

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE,
C.N.R. LABORATORY, UNIVERSITÀ DI MILANO, MILAN, ITALY**Kinetic Studies of Group VII Metal Carbonyls. II.
Cleavage of Halogen-Bridged Carbonyl Complexes of Manganese(I)**

BY FRANCO ZINGALES AND UGO SARTORELLI

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Rate data for the reactions of tetracarbonyl halide dimers of manganese, $[\text{Mn}(\text{CO})_4\text{X}]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$), with different reagents L ($\text{L} = \text{pyridine}, \gamma\text{-picoline}, \text{or } 3\text{-chloropyridine}$) to yield $\text{Mn}(\text{CO})_3\text{XL}_2$ are reported. The reactions proceed according to the two-term rate law

$$\text{rate} = k_1[\text{Mn}(\text{CO})_4\text{X}]_2 + k_2[\text{Mn}(\text{CO})_4\text{X}]_2[\text{L}]$$

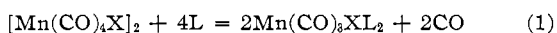
For the same reagent the rates decrease with increasing atomic number of the coordinate halide X and are not greatly affected by changing the solvent. Possible mechanisms for the reaction are presented.

Introduction

Several kinetic studies have been performed concerning carbon monoxide exchange and substitution reactions of mononuclear metal carbonyl compounds. Much less attention has been given so far to binuclear metal carbonyl complexes although many such compounds are known.¹

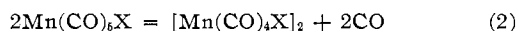
Earlier we have reported that the tetracarbonyl halide dimers of rhenium, $[\text{Re}(\text{CO})_4\text{X}]_2$, where $\text{X} = \text{Cl}, \text{Br}, \text{or I}$, undergo substitution reactions with various reagents L to yield the compounds $\text{Re}(\text{CO})_4\text{XL}$, the reactions being first order in both metal carbonyl and ligand concentration.²

The present work deals with the kinetic study of the formation of $\text{Mn}(\text{CO})_3\text{XL}_2$ by allowing $[\text{Mn}(\text{CO})_4\text{X}]_2$ to react with pyridine or pyridine derivatives, according to the stoichiometry

**Experimental Section**

Compounds and Solvents.—Decacarbonyldimanganese was prepared by the method of Calderazzo.³

The compounds $[\text{Mn}(\text{CO})_4\text{I}]_2$, $[\text{Mn}(\text{CO})_4\text{Br}]_2$, and $[\text{Mn}(\text{CO})_4\text{Cl}]_2$ were prepared by heating the halogenopentacarbonylmanganese derivatives according to a slightly modified literature procedure⁴



Reaction 2 was carried out in refluxing *n*-heptane at 98° for $\text{X} = \text{I}$, 60° for $\text{X} = \text{Br}$, and 45° for $\text{X} = \text{Cl}$. At these temperatures the thermal decomposition of the pentacarbonyls is very limited.

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y. 1967, Chapter 7; R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586 (1965); J. R. Graham and R. J. Angelici, *ibid.*, **87**, 5590 (1965); H. G. Schuster-Woldan and F. Basolo, *ibid.*, **88**, 1657 (1966); S. Breitschaft and F. Basolo, *ibid.*, **88**, 2702 (1966); F. Zingales, A. Chiesa, and F. Basolo, *ibid.*, **88**, 2707 (1966); L. R. Kangas, R. F. Heck, P. M. Henry, S. Breitschaft, E. M. Thorsteinson, and F. Basolo, *ibid.*, **88**, 2334 (1966); H. Werner, *J. Organometal. Chem.* (Amsterdam), **5**, 100 (1966); H. Werner and R. Prinz, *ibid.*, **5**, 79 (1966); R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **88**, 3658 (1966); I. A. Cohen and F. Basolo, *J. Inorg. Nucl. Chem.*, **28**, 511 (1966); F. Zingales, F. Canziani, and F. Basolo, *J. Organometal. Chem.* (Amsterdam), **7**, 461 (1967); F. Zingales, M. Graziani, and U. Belluco, *J. Am. Chem. Soc.*, **89**, 256 (1967).

(2) F. Zingales, U. Sartorelli, F. Canziani, and M. Raveglia, *Inorg. Chem.*, **6**, 154 (1967).

(3) F. Calderazzo, *ibid.*, **4**, 293 (1965).

(4) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

Pyridine, γ -picoline, and 3-chloropyridine (British Drug Houses Ltd.) were distilled before use. All of the solvents were distilled under nitrogen. Thiophene-free benzene was refluxed over sodium wire and then distilled. The *s*-tetrachloroethane was shaken with concentrated H_2SO_4 , washed with water, dried over CaCl_2 , and distilled.

Preparation of Complexes.—The preparation of $\text{Mn}(\text{CO})_3\text{I}(\text{py})_2$ has been described by Abel and Wilkinson.⁴ Since all of the complexes were prepared in the same manner, we present only a general method for their preparation. A reaction mixture containing $[\text{Mn}(\text{CO})_4\text{X}]_2$ (0.0004 mole) and *ca.* 0.0018 mole of ligand in 100 ml of *n*-heptane was allowed to stand under nitrogen at 50° for 1–5 hr. During this time yellow crystals separated from the solution. The product was filtered under nitrogen, washed with pentane, and dried under vacuum. Purification was effected by recrystallization from carbon tetrachloride. The yields were about 80%. All of the compounds were slightly soluble in carbon tetrachloride, chloroform, *s*-tetrachloroethane, and benzene and insoluble in aliphatic hydrocarbons. The compounds, when dry, did not decompose in the presence of air for several days. Elemental analyses and other data on the complexes are given in Tables I and II. The compounds reported in Table I are new.

Kinetic Studies.—The infrared data were obtained with a Perkin-Elmer Model 621 spectrophotometer.

The rates of the substitution reactions were followed by observing changes in the infrared spectra of the reaction mixtures. More details about this method have been given previously.³ All of the kinetic studies were carried out under pseudo-first-order conditions, using at least a tenfold excess of reagent. Light and air were excluded. The concentration range of the substrate was *ca.* 0.0005–0.0015 *M*.

The reactions were carried out in foil-wrapped, nitrogen-filled flasks kept in constant-temperature baths ($\pm 0.1^\circ$). Aliquots were withdrawn from the flasks through a serum cap and transferred to a 1-mm NaCl cell; the infrared spectra were compensated with a reference solution containing the same concentration of the ligand. For the reactions with $k_{\text{obsd}} > 100 \text{ sec}^{-1}$ the reaction mixture was kept in a thermostated ($\pm 0.2^\circ$) Perkin-Elmer 1-mm infrared cell, and the change in transmittance with time was recorded. In the case of $[\text{Mn}(\text{CO})_4\text{Cl}]_2$ the reactions were too fast to be followed by the conventional point-by-point method, and they had to be observed continuously. In such instances, the reactants were first thermostated at 25° for a sufficient length of time and rapidly mixed, and then an aliquot was transferred to a thermostated Perkin-Elmer 1-mm infrared cell. With the frequency set on the instrument at that corresponding to the high-energy carbonyl band of $[\text{Mn}(\text{CO})_4\text{Cl}]_2$, the change in transmittance at this frequency was observed continuously with time. The reactions followed by this method were complete in 4 min or less.

The rate constants were reproducible to within 10% or better.

TABLE I
ANALYTICAL DATA FOR $Mn(CO)_3XL_2$

Complex	Color	Mp, °C ^a	Mol wt ^b		% calcd			% found		
			Calcd	Found	C	H	N	C	H	N
$Mn(CO)_3I(3-Clpy)_2$	Orange	160	493	514	31.7	1.62	5.68	31.1	1.81	5.35
$Mn(CO)_3Br(3-Clpy)_2$	Yellow	150 dec	446	441	35.0	1.79	6.28	34.6	1.73	5.95
$Mn(CO)_3Cl(3-Clpy)_2$	Yellow	150 dec	401	387	38.9	1.99	6.97	38.2	2.21	6.76
$Mn(CO)_3I(\gamma-pic)_2$	Orange	140	452	455	39.8	3.10	6.19	39.7	3.28	6.01

^a Determined with a melting-point block and uncorrected. ^b Osmometry ($10^{-2} M$ solution in $CHCl_3$) with a Mechrolab Model 301-A instrument.

TABLE II
CARBONYL STRETCHING FREQUENCIES IN CCl_4 SOLUTION^a

Compound	ν , cm^{-1}
$[Mn(CO)_4I]_2$	2087 m, 2033 vs, 2008 s, 1974 vs
$[Mn(CO)_4Br]_2$	2098 m, 2041 vs, 2012 s, 1975 vs
$[Mn(CO)_4Cl]_2$	2104 m, 2045 vs, 2012 s, 1975 vs
$Mn(CO)_3I(3-Clpy)_2$	2027 s, 1951 s, 1911 s
$Mn(CO)_3I(py)_2$	2024 s, 1947 s, 1906 s
$Mn(CO)_3I(\gamma-pic)_2$	2022 s, 1942 s, 1903 s
$Mn(CO)_3Br(3-Clpy)_2$	2032 s, 1956 s, 1909 s
$Mn(CO)_3Cl(3-Clpy)_2$	2035 s, 1956 s, 1907 s

^a All spectra recorded on a Perkin Elmer Model 621 spectrophotometer. Abbreviations: vs, very strong; s, strong; m, medium.

Results and Discussion

The infrared⁵ and X-ray⁶ studies of the compounds $[Mn(CO)_4X]_2$ have established a structure with bridging halogens. It has also been reported⁴ that $[Mn(CO)_4X]_2$ compounds undergo a substitution reaction with several reagents in the absence of solvent at 100° to yield disubstitution products, according to reaction 1.

We have now found that reaction 1 occurs also in solution at room temperature with pyridine or substituted pyridines. The products have been isolated and characterized by analyses and molecular weights (Table I). The infrared spectra of the $Mn(CO)_3XL_2$ compounds in the range 2100–1900 cm^{-1} (Table II) are consistent with a structure in which the two L groups are *cis* to the X as well as to each other.⁷

The rates of reaction 1 were followed by observing the changes in the infrared spectrum of the reaction mixtures. The bands due to the C–O stretching vibrations of the starting material were gradually replaced by the bands of the final product $Mn(CO)_3XL_2$. No evidence for the presence of monosubstituted complexes, $Mn(CO)_4XL$, was found.

Linear plots of the pseudo-first-order rate constants, k_{obsd} (sec^{-1}) (Table III), vs. the concentration of L are obtained with a nonzero intercept (Figure 1). The general rate law is therefore

$$\text{rate} = k_1[[Mn(CO)_4X]_2] + k_2[[Mn(CO)_4X]_2][L] \quad (3)$$

The intercept is k_1 (sec^{-1}), and the slope is k_2 ($M^{-1} sec^{-1}$). As expected for the general rate law (3), k_1 is practically independent of the nature of L (the deviations are relatively small), while k_2 definitely depends upon the nature of L. The values of the specific rate

TABLE III
RATES OF REACTIONS OF $[Mn(CO)_4X]_2$
WITH DIFFERENT LIGANDS AT 25°

$10^2[\text{ligand}], M$	$10^3k_{obsd}, sec^{-1}$	$10^2[\text{ligand}], M$	$10^3k_{obsd}, sec^{-1}$
[$Mn(CO)_4I]_2$ + 3-Clpy in CCl_4			
	5.60	17.0	18.2
2.11	7.10	20.7	21.4
3.61	8.06	1.02	20.0 ^a
4.34	9.21	2.05	22.6 ^a
5.92	10.4	4.36	28.3 ^a
7.82	11.5	5.29	29.9 ^a
9.00	13.0	9.15	39.9 ^a
10.6	15.5	12.7	48.4 ^a
[$Mn(CO)_4I]_2$ + 3-Clpy in <i>s</i> - $C_2H_5Cl_4$			
1.98	5.10	7.83	9.40
4.50	7.30	12.1	12.0
6.62	8.46	15.3	14.0
[$Mn(CO)_4I]_2$ + 3-Clpy in C_6H_6			
2.74	10.7	9.76	19.3
3.89	13.5	12.7	20.9
5.96	15.1	17.0	25.5
[$Mn(CO)_4I]_2$ + py in CCl_4			
1.34	8.52	5.13	21.1
2.54	12.5	6.33	25.3
3.46	15.4	8.41	32.1
3.66	16.1	11.4	42.2
4.11	17.5	12.9	47.4
[$Mn(CO)_4I]_2$ + γ -pic in CCl_4			
1.28	12.6	4.03	28.8
1.97	16.3	4.79	31.9
3.12	22.4	6.75	43.7
[$Mn(CO)_4Br]_2$ + 3-Clpy in CCl_4			
0.629	136	6.10	224
1.81	150	6.37	226
2.56	159	7.34	242
3.36	180	8.66	265
4.41	201	10.4	295
5.14	213		
[$Mn(CO)_4Cl]_2$ + 3-Clpy in CCl_4			
0.890	1210	5.99	1450
2.35	1290	9.05	1640
5.30	1460	11.9	1790

^a At 35° .

constants calculated from the data by a least-squares fit are listed in Table IV.

The reactions have been carried out in carbon tetrachloride, benzene, and *s*-tetrachloroethane. Solvents of high dielectric constant and/or of high coordinating ability such as acetone, nitromethane, nitrobenzene, and tetrahydrofuran give very poor resolution of the higher strong carbonyl absorption of $[Mn(CO)_4X]_2$ so that the reactions could not be followed in these conditions.

(5) M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963).

(6) L. F. Dahl and C. H. Wei, *Acta Cryst.*, **16**, 611 (1963).

(7) R. J. Angelici, F. Basolo, and A. J. Poë, *J. Am. Chem. Soc.*, **85**, 2215 (1963).

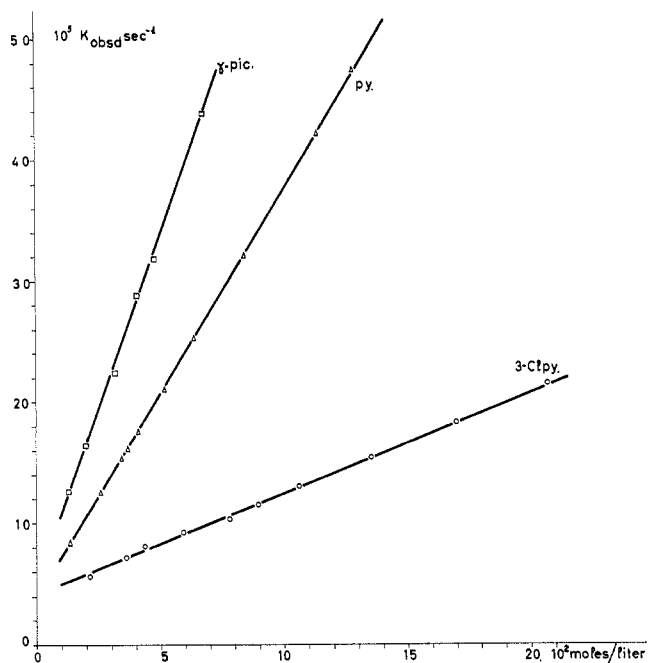


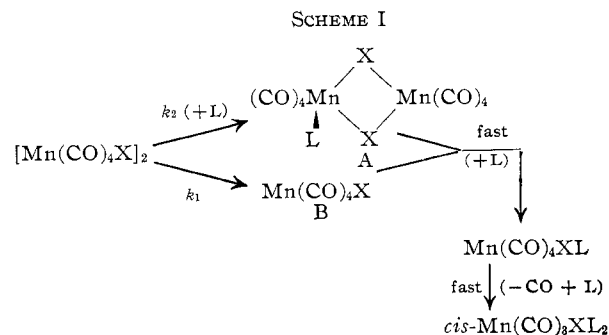
Figure 1.—Plots of the experimental rate constants, k_{obsd} , for the reaction of $[\text{Mn}(\text{CO})_4\text{I}]_2$ with pyridines at 25° in carbon tetrachloride.

TABLE IV
FIRST- AND SECOND-ORDER RATE CONSTANTS FOR REACTIONS OF
HALOGEN-BRIDGED COMPLEXES WITH LIGANDS IN
CARBON TETRACHLORIDE SOLUTION

$[\text{Mn}(\text{CO})_4\text{X}]_2$	L	Temp, $^\circ\text{C}$	10^3k_1 , sec^{-1}	10^3k_2 , $M^{-1}\text{sec}^{-1}$
$[\text{Mn}(\text{CO})_4\text{I}]_2$	3-Clpy	25	4.1	0.83
		35	17	2.4
		25^a	5.2	0.52
		25^b	9.1	0.97
	py	25	3.8	3.4
$[\text{Mn}(\text{CO})_4\text{Br}]_2$	3-Clpy	25	120	17
		$[\text{Mn}(\text{CO})_4\text{Cl}]_2$	3-Clpy	25

^a In *s*-tetrachloroethane. ^b In benzene.

According to the kinetic data, we proposed for the cleavage reactions the mechanism shown in Scheme I, involving the initial simultaneous formation of either an activated halogen-bridged complex (A) of higher coordination number or the five-coordinate complex (B), the latter probably arising from a single-bridged species



as intermediate. It can be noted that the nitrogen ligands always yield the disubstituted product of the halogenopentacarbonylmanganese derivatives, giving no evidence for a monosubstituted intermediate.⁸

An alternative mechanism involves a rapid preequilibrium between the original dibridged complex (I) and a complex (II) with an X bridge partially labilized reminiscent of the primary structure. The latter reacts then by a dissociative path (k_1) and simultaneously undergoes a nucleophilic attack (k_2) by the entering group (Figure 2).

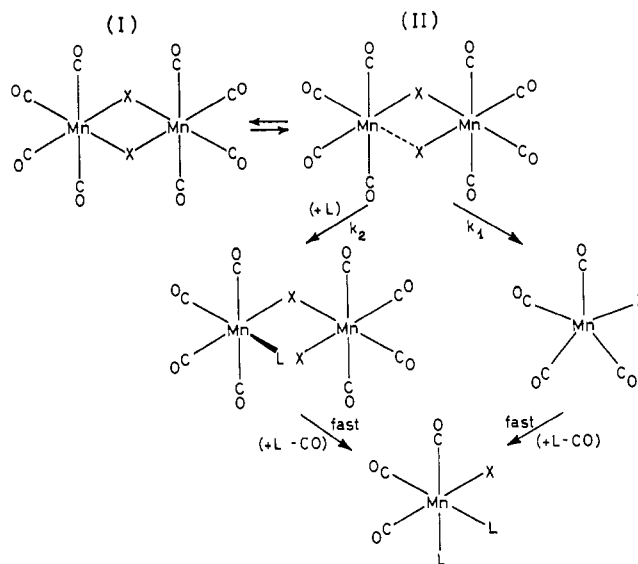


Figure 2.

The comparison of the kinetic data for the reactions of analogous rhenium² and manganese carbonyl dimers of the type $[\text{M}(\text{CO})_4\text{X}]_2$ shows that (i) the k_2 values are significantly larger for rhenium than for manganese and (ii) there is no dissociative pathway (k_1) in the case of rhenium reactions. Point i can be explained by the larger covalent radius of rhenium which makes the formation of the heptacoordinate transition state more favorable. Concerning point ii, the relatively large values of k_1 for the manganese compounds suggest that in tetracarbonyl halide dimers of manganese the bond strength Mn-X is lower than that of its parents Re-X. It can be noted that the $\nu(\text{Mn-X})$ vibration in $\text{Mn}(\text{CO})_5\text{X}$ occurs at essentially the same frequency as the $\nu(\text{Re-X})$ mode of $\text{Re}(\text{CO})_5\text{X}$.⁹ This result presumably implies that the Re-X bond in $\text{Re}(\text{CO})_5\text{X}$ is stronger than the Mn-X bond in $\text{Mn}(\text{CO})_5\text{X}$, because on a mass basis alone it would be expected that $\nu(\text{Re-X}) < \nu(\text{Mn-X})$. Unfortunately, the corresponding $\nu(\text{M-X})$ for the dimers $[\text{Mn}(\text{CO})_4\text{X}]_2$ and $[\text{Re}(\text{CO})_4\text{X}]_2$ are not known.

A comparison of the kinetic data for the reactions of the three $[\text{Mn}(\text{CO})_4\text{X}]_2$ with 3-chloropyridine shows that k_2 decreases in the order $\text{Cl} > \text{Br} > \text{I}$. Such a reactivity order can be rationalized in terms of the different halide electronegativity: the more electronegative group will induce less electron density on the Mn, making it more sensitive to the nucleophilic attack. As far as the dissociative path (k_1) is concerned, the

(8) R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, **84**, 2495 (1962); R. J. Angelici, *J. Inorg. Nucl. Chem.*, **28**, 2627 (1966).

(9) M. A. Bennett and R. J. H. Clark, *J. Chem. Soc.*, 5560 (1964).

reactivity order found, $\text{Cl} > \text{Br} > \text{I}$, is consistent with the increasing order of the bond strength of $\text{M}-\text{X}$ when the metal is of class b¹⁰ or "soft"-acid type,¹¹ *i.e.*, $\text{I} > \text{Br} > \text{Cl}$.

Temperature-dependence studies permit calculations of the activation parameters for the reaction of $[\text{Mn}(\text{CO})_4\text{I}]_2$ with 3-chloropyridine in carbon tetrachloride solution: $\Delta H_1^* = 26$ kcal/mole, $\Delta S_1^* = 8$ eu, $\Delta H_2^* = 19$ kcal/mole, and $\Delta S_2^* = -8$ eu. The positive activation entropy for the first-order pathway (k_1) has to be expected for a dissociation process where in the transition state some freedom degrees are gained. The activation entropy for the second-order path (k_2) is negative as generally found for bimolecular processes.

It was reported that in CCl_4 solution the tetracarbonyl halide dimers of manganese decompose slowly

(10) S. Ahrlund, J. Chatt, and N. R. Davies, *Quart. Rev. (London)*, **12**, 265 (1958).

(11) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

giving an insoluble residue.¹² On the other hand it is well known that CCl_3 radicals are readily obtained from CCl_4 under irradiation. However, using CCl_4 as solvent, we never observed, under our reaction conditions, the formation of any insoluble product. Also the two-term rate law (3) was found to hold for all solvents used. Moreover, the nature of the solvent does not significantly affect the rate constants of the examined reaction, as generally observed for the reactions involving carbonyl derivatives of the transition metals.¹ Our kinetic measurements were carried out mainly in CCl_4 solution, because of the high solubility of both reagents and reaction products and of the good resolution of the absorption bands in the carbonyl stretching region.

Acknowledgments.—The authors wish to thank Dr. F. Calderazzo and Dr. U. Belluco for helpful discussions.

(12) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962).

Notes

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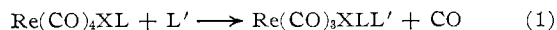
Kinetic Studies of Group VII Metal Carbonyls. III. Kinetics of the Reaction of Monosubstituted Rhenium Pentacarbonyl Halides with Different Reagents

BY FRANCO ZINGALES, UGO SARTORELLI, AND ALDO TROVATI

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The reaction mechanism of the tetracarbonyl halide dimers of rhenium, $[\text{Re}(\text{CO})_4\text{X}]_2$, with various ligands to form *cis*-monosubstituted compounds, $\text{Re}(\text{CO})_4\text{XL}$, have been recently reported.¹ It was found that the reactions were first order in both the metal carbonyl and the ligand concentrations.

The present article reports the formation of $\text{Re}(\text{CO})_3\text{XLL}'$, by the reaction between $\text{Re}(\text{CO})_4\text{XL}$ and L' in solution at different temperatures



Experimental Section

Preparation and Purification of Materials.—The compounds $\text{Re}(\text{CO})_5\text{X}$ and $[\text{Re}(\text{CO})_4\text{X}]_2$ (where $\text{X} = \text{Cl}, \text{Br}, \text{or I}$) were prepared according to the procedure described in the literature.^{2,3}

Triphenylphosphine, commercial reagent grade, was recrystallized from petroleum ether. Tributylphosphine (Fluka), pyridine, and γ -picoline (British Drug Houses) were distilled

before use. The method described in the literature was used to prepare ethyldiphenylphosphine.⁴

Carbon tetrachloride (Analar, British Drug Houses) was distilled and stored under nitrogen. Toluene was refluxed over sodium wire and then distilled.

The preparation of monosubstituted complexes, $\text{Re}(\text{CO})_4\text{XL}$, has been previously described.¹ Analytical data for the new compound $\text{Re}(\text{CO})_4\text{BrP}(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5)$ are given in Table I. The monosubstituted derivative $\text{Re}(\text{CO})_4\text{BrP}(n\text{-C}_4\text{H}_9)_3$ has not been isolated, but it was prepared *in situ* under the kinetic conditions.

Some of the disubstituted complexes, $\text{Re}(\text{CO})_3\text{XLL}'$, were prepared and characterized by means of analyses and infrared spectra (Tables I and II). The infrared spectra of the $\text{Re}(\text{CO})_3\text{XLL}'$ compounds are consistent with a structure in which L and L' are *cis* to the X as well as to each other.⁵ A general procedure for the synthesis of $\text{Re}(\text{CO})_3\text{XLL}'$ has been used. $\text{Re}(\text{CO})_4\text{XL}$ (0.0007 mole) and *ca.* 0.001 mole of ligand L' dissolved in 100 ml of carbon tetrachloride were allowed to react at 60°. Progress of the reaction was monitored by infrared spectroscopy. When no more $\text{Re}(\text{CO})_4\text{XL}$ could be detected, the solution was cooled to room temperature and the product was precipitated by adding *n*-pentane. The compound was filtered, washed with pentane, and dried under vacuum. The yields are about 80%. Purification was obtained by recrystallization from carbon tetrachloride. All of the compounds are slightly soluble in organic solvents.

Kinetic Studies.—The reactions were carried out in foil-wrapped flasks kept in constant-temperature baths ($\pm 0.1^\circ$). Aliquots were withdrawn from the flasks through a serum cap and transferred to a 1-mm NaCl cell; their infrared spectra were measured against that of a reference solution containing the same concentration of the ligand. Measurements were performed on a Perkin-Elmer Model 621 spectrophotometer. In most cases, rates were determined from the disappearance of the intense carbonyl band next to the highest energy absorption. More details

(1) F. Zingales, U. Sartorelli, F. Canziani, and M. Raveglia, *Inorg. Chem.*, **6**, 154 (1967).

(2) W. J. Kirkham, A. G. Osborne, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 550 (1965).

(3) E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *ibid.*, 3149 (1958).

(4) J. Meisenheimer, J. Casper, M. Höring, W. Lauter, L. Lichtenstadt, and W. Samuel, *Ann. Chem.*, **449**, 213 (1926).

(5) U. Sartorelli, F. Canziani, and F. Zingales, *Inorg. Chem.*, **5**, 2233 (1966).