I_2 with $M_2(CO)_8L_2$ in Cyclohexane

M_2	L	ΔH^\ddagger , kcal mol^{-1}	ΔS_3^\ddagger , $\text{cal K}^{-1}\text{mol}^{-1}$	$\sigma(k_{\text{obsd}})$, %
Mn_2	PEt_3	1.36 ± 0.21	-34.0 ± 0.70	2.3
Mn_2	PEt_2Ph	1.08 ± 0.39	-32.0 ± 1.3	7.0
$MnRe$	PPh_3	0.71 ± 0.31	-41.2 ± 1.0	5.2
Re_2	PPh_3	2.70 ± 0.72	-26.5 ± 2.4	12.3
Re_2	PPh_3^a	ca. 4.5	ca. -36	ca. 7
Mn_2	PBu_3	3.3 ± 1.2	-24.7 ± 3.9	

^a Data for $Re_2(CO)_8PPh_3$.

of Br_2 with these complexes. The least-squares plot of $\log k_2$ against ν_{CO} for phosphine substituents other than $P(C_6H_{11})_3$ has a gradient of -0.22 cm , r being -0.88 and the mean deviation 0.46. The point for $L = P(C_6H_{11})_3$ lies 3 log units below the line and those for $L = P(OMe)_3$ and $P(OPh)_3$ lie respectively 1.7 and a rather surprising 4.8 log units above the line. These trends enable it to be argued that the π -acid character of the substituent does not play a major role in determining the rates of the reaction. The values of ν_{CO} for $Mn_2(CO)_8[P(OMe)_3]_2$ and $Mn_2(CO)_8[P(OPh)_3]_2$ are ca. 8 and 17 cm^{-1} above a plot of ν_{CO} against $\Delta(\text{hnp})$ of L for the phosphine complexes $Mn_2(CO)_8L_2$. (The corresponding values for the complexes $Ni(CO)_3L$ are 10 and 8 cm^{-1} , respectively.²¹) The simplest explanation for this is that the higher π acidity of the phosphites raises ν_{CO} above what would be expected from their Brønsted basicity or σ -donor character. The fact that phosphines and phosphite complexes do share the same dependence of $\log k_3$ on $\Delta(\text{hnp})$ but do not share the same dependence of $\log k_3$ on ν_{CO} indicates that the substituents' effect on the kinetics operates through their σ -bonding character.

The values of ΔH_3^\ddagger shown in Table VI are all quite small and those of ΔS_3^\ddagger quite negative, as expected for third-order reactions. In the case of $Mn_2(CO)_8(PBu_3)_2$ the low value of ΔH_3^\ddagger can be seen to be largely due to a negative value for ΔH_1° (Table I), formation of the adduct with one I_2 molecule being quite exothermic. No very informative trends are discernible. The two very similar substituents PBu_3 and PEt_3 lead to small but significant differences in activation parameters such that the temperature would have to be lowered to ca. -60°C before the values of k_3 became equal. Lowering the temperature to -60°C would increase the difference in rate be-

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tween $\text{Mn}_2(\text{CO})_8(\text{PEt}_3)_2$ and $\text{Mn}_2(\text{CO})_8(\text{PEt}_2\text{Ph})_2$, so the scatter shown in Figure 4 cannot be removed by a different choice of temperature and must reflect nonsystematic, though fairly small, variations in the activation parameters. The fact that $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ reacts a factor of ca. 60 faster than $\text{MnRe}(\text{CO})_8(\text{PPh}_3)_2$ is because the former has a much less negative value of ΔS_3^\ddagger and this more than offsets its higher value of ΔH_3^\ddagger . The stabilizing effect of the second PPh_3 in $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ is caused by a lowering of ΔH_3^\ddagger reinforced by an increase in ΔS_3^\ddagger .

Formation Constants of the Adducts. Several of these reactions, in C_6H_{12} or in other solvents, show clear kinetic evidence for the formation of the proposed adducts. Some spectroscopic evidence for interaction between $\text{Mn}_2(\text{CO})_{10}$ and I_2 has been observed,³ but the small changes were not compatible with the formation of an adduct with only one I_2 molecule, and no further quantitative studies were undertaken. The measurably slow reaction between Br_2 and $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$ was preceded by a very fast spectroscopic change indicative of adduct formation, but the quantitative investigation of the change was difficult and was not pursued.⁷ The kinetic data reported here, however, provide quite precise values for the formation constants of the adducts as shown in Table V.

The values of β_1 for complexes in cyclohexane increase along the series $\text{L} = \text{P}(\text{OPh})_3 < \text{PEtPh}_2 < \text{P}(\text{OMe})_3 < \text{PBu}_3$, and the order of β_2 is $\text{P}(\text{OPh})_3 < \text{PEtPh}_2 < \text{P}(\text{OMe})_3$. No term containing β_2 was detected for $\text{L} = \text{PBu}_3$. For those complexes for which a β_2 value was obtained, we find $k_3/\beta_2 = k_2' = 3.2 \times 10^{-4} \text{ s}^{-1}$ ($\text{L} = \text{P}(\text{OPh})_3$), 0.04 s^{-1} ($\text{L} = \text{P}(\text{OMe})_3$), and 0.08 s^{-1} ($\text{L} = \text{PEtPh}_2$). This sequence shows a good correlation between $\log k_2'$ and $\Delta(\text{hnp})$. For those complexes where no values of β_1 were detected it might be thought that upper limits could be obtained from the inequality $\beta_1[\text{I}_2] \lesssim 0.1$ at the highest value of $[\text{I}_2]$ used. Unfortunately, this is unlikely to give reliable limits as the effect of a significant term $\beta_1[\text{I}_2]$ in the denominator could be masked by a term higher order in $[\text{I}_2]$ in the numerator so that both terms go undetected. This would have been the case for the $\text{Mn}_2(\text{CO})_8(\text{PPhEt}_2)_2\text{-Br}_2$ system if a large number of precise measurements had not been made.⁷ It does not seem justified, therefore, to attempt any more detailed analysis of the values of β_n that were obtained. However, the importance of detectable adduct formation is clearly much greater for reactions with I_2 than for those with Br_2 .⁷

Solvent Effects. The effect of solvent on the values of β_1 can be very pronounced. For $\text{Mn}_2(\text{CO})_8(\text{PEt}_3)_2$ in cyclohexane no value was detected, but in CCl_4 $\beta_1 = 1440 \text{ M}^{-1}$. For this complex in CH_2Cl_2 and MeOH the rate equation has undergone a drastic change (from (4) to (1)), and substantial values of k_1 are obtained. We consider this to be most probably due to even higher values of β_1 in these solvents so that $\beta_1[\text{I}_2] \gg 1$ even at the lowest $[\text{I}_2]$ used. This implies that $\beta_1 \gtrsim 5 \times 10^4 \text{ M}^{-1}$ in CH_2Cl_2 and $\gtrsim 10^4 \text{ M}^{-1}$ in MeOH . In view of the large change from cyclohexane (where no evidence for a term $\beta_1[\text{I}_2]$ was obtained) to CCl_4 a further large change on going to CH_2Cl_2 or MeOH does not seem unreasonable. The values of β_1 are therefore in the order $\text{C}_6\text{H}_{12} < \text{CCl}_4 < \text{MeOH}, \text{CH}_2\text{Cl}_2$. The values of k_1 found in CH_2Cl_2 and MeOH are, therefore, equal to k_1' . Since reaction in CCl_4 does not show a term in $k_2[\text{I}_2]$, no value of k_1' is available, but the value of k_3/β_1 found in CCl_4 ($51 \text{ M}^{-1} \text{ s}^{-1}$) can be compared with the values of k_2 for reactions in CH_2Cl_2 and MeOH , i.e., $\text{CCl}_4 < \text{MeOH} < \text{CH}_2\text{Cl}_2$. The values of k_2 found in CH_2Cl_2 and MeOH can be compared to the k_3 values in C_6H_{12} and CCl_4 by multiplying them by the corresponding limiting values for β_1 , and the sequence of k_3 is then $\text{C}_6\text{H}_{12} < \text{CCl}_4 \ll \text{MeOH} \leq \text{CH}_2\text{Cl}_2$. The sequences for reaction of Br_2 with $\text{Mn}_2(\text{CO})_8[\text{P}(\text{OMe})_3]_2$ are $\text{C}_6\text{H}_{12} \ll \text{CCl}_4 <$

CH_2Cl_2 for k_2 , $\text{C}_6\text{H}_{12} \ll \text{MeOH}$ for k_3 , and $\text{C}_6\text{H}_{12} < \text{CCl}_4 < \text{CH}_2\text{Cl}_2 < \text{MeOH}$ for β_1 , so quite similar solvent effects are evident for all these parameters. The rate equations for reaction of I_2 with $\text{Mn}_2(\text{CO})_8[\text{P}(\text{OMe})_3]_2$ also depend on the solvent. They become increasingly complex along the series $n\text{-Bu}_2\text{O}$ (eq 3), EtOAc (eq 4), and C_6H_{12} (eq 6). The values of k_3 parallel the values of β_1 . In general the tendency to form an adduct with one molecule of I_2 increases along the series $n\text{-Bu}_2\text{O} < \text{C}_6\text{H}_{12} < \text{EtOAc} < \text{CCl}_4 < \text{CH}_2\text{Cl}_2 \approx \text{MeOH}$.

The Intimate Mechanism. The rate equations clearly confirm the general nature of the stoichiometric mechanism of these reactions as described by eq 13 and 14. The trends confirm that reaction involves electrophilic attack by the halogen, the rates increasing with ease of oxidation of the metal as determined by the actual metals involved or, even more so, by the substituents attached to the metal. The absence of pronounced substituent steric effects (other than that for the very largest substituent) suggests that adduct formation occurs by attachment of halogen molecules at or near the O atoms of the CO ligands. The detailed nature of the electron-transfer process is not defined by the kinetics. However, the occurrence of terms $k_4[\text{I}_2]^3$ and even $k_5[\text{I}_2]^4$ in the rate equations, as well as of terms such as $\beta_3[\text{I}_2]^3$, suggests that the complexes could be acting as polyfunctional Lewis bases capable of forming quite strong attachments to several separate I_2 molecules.²³ I_2 is known to form such adducts more readily than Br_2 .²³ The I_2 molecules will tend to withdraw electrons from the metal atoms in the complex through the carbonyl ligands, so weakening the metal-metal bonds and leading to enhanced ease of homolytic or, more probably, heterolytic fission. If the metal-metal bonds do, in fact, undergo heterolytic fission, the reactions can be regarded as S_E in nature. An increasingly close proximity of the I_2 molecules to the metal atoms as the metal-metal bonds stretch would ensure their availability to react with the two fragments while they are forming or immediately they are formed.

These results bear some relationship to reactions such as those of I_2 with ArSnR_3 in CCl_4 to form ArI and ISnR_3 .²⁴ These reactions are second order in $[\text{I}_2]$ and are believed to go via adducts in which an I_2 molecule is attached to the benzenoid ring. The role of the second I_2 molecule is supposed to be the stabilization of the developing negative charge on the first one. It does not seem an improbable alternative for the second I_2 molecule also to be attached to the benzenoid ring in the transition state, thereby inductively enhancing the ease of heterolytic weakening of the Ar-Sn bond. In the reactions described here the negative end developing in one I_2 molecule (whose positive end is attached to an O atom of a CO on one metal) could become close to a relatively electrophilic C atom on a CO ligand on the other metal. This arises because of the staggered nature of the two sets of four CO ligands on the two metals.²⁵ If the contact between the I_2 molecule and the complex is as intimate as this analysis implies, then it is not surprising that the quasi-LFER plots in Figures 4 and 5 should be rather scattered. Rather small variations in the shape of the substituents could easily have effects of the size needed to account for the scatter. The fact that there is no correlation of the rates with the intrinsic ease of homolytic fission of the metal-metal bonds^{11,15} shows that the electron rearrangement in the complexes, caused by the halogen molecules in the adducts, does not provide some sort of constant weakening of the metal-metal bonds but, rather,

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that the ease of electron rearrangement, as determined by the nature of the substituents, is the deciding factor.

The results can also be related to kinetic studies of reactions of halogens with other metal-carbonyl complexes containing metal-metal bonds. The most extensive is a series of studies, by Chipperfield et al.,²⁶⁻³⁰ of the reactions of halogens with a number of complexes containing a group 4 metal attached to a transition-metal carbonyl moiety. Reactions were generally only first order in [halogen] although reaction of I₂ with (η^5 -C₅H₅)Fe(CO)₂(SnPh₃) also showed a term in [I₂]².²⁸ High orders were less likely to be seen in these reactions since they were followed by measuring the decrease of [I₂] at relatively low values of [I₂]. The values of *k*₂ for reaction of I₂ with Mn(CO)₅(ER₃) (E = Si, Ge, Sn, and Pb; R = alkyl) increased²⁸ with increasing electron-releasing power of ER₃, the range in values being ca. 3 × 10⁴. The order of values for E = Sn was R = Me < Et ≲ Bu > C₆H₁₂ although the range of values was only a factor of ca. 8. However, the inevitably linear plot of log *k*₂ for the first three complexes against the value of ν_{CO} for the most intense band in the C-O stretching region has a gradient of -0.14 cm, and the value of log *k*₂ for R = C₆H₁₁ lies 0.4 log unit below this line. The qualitative agreement between this trend and those listed above for reactions of Br₂ or I₂ is interesting, and the much smaller steric deviation of log *k*₂ for reaction of I₂ with (C₆H₁₁)₃SnMn(CO)₅ is exactly what would have been expected. Chipperfield et al. propose^{28,29} that the reaction involves electrophilic attack at the Mn atom, so that there would be substantial Mn-I₂ bonding in the transition state. Differences in rate between Me₃SnMn(CO)₅ and Me₃SnRe(CO)₅ were ascribed to steric effects, the latter reacting faster supposedly because of the larger radius of the Re atom. We believe that rate-determining

attack directly at the metal would be virtually impossible, especially when the necessary electron density is readily available at and through the CO ligands. The very pronounced increase in rate along the series Re₂(CO)₁₀, Re₂(CO)₉(PPh₃), and Re₂(CO)₈(PPh₃)₂ is hardly in accord with a steric control, and the more ready oxidation of Re compared to Mn seems a more likely explanation of the relative rates of the Me₃Sn complexes.

Spectroscopic^{31,32} and kinetic³³ studies of reactions of halogens with Fe(CO)₅ have also shown the formation of Fe(CO)₅·X₂ adducts although their precise formulation seems to depend on the solvent.^{30,31} Kinetics also show that two molecules of I₂ can be involved in the transition state.³³ It seems likely that initial electrophilic attack by a halogen molecule at the periphery of the complex could play a role in these reactions although the five-coordinate nature of the carbonyl does allow for a wider variety of structures. Similar attack could occur in a wide range of reactions involving electrophilic reaction with metal-carbonyl complexes containing metal-alkyl bonds.³⁴ The possibility that variation in the number of halogen molecules in the adducts could affect the stereochemistry of the alkyl halide products is a real one.

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Registry No. I₂, 7553-56-2; Mn₂(CO)₈(PBu₃)₂, 15609-33-3; Mn₂(CO)₈[P(OMe)₃]₂, 15529-61-0; Mn₂(CO)₈(PPh₂Et)₂, 15444-76-5; Mn₂(CO)₈[P(OPh)₃]₂, 15228-70-3; Mn₂(CO)₁₀, 10170-69-1; Mn₂(CO)₈[P(C₆H₁₁)₃]₂, 15662-81-4; Mn₂(CO)₈[P(*p*-MeOC₆H₄)₃]₂, 15662-85-8; Mn₂(CO)₈(PET₃)₂, 15202-23-0; Mn₂(CO)₈(PPhEt)₂, 15444-75-4; Mn₂(CO)₈(PPh₃)₂, 15279-67-1; MnRe(CO)₈(PPh₃)₂, 51371-63-2; Re₂(CO)₁₀, 14285-68-8; Re₂(CO)₈(PPh₃)₂, 27770-64-5; Re₂(CO)₉PPh₃, 51371-62-1; Br₂, 7726-95-6.

Supplementary Material Available: Tables of kinetic data (11 pages). Ordering information is given on any current masthead page.

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