reactivity order found, Cl > Br > I, is consistent with the increasing order of the bond strength of M–X when the metal is of class b[10] or "soft"-acid type,[11] *i.e.*, I > Br > Cl.

Temperature-dependence studies permit calculations of the activation parameters for the reaction of $[\mathrm{Mn(CO)_4I}]_2$ 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 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.

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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

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The reaction mechanism of the tetracarbonyl halide dimers of rhenium, $[\mathrm{Re(CO)_4X}]_2$, with various ligands to form *cis*-monosubstituted compounds, $\mathrm{Re(CO)_4XL}$, 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 $\mathrm{Re(CO)_3XLL'}$, by the reaction between $\mathrm{Re(CO)_4XL}$ and L′ in solution at different temperatures

$$\mathrm{Re(CO)_4XL} + \mathrm{L'} \longrightarrow \mathrm{Re(CO)_3XLL'} + \mathrm{CO} \qquad (1)$$

Experimental Section

Preparation and Purification of Materials.—The compounds $\mathrm{Re(CO)_5X}$ and $[\mathrm{Re(CO)_4X}]_2$ (where X = Cl, Br, 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, $\mathrm{Re(CO)_4XL}$, has been previously described.[1] Analytical data for the new compound $\mathrm{Re(CO)_4BrP(C_6H_5)_2(C_2H_5)}$ are given in Table I. The monosubstituted derivative $\mathrm{Re(CO)_4BrP(}n\mathrm{\text{-}C_4H_9)_3}$ has not been isolated, but it was prepared *in situ* under the kinetic conditions.

Some of the disubstituted complexes, $\mathrm{Re(CO)_3XLL'}$, were prepared and characterized by means of analyses and infrared spectra (Tables I and II). The infrared spectra of the $\mathrm{Re(CO)_3XLL'}$ 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 $\mathrm{Re(CO)_3XLL'}$ has been used. $\mathrm{Re(CO)_4XL}$ (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 $\mathrm{Re(CO)_4XL}$ 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 (±0.1°). 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

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[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).

TABLE I

Complex	Color	Mp, °C		%C	%H	%N
$Re(CO)_3ClP(C_6H_5)_3(py)$	White	138	Calcd	48.26	3.11	2.16
			Found	47.9	3.02	2.45
$Re(CO)_3Br(\gamma\text{-pic})_2$	White	168	Calcd	33.58	2.63	5.22
			Found	33.88	2.84	5.17
$Re(CO)_3Br[P(C_6H_5)_3]_2$	White	181	Calcd	53.55	3.46	
			Found	53.1	3.15	
$Re(CO)_4BrP(C_6H_5)(C_2H_5)$	White	82	Calcd	36.49	2.55	
			Found	36.75	2.47	
$Re(CO)_3Br[P(C_6H_5)_2(C_2H_5)]_2$	White	141	Calcd	47.82	3.88	
			Found	48.1	3.95	
$Re(CO)_3I(py)_2$[a]	Yellow	196	Calcd	28.11	1.81	5.04
			Found	27.9	1.75	5.15

[a] This compound has been reported elsewhere.[3]

TABLE II
CARBONYL STRETCHING FREQUENCIES OF
SOME NEW HALOGENOCARBONYLRHENIUM DERIVATIVES[a]

Compound	ν, cm⁻¹
$Re(CO)_4BrP(C_6H_5)_2(C_2H_5)$	2104 m, 2019 s, 2001 vs, 1939 s
$Re(CO)_4BrP(n\text{-}C_4H_9)_3$	2101 m, 2000 vs, 1972 vs, 1926 s
$Re(CO)_3ClP(C_6H_5)_3(py)$	2034 s, 1945 s, 1893 s
$Re(CO)_3Br(\gamma\text{-pic})_2$	2026 s, 1929 s, 1884 s
$Re(CO)_3Br(py)_2$	2027 s, 1933 s, 1887 s
$Re(CO)_3Br[P(C_6H_5)_3]_2$	2037 s, 1960 s, 1899 s
$Re(CO)_3BrP(C_6H_5)_3(py)$	2035 s, 1943 s, 1891 s
$Re(CO)_3Br[P(C_6H_5)_2(C_2H_5)]_2$	2032 s, 1952 s, 1902 s
$Re(CO)_3Br[P(C_6H_5)_2(C_2H_5)](py)$	2030 s, 1941 s, 1887 s
$Re(CO)_3BrP(n\text{-}C_4H_9)_3P(C_6H_5)_3$	2034 s, 1955 s, 1896 s
$Re(CO)_3I(\gamma\text{-pic})_2$	2028 s, 1931 s, 1886 s

[a] All spectra recorded on a Perkin-Elmer Model 621 spectrophotometer, in carbon tetrachloride solution. Abbreviations: vs, very strong; s, strong; m, medium. For other data see ref 1 and E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

TABLE III
RATE CONSTANTS FOR REACTION 1 IN CCl_4 SOLUTION[a]

$$Re(CO)_4XL + L' \longrightarrow Re(CO)_3XLL' + CO$$

L	L'	Temp, °C	10^5k, sec⁻¹
	Rates for $Re(CO)_4ClL$		
Pyridine	Pyridine	30	7.7
		35	17
		40	35
$P(C_6H_5)_3$	$P(C_6H_5)_3$	45	8.7
		50	18
		60	65
		50	16[b]
$P(C_6H_5)_3$	Pyridine	60	71
	Rates for $Re(CO)_4BrL$		
γ-Picoline	γ-Picoline	60	87
Pyridine	Pyridine	40	5.5
		50	22
		60	86
		60	75[b]
Pyridine	$P(C_6H_5)_3$	60	85
$P(C_6H_5)_3$	$P(C_6H_5)_3$	55	6.4
		60	14
		67.5	38
$P(C_6H_5)_3$	Pyridine	60	15
$P(C_6H_5)_2(C_2H_5)$	$P(C_6H_5)_2(C_2H_5)$	60	4.4
$P(C_6H_5)_2(C_2H_5)$	Pyridine	60	4.3
$P(n\text{-}C_4H_9)_3$	$P(C_6H_5)_3$	60	2.9
	Rates for $Re(CO)_4IL$		
γ-Picoline	γ-Picoline	60	9.4
Pyridine	Pyridine	60	9.4
		65	18
		70	35
		60	8.0[b]

[a] Supplementary material (specific kinetic data used to estimate values in this table) has been deposited as Document No. 9387 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks payable to: Chief, Photoduplication Service, Library of Congress. [b] Toluene as the solvent.

about this method have been given previously.[1] All of the kinetic studies were carried out under pseudo-first-order conditions: the concentration of the metal complexes was kept at approximately 10^{-3} *M*; the concentration of the ligands was varied from 10^{-2} to 5×10^{-1} *M*. Usually about 20 measurements were done during a period of 3 half-lives. All of the reactions proceeded to completion. The rate constants have been measured with an accuracy which is believed to be 10% or better.

The infrared spectrum in the carbonyl region of a given derivative was in good agreement with that of the reaction mixture at infinite time containing the same reagent. Reaction mixtures for which the product was not isolated gave infrared spectra analogous to the disubstituted derivatives (Table II).

Kinetic measurements and infrared spectral evidence indicate that reaction 1 of $Re(CO)_4Br(py)$ with $P(C_6H_5)_3$ is not a simple one. The scheme in this case is very probably

$$\begin{tikzcd} Re(CO)_4Br(py) \arrow[r, "+P(C_6H_5)_3", "-CO"'] \arrow[d, "-py"', "+P(C_6H_5)_3"] & Re(CO)_3Br(py)P(C_6H_5)_3 \\ Re(CO)_4BrP(C_6H_5)_3 \arrow[r, "+P(C_6H_5)_3", "-CO"'] & Re(CO)_3Br[P(C_6H_5)_3]_2 \end{tikzcd} \quad (2)$$

Results and Discussion

The pseudo-first-order rate constants of reactions of $Re(CO)_4XL$ with various ligands (eq 1) were found to be zero order in L′ as well as independent of the nature of L′ (Table III). Thus the general rate law is

$$\frac{-d[Re(CO)_4XL]}{dt} = k[Re(CO)_4XL] \quad (3)$$

According to the rate law (3), the rate-determining step is the dissociation of a CO group from the complex, followed by the rapid entry of L′. Recently it has been shown that $Mo(CO)_6$, which previously had been reported to react with neutral monodentate ligands by a first-order mechanism,[6] at high ligand concentration follows a two-term rate law[7]

$$\text{rate} = k_1[Mo(CO)_6] + k_2[Mo(CO)_6][L] \quad (4)$$

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(6) H. Werner, *J. Organometal. Chem.*, (Amsterdam), **5**, 100 (1966).
(7) J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, **88**, 3658 (1966).

On the contrary, in reaction 1 also at high concentrations of the ligand L′, the rates of reaction do not depend on the nature and concentration of L′. As an example, the values of the pseudo-first-order rate constants, k_{obsd} (sec^{-1}), for the reaction of $\mathrm{Re(CO)_4BrP(C_6H_5)_3}$ with $\mathrm{L' = P(C_6H_5)_3}$ at 60° in $\mathrm{CCl_4}$ are 13.9×10^{-5} ($L' = 0.02\ M$) and 13.8×10^{-5} ($L' = 0.208\ M$). For the analogous reaction with L′ = pyridine in the same experimental condition, the values found are 15.2×10^{-5} ($L' = 0.0188\ M$) and 15.3×10^{-5} ($L' = 0.424\ M$). Similar results are obtained in the case of other examined substrates.

Data in Table III show that the rate constants for reaction 1 decrease with changes in X in the order Cl > Br > I. This is the same reactivity order as found for the reactions of the analogous manganese compounds.[8, 9] This has been explained on the basis of the difference in electronegativity of halogen ligands: the more electronegative chlorine causes a lower electron density on rhenium which in turn means less back-donation of d electrons, lower metal–CO bond strength, and therefore faster reaction.

Furthermore the data in Table III indicate a decrease in the rate of reaction 1 with changes in the coordinated ligand L in the order: γ-pic = py ≫ $\mathrm{P(C_6H_5)_3}$ > $\mathrm{P(C_6H_5)_2(C_2H_5)}$ > $\mathrm{P(\mathit{n}\text{-}C_4H_9)_3}$. It has been reported that the rates of reaction

$$\mathrm{Mn(CO)_4XL + L' \longrightarrow Mn(CO)_3XLL' + CO} \qquad (5)$$

were independent of L′ concentration and were decreased by reducing the bulkiness of the coordinated ligand L.[9] Our results for $\mathrm{Re(CO)_4XL}$ are in agreement with a similar behavior when the coordinated ligands L are bases with the same donor atom (*i.e.*, $\mathrm{P(C_6H_5)_3}$, $\mathrm{P(C_6H_5)_2(C_2H_5)}$, $\mathrm{P(\mathit{n}\text{-}C_4H_9)_3}$). Conversely, when L is pyridine or substituted pyridine, the rates of reaction 1 are considerably larger. The decreasing first-order rate constant with change in the donor atom of the coordinated L is opposite to that expected on the basis of the decreasing metal–CO bond order in the ground state with increasing π-acceptor properties of the coordinated ligand L. Thus a reason for such behavior ought to be found in a different stabilization imposed by the σ-donor pyridine in comparison to the π-acceptor phosphine upon the coordinately unsaturated complex in the transition state. The same type of reasoning applied to the comparison between the rate constants when $\mathrm{L = P(C_6H_5)_3}$ and $\mathrm{P(\mathit{n}\text{-}C_4H_9)_3}$ would predict a larger rate for $\mathrm{P(\mathit{n}\text{-}C_4H_9)_3}$, which is not the case. However, in this particular case, it should be considered that a steric acceleration by $\mathrm{P(C_6H_5)_3}$ probably overrides the electronic effect of $\mathrm{P(C_6H_5)_3}$.

TABLE IV
ACTIVATION PARAMETERS FOR REACTION 1 IN $\mathrm{CCl_4}$ SOLUTION

$$\mathrm{Re(CO)_4XL + L' \longrightarrow Re(CO)_3XLL' + CO}$$

$\mathrm{Re(CO)_4XL}$	L′	ΔH^*, kcal/mole	ΔS^*, eu
$\mathrm{Re(CO)_4Cl(py)}$	Pyridine	28	15
$\mathrm{Re(CO)_4Br(py)}$	Pyridine	29	14
$\mathrm{Re(CO)_4I(py)}$	Pyridine	29	10
$\mathrm{Re(CO)_4ClP(C_6H_5)_3}$	$\mathrm{P(C_6H_5)_3}$	28	11
$\mathrm{Re(CO)_4BrP(C_6H_5)_3}$	$\mathrm{P(C_6H_5)_3}$	34	26

Some activation parameters for reaction 1 are given in Table IV.

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

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[8] R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, **84**, 2495 (1962).

[9] R. J. Angelici and F. Basolo, *Inorg. Chem.*, **2**, 728 (1963).

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Tetra(methylgermanium) Hexasulfide

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As evidenced by recent reviews,[1] organogermanium sulfur compounds have received little attention in the past, although corresponding compounds of silicon or tin are quite well known. Examples of organogermanium sulfides of the general formula $\mathrm{(R_3Ge)_2S}$ and $\mathrm{(R_2GeS)_3}$ have been described previously. However, crystalline species of the corresponding sulfides based on monoalkylgermanium moieties, having the general formula $\mathrm{(RGeS_{1.5})}$, do not seem to have been reported, although amorphous aryl derivatives[1] have been described.

Owing to the ready availability of alkylhalogermanes by an improved version[2] of the direct synthesis,[3] the latter are now conveniently accessible so that synthesis of a prototype of the missing low molecular weight sulfide has been undertaken. A method of preparation has been used which was previously applied to the synthesis of analogous monoalkylsilicon sulfides,[4,5] $\mathrm{(RSiS_{1.5})_4}$. It is based on the reaction

$$\mathrm{4CH_3GeBr_3 + 6H_2S + 12N(C_2H_5)_3 \longrightarrow (CH_3GeS_{1.5})_4 + 12N(C_2H_5)_3 \cdot HBr} \qquad (1)$$

The tetra(methylgermanium)hexasulfide thus prepared is a stable, crystalline, high-melting material which, because of its molecular weight and mass spectroscopic cracking pattern, must consist of four $\mathrm{(CH_3GeS_{1.5})}$ moieties—probably arranged in a structure of the type I or II.

The "adamantane" skeleton of structure I, which is found in some organic and inorganic compounds,[6] is

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[1] D. Quane and R. S. Bottei, *Chem. Rev.*, **63**, 403 (1963). See also O. H. Johnson, *ibid.*, **48**, 259 (1951).

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[3] E. G. Rochow, *J. Am. Chem. Soc.*, **69**, 1729 (1947).

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[6] H. Stetter, *Angew. Chem. Intern. Ed. Engl.*, **1**, 286 (1962).