even in the presence of air: no changes in its infrared spectrum were detected over a period of 2 months. It decomposes without melting.

$[Re(CO)_2(NO)X_2]_2$ (X = Br, I).—The chloride dimer (0.2 g) was dissolved in 80 ml of acetone and treated with an excess of potassium bromide or iodide at reflux with stirring. After 12 hr the suspension was filtered and the filtrate was taken to dryness under reduced pressure. The residue was taken up with 30 ml of 1,2-dichloroethane to give a suspension containing the potassium halide as insoluble residue. Filtration and addition of *n*-pentane or very cold carbon tetrachloride gave the products $[Re(CO)_2(NO)X_2]_2$ (X = Br, I) as crystalline precipitates. These were filtered off, washed with *n*-pentane, and dried *in vacuo* (yields *ca.* 60%). The compounds are soluble in most organic solvents, except for aliphatic hydrocarbons and carbon tetrachloride. They are quite stable both in the solid and in solution and decompose without melting.

$Re(CO)_2(NO)Cl_2L$ (L = Pyridine, 4-Picoline, 3,4-Lutidine, Pyridine Oxide, Triphenylphosphine Oxide, Tetrahydrothiophene).—$[Re(CO)_2(NO)Cl_2]_2$ (0.2 g) dissolved in 100 ml of carbon tetrachloride was treated with a slight excess of ligand L at reflux. All the reactions went to completion in 2–3 hr. The solutions were filtered and concentrated to a small volume under reduced pressure, and the complexes were precipitated by addition of *n*-pentane and storage in a refrigerator overnight. The yellow crystalline products were filtered off, washed with *n*-pentane, and dried *in vacuo*. The yields were practically quantitative.

$Re(CO)_2(NO)X_2L$ (X = Br, I; L = Pyridine).—These were prepared with the same method as above, except for the use of nitromethane as solvent, owing to the low solubility of the starting bromide and iodide complexes in carbon tetrachloride. Conversion was practically quantitative in *ca.* 20 hr for the bromo complex and in *ca.* 40 hr for the iodide.

Preparation of $Re(CO)_2(NO)Cl_2L$ from $Re(CO)_4ClL$.—About 0.3 g of $Re(CO)_4ClL$ dissolved in 100 ml of thiophene-free benzene was heated at reflux with a stream of nitric oxide and gaseous HCl for 6 days. The solution was evaporated to a small volume under reduced pressure and the products were precipitated by addition of *n*-pentane. After filtration, they were recrystallized from carbon tetrachloride–pentane (1:10). The yield was 50%.

Preparation of $Re(CO)_2(NO)Cl_2L$ from $Re(CO)_3ClL_2$.—These reactions, carried out under conditions similar to those previously described, did not go to completion. After 15 days, the starting material could still be detected. The solution was evaporated to dryness and the residue was treated with boiling ligroin (bp 80–110°) with vigorous stirring. After filtration, the reaction products were isolated from the solution after standing in a refrigerator overnight. The yield was very low (10–15%).

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Mechanism of Cleavage of Halogen-Bridged Rhenium Carbonyl Nitrosyl Complexes

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Kinetic experiments are reported for chloride bridge cleavage reactions of $[Re(CO)_2(NO)Cl_2]_2$ with nitrogen-bearing monodentate ligands (L) in carbon tetrachloride or trichloroethylene which yield $Re(CO)_2(NO)Cl_2L$ (L = chloro-, fluoro-, or cyanopyridine). Reaction rates are first order both in substrate and ligand concentrations. Activation parameters are reported. Two alternative mechanisms are proposed. Slow bimolecular attack by L may occur at the vacant coordination site of one rhenium atom in a mono-bridged intermediate formed in a preequilibrium step. Subsequent fast attack by L leads to the final product. Alternatively, nucleophilic attack by L may take place directly at one rhenium atom in a slow step leading to a dibridged intermediate of a higher coordination number. This may then react rapidly with a further L to yield the final product. Factors affecting the reactivity of this system are discussed. The new complexes $Re(CO)_2(NO)Cl_2L$ are described.

Introduction

Studies on the kinetic behavior of transition metal carbonyl and carbonyl nitrosyl derivatives are of considerable current interest.[1] A great number of substrates have been examined to date,[2] particularly simple and substituted mononuclear carbonyl complexes. By contrast, rather few binuclear and carbonyl nitrosyl derivatives have been investigated kinetically. Earlier we reported kinetic studies on halide bridge cleavage reactions of binuclear complexes of the type $[M(CO)_4X]_2$ where M = Mn, Re; X = Cl, Br, I.[3,4] Recently we have described the preparation of the first halide-bridged carbonyl nitrosyl rhenium derivatives, $[Re(CO)_2(NO)X_2]_2$ (X = halide), and some of the products that can be obtained from these by halide bridge cleavage reactions with neutral monodentate ligands bearing N, P, O, or S as donor atoms.[5]

With the aim to gain information on the factors which affect halide bridge cleavage reactions and on the

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TABLE I

ANALYTICAL DATA FOR SOME NEW COMPLEXES OF THE TYPE $Re(CO)_2(NO)Cl_2L$

				Analyses, %							
		Mol wt[b]		C		H		N		Halogen	
Complex[c]	Mp,[a] °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Re(CO)_2(NO)Cl_2$(3-CNpy)	193	447	428	21.48	21.05	0.90	0.86	9.40	9.47	15.85	15.50
$Re(CO)_2(NO)Cl_2$(2-Cl(py))	185	457	442	18.41	19.13	0.88	0.86	6.14	6.34	23.29	22.72
$Re(CO)_2(NO)Cl_2$(4-CNpy)	169	447	462	21.48	22.00	0.90	0.87	9.40	9.65	15.85	15.75
$Re(CO)_2(NO)Cl_2$(2-Fpy)	186	440	428	19.10	19.10	0.91	0.86	6.36	6.38	...	...
$Re(CO)_2(NO)Cl_2$(3-Cl(py))	165	457	447	18.41	18.32	0.88	0.85	6.14	6.53	23.29	22.23

[a] Determined in evacuated tubes and uncorrected. [b] Determined in chloroform solution using a Mechrolab Model 301 A osmometer. [c] All complexes are yellow.

influence of the coordinated NO group, we have now carried out a kinetic study of the reactions

$$[Re(CO)_2(NO)Cl_2]_2 + 2L \longrightarrow 2Re(CO)_2(NO)Cl_2L \qquad (1)$$

(L = 2- and 4-cyanopyridine, 2- and 3-chloropyridine, and 2-fluoropyridine) in carbon tetrachloride or trichloroethylene and shall report the results in this paper, along with a description of the new complexes $Re(CO)_2(NO)Cl_2L$.

Results and Discussion

(1) **Reaction Products.**—Analytical data, physical properties, and selected infrared bands for the products of reactions 1 are reported in Tables I and II.

TABLE II

C–O, N–O, AND Re–Cl STRETCHING FREQUENCIES (cm^{-1})[a]

Complex	ν(CO)[b]	ν(NO)[b]	ν(Re–Cl)[c]
$[Re(CO)_2(NO)Cl_2]_2$[d]	2106 vs 2047 vs	1803 vs	331 s 287 s 252 m
$Re(CO)_2(NO)Cl_2$(3-CNpy)	2109 vs 2036 vs	1769 vs	323 s 296 s
$Re(CO)_2(NO)Cl_2$(2-Cl(py))	2107 vs 2036 vs	1776 vs	325 s 295 s
$Re(CO)_2(NO)Cl_2$(4-CNpy)	2112 vs 2036 vs	1770 vs	327 s 298 s
$Re(CO)_2(NO)Cl_2$(2-Fpy)	2107 vs 2035 vs	1777 vs	325 s 294 s
$Re(CO)_2(NO)Cl_2$(3-Cl(py))	2107 vs 2033 vs	1766 vs	320 s 296 s

[a] All spectra recorded using a Perkin-Elmer Model 621 spectrophotometer. Abbreviations: vs, very strong; s, strong; m, medium. [b] In CCl_4 solution. [c] In Nujol mull. [d] From ref 5.

The infrared spectra in solution in the 2200–1700-cm^{-1} region show two strong bands assigned to terminal carbonyl stretching vibrations and one strong absorption due to ν(NO). The far-infrared spectra show two medium strong bands in the range 330–290 cm^{-1} attributed to ν(Re–Cl). Based on their infrared spectra for these compounds we also propose a structure analogous to the similar $Re(CO)_2(NO)X_2L$ complexes described earlier.[5]

(2) **Kinetics.**—All kinetic runs were carried out under pseudo-first-order conditions by the use of at least a tenfold excess of ligand L over the substrate concentration. Rates of reaction 1 were determined by following the disappearance of the NO stretching band at 1803 cm^{-1} in the infrared spectrum of the starting dimeric complex in solution. During the reactions, such a band was gradually replaced by the analogous bands of the reaction products which occur at lower frequencies (Table II). All the reactions went to completion, as shown by a comparison of the spectra of the final reaction mixtures with those of the expected products. Carbon tetrachloride or trichloroethylene was used as the solvent. Media with higher dielectric constant or coordinating ability, such as acetone, nitromethane, nitrobenzene, or tetrahydrofuran, were found to be unsuitable because of the poor resolution they afford in the NO stretching region.

The pseudo-first-order rate constants, k_{obsd} (sec^{-1}) (Table III), when plotted *vs.* the concentration of ligand L gave straight lines with zero intercepts at all temperatures examined (see Figure 1), so that the rate law is of the form

$$\text{rate} = k_2[\text{complex}][L]$$

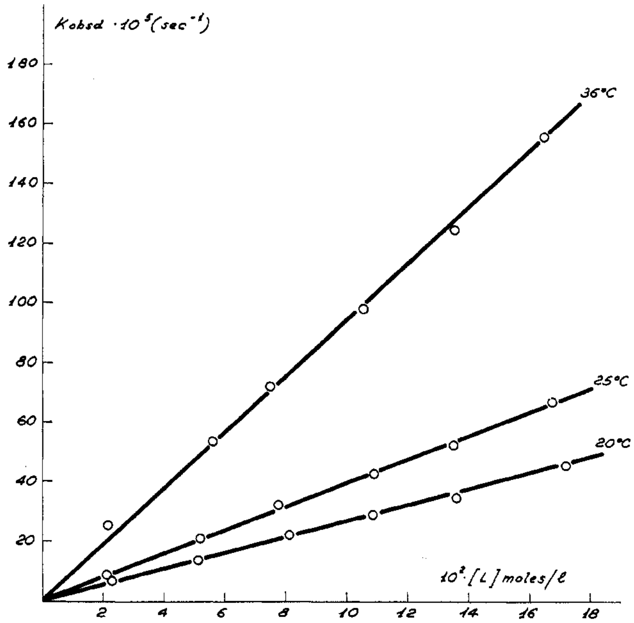


Figure 1.—Plot of k_{obsd} *vs.* 3-CNpy concentrations for the reaction of $[Re(CO)_2(NO)Cl_2]_2$ with 3-CNpy in carbon tetrachloride at three temperatures.

There appears to be no detectable contribution of a first-order path to the rate of reaction under the conditions of these experiments. Values for the slopes, k_2 (M^{-1} sec^{-1}), calculated from the data by a least-squares fit are listed in Table IV.

TABLE III

RATES OF THE REACTION

$[Re(CO)_2(NO)Cl_2]_2 + 2L \longrightarrow 2Re(CO)_2(NO)Cl_2L$

AT DIFFERENT TEMPERATURES IN CCl_4 SOLUTION

20°		25°		36°	
$10^2[L]$, *M*	10^5k_{obsd}, sec^{-1}	$10^2[L]$, *M*	10^5k_{obsd}, sec^{-1}	$10^2[L]$, *M*	10^5k_{obsd}, sec^{-1}
		L = 3-CNpy			
2.30	7.18	2.04	9.52	2.06	23.1
5.09	13.9	5.19	20.8	5.65	54.9
8.10	22.2	7.75	32.2	7.40	72.7
10.9	29.0	10.9	42.2	10.6	97.9
13.5	34.7	13.5	52.1	13.5	125
17.1	45.5	16.8	66.5	16.5	155
		L = 3-CNpy[a]			
...	...	2.16	8.52	2.21	19.4
...	...	4.93	16.7	4.84	32.1
...	...	7.63	22.9	7.63	50.1
...	...	11.0	31.5	11.0	78.8
...	...	13.3	36.5	13.3	84.0
...	...	16.5	45.0	16.9	115
		L = 2-Cl(py)			
1.88	8.75	2.01	12.2	2.74	39.1
4.02	16.4	4.78	29.1	4.47	61.6
6.71	28.3	8.77	55.0	6.51	88.1
9.42	39.7	11.4	70.5	8.68	110
12.8	54.5	14.5	95.4	10.9	133
16.2	75.0	16.8	110	12.8	154
				15.3	194
				16.9	220
		L = 4-CNpy			
1.82	9.78	1.47	11.7	1.38	25.5
5.07	22.2	5.67	36.2	5.09	82.1
8.75	37.5	7.90	53.2	8.04	123
12.7	53.7	10.3	62.9	10.9	171
15.8	68.4	13.1	86.4	12.8	199
		L = 2-Fpy			
1.79	8.56	2.23	10.7	2.52	40.9
5.65	24.2	3.14	19.7	3.67	61.8
8.49	36.5	6.49	39.4	5.82	88.8
12.0	51.2	9.59	57.2	8.35	129
15.2	62.8	12.8	77.7	11.0	176
17.5	69.5	15.4	89.4	11.9	190
		L = 3-Cl(py)			
...	...	1.45	16.7	...	...
...	...	2.89	31.8	...	...
...	...	4.69	52.1	...	...
...	...	6.13	72.9	...	...
...	...	8.43	111	...	...

[a] Trichloroethylene as the solvent.

TABLE IV

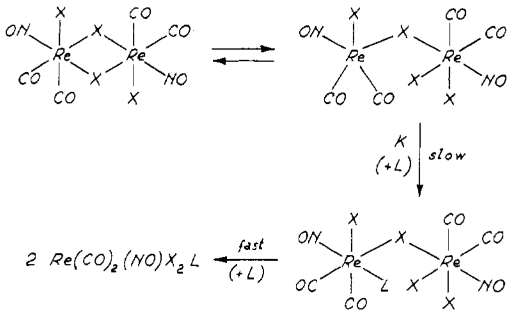
SECOND-ORDER RATE CONSTANTS FOR REACTIONS OF HALOGEN-BRIDGED COMPLEXES WITH LIGANDS IN CARBON TETRACHLORIDE SOLUTION

L	10^3k_2, M^{-1} sec^{-1} 20°	25°	36°
3-CNpy	2.56	3.82–2.51[a]	9.04–6.52[a]
2-Cl(py)	4.49	6.31	12.3
4-CNpy	4.17	6.29	15.2
2-Fpy	3.95	5.95	15.7
3-Cl(py)	...	11.4	...
Pyridine	Very fast	...	...

[a] In trichloroethylene solution.

From the kinetic data two alternative mechanisms for the cleavage reactions can be proposed, as shown by Schemes I and II. According to the mechanism in Scheme I a rapid preequilibrium (lying far over to the left) exists in solution between the original dibridged complex and one containing a single halogen bridge. A slow, rate-controlling nucleophilic attack by the ligand L takes place then at the vacant coordination site of one rhenium atom, with formation of a monobridged active intermediate. This rapidly adds an additional L molecule to give the final product. In the mechanism of Scheme II the nucleophilic attack by L takes place directly at one rhenium atom in a slow, primary step, giving rise to a bridged labile intermediate with a higher coordination number which then reacts rapidly with a further L to yield the final product. Activation parameters, calculated by a least-squares fit from rate constants at three temperatures, are listed in Table V and support a bimolecular SN2-type mechanism. The activation enthalpies are of the order of those commonly observed in reactions of this type (11–15 kcal/mol) wherein the incoming ligand L coordinates rather firmly to give the activated complex; the negative values of activation entropies also suggest SN2-type reactions, wherein some degrees of freedom are lost in the formation of the transition state. It

SCHEME I



SCHEME II

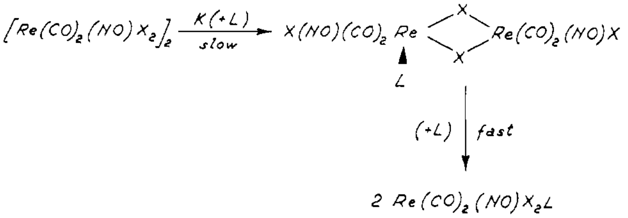


TABLE V

ACTIVATION PARAMETERS FOR THE REACTION

$[Re(CO)_2(NO)Cl_2]_2 + 2L \longrightarrow 2\,Re(CO)_2(NO)Cl_2L$

IN CARBON TETRACHLORIDE SOLUTION

L	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	L	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
3-CNpy	14	−22	4-CNpy	14	−20
	16[a]	−18[a]	2-Fpy	16	−16
2-Cl(py)	11	−30			

[a] In trichloroethylene solution.

should be recalled at this point that the majority of nitrosyl carbonyl transition metal complexes undergo substitution reactions with a purely SN2-type mechanism.[6–10] A "mixed" type of mechanism, SN1 + SN2, was found to the operative in a few particular cases,[6,7,9,11] the second-order path always being, however, much faster than the first-order one. The preference for bimolecular displacements displayed by metal nitrosyls has been explained[12] by the assumption that, although the NO group is formally bonded to the metal as NO^+ in the ground state,[13] it may accommodate a bonding pair of electrons from the metal in the transition state. This would make available an empty orbital of low energy, thereby facilitating the attack by an electron pair of the incoming nucleophile in a bimolecular reaction. This explanation can well be applied to the kinetic behavior of our nitrosyl substrate, $[Re(CO)_2(NO)Cl_2]_2$. The presence of the NO group compounded with two electronegative chlorine atoms bonded to the central metal atom can be expected to render this complex highly reactive toward nucleophiles. This expectation is fully confirmed by our results: kinetic runs for the halogen bridge cleavage reaction (eq 1) could only be followed at relatively mild temperatures by the use of poor nucleophiles, such as pyridine derivatives bearing strong electronegative substituents as F, Cl, or CN. With pyridine the rate of reaction was too fast to measure by our standard spectrophotometric methods even at 20°. Consistently, an inspection of Table IV will show that in analogy with other systems where an SN2 mechanism is operative, the rates of reaction 1 decrease with decreasing polarizability of the entering ligand L, the reactivity order being py $\gg$ 3-Cl(py) $>$ 2-Cl(py) $\sim$ 4-Cl(py) $>$ 2-F(py) $>$ 3-CN(py). As expected, both the nature and the position of the substituent in the pyridine ring affect the nucleophilic ability of the ligand.

A comparison of reaction 1 with halogen bridge splitting reactions of $[Re(CO)_4Cl]_2$[4] may be significant in this context. This latter complex reacts much slower than $[Re(CO)_2(NO)Cl_2]_2$ even with good nucleophiles to yield bridge-cleavage products, other things being equal. Apparently, the transition states of reaction 1 are more stabilized than those of $[Re(CO)_4Cl]_2$, owing to the greater ability of NO to act as a π-acceptor ligand relative to CO.[14,15]

Experimental Section

Materials and Complexes.—The complex $[Re(CO)_2(NO)Cl_2]_2$ was prepared as described earlier.[5] The reaction products $Re(CO)_2(NO)Cl_2L$ were prepared by mere extension of the already reported procedure.[5] Pyridine, 2-chloropyridine, 3-chloropyridine, and 2-fluoropyridine (Fluka A.G.) were distilled prior to use. 4-Cyanopyridine and 3-cyanopyridine were used as purchased from Fluka A.G. without further purification.

Carbon tetrachloride (Analar, BDH Ltd.) was purified by distillation under nitrogen. Trichloroethylene (C. Erba RS) was shaken with concentrated H_2SO_4, washed with water, dried over calcium chloride, and distilled under nitrogen.

Kinetics.—Measurements of reaction rates were carried out by monitoring the disappearance of the NO stretching band of the starting complex (1803 cm^{-1}) which was gradually replaced by the corresponding, lower frequency band of the products during kinetic runs. Preliminary experiments showed the intensity of this band to obey the Lambert–Beer law. A Perkin-Elmer 621 spectrophotometer was used. All kinetic runs were carried out under pseudo-first-order conditions by the use of at least a tenfold excess of entering ligand L over the substrate. In a typical run solutions of the substrate (5×10^{-4}–1.8×10^{-3} M) and of the ligand L (at the desired concentration) were thermostated for 20 min in two separate aluminium foil wrapped flasks placed in a high-precision thermostat at the desired temperature ±0.1°. At zero time the solutions were mixed and well stirred. At time intervals aliquots of the reaction mixture were withdrawn with a syringe and introduced into a 1-mm thick NaCl-windowed infrared cell, and the infrared spectrum in the NO stretching region was recorded promptly. A reference cell containing a solution of L at the same concentration was used. For reactions with $k_{obsd} > 90$–100 sec^{-1}, spectral changes were recorded with the reaction mixture being placed in a 1-mm thermostated (±0.2°) Perkin-Elmer cell. Usually *ca.* 20 measurements were taken over a period of 3 half-lives, since all the reactions went to completion. On plotting log (log T_∞/T) *vs.* time (T is transmittance) straight lines were obtained from the slopes of which the k_{obsd} values were calculated. The k_{obsd} values were accurate within 5% or better. Values of activation parameters calculated by a least-squares fit are believed to be accurate within ±1 kcal/mol for ΔH^* and ±2 eu for ΔS^*.

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