2.5 l. of gas evolved at room temperature. The reaction mixture was poured into 1 l. of water, and the product was extracted with methylene chloride and chromatographed as in the preceding experiment. There was obtained 20.4 g (36.8%) of bluish solid which was recrystallized from methylene chloride–ethanol; mp 226–230°.

Anal. Calcd for $C_{24}H_{27}BMoN_6O_3$: C, 52.0; H, 4.87; Mo, 17.3; N, 15.1; O, 8.67; mol wt 554. Calcd for $C_{23}H_{27}BMoN_6O_3$: C, 51.0; H, 4.99; Mo, 17.7; N, 15.5; O, 8.87; mol wt 542. Found: C, 51.0; H, 4.97; Mo, 17.7; N, 14.8; O, 8.75; mol wt 539 (osmometry in chloroform). Ir (cyclohexane): 1956 (w), 1865 (vs), 1840 cm^{-1} (w). Nmr: m ~2.8; m ~3.4; singlets at 5.16, 5.25, 8.60, 8.66, 8.67, and 9.02 in 2:3:1:2:3:6:3:6 ratio.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratooxomolybdenum Dichloride.—Into a stirred slurry of 31 g (0.05 mol) of $(C_2H_5)_4N$-$HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3$ in 300 ml of methylene chloride was added dropwise thionyl chloride until all gas evolution ceased. The slurry was stirred with 500 ml of water and the red organic layer was separated. It was diluted to 500 ml with methylene chloride and slurried with about 250 ml of Merck acid-washed alumina. When the color changed to green, the mixture was filtered, and the filtrate was stripped yielding a green solid which was stirred with CH_3OH and filtered. There was obtained 14.0 g (58.4%) of green crystals. After recrystallization from chlorobenzene, the product decomposes gradually from 350°.

Anal. Calcd for $C_{15}H_{22}BCl_2MoN_6O$: C, 37.5; H, 4.58; Cl, 14.8; Mo, 20.0; N, 17.5; O, 3.33; mol wt 480. Found: C, 37.4; H, 4.51; Cl, 15.4; Mo, 20.0; N, 17.3; O, 3.29; S absent; mol wt 482 (by osmometry in chloroform). The infrared spectrum is devoid of carbonyl bands but has a strong BH spike at ~2580 cm^{-1}.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratodicarbonylmolybdenum Phenylselenide.—To a solution of 0.02 mol of $KHB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3$ prepared *in situ* was added 0.01 mol of phenyl diselenide, followed by 0.01 mol of bromine dissolved in 20 ml of carbon tetrachloride. The mixture was heated whereupon it started turning red and the solids dissolved. When a total of 0.6 l. of gas was evolved, the solution was poured into water. The product was extracted with methylene chloride and the extracts were chromatographed on alumina yielding 3.6 g (61%) of a dark red solid. It was recrystallized from dimethylformamide; mp 258–260° dec.

Anal. Calcd for $C_{22}H_{27}BMoN_6O_2Se$: C, 44.5; H, 4.56; N, 14.1. Found: C, 44.3; H, 4.67; N, 13.8. Ir (cyclohexane): 1957, 1859 cm^{-1}. Nmr: m 2.80; singlets at 3.88, 4.33, 7.34, 7.54, and 8.82 in 5:1:2:6:6:6 ratio.

Hydrotris(3,5-diethyl-1-pyrazolyl)boratodicarbonylnitrosylmolybdenum.—This compound was prepared in 28% overall yield by a method analogous to that employed for the 3,5-dimethyl analog,[1] but employing 3,5-diethylpyrazole[16] as the starting material. The product was recrystallized from toluene; it crystallizes as an orange solvate. Drying gives yellow crystals, mp 238–240°.

Anal. Calcd for $C_{23}H_{24}BMoN_7O_3$: C, 49.0; H, 6.04; N, 17.4. Found: C, 48.7; H, 6.18; N, 17.4. Ir (cyclohexane): 2014 (CO), 1924 (CO), and 1670 cm^{-1} (NO).

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CONTRIBUTION FROM THE CATTEDRA DI CHIMICA,
FACOLTÁ DI INGEGNERIA, UNIVERSITÁ DI PADOVA, PADUA, ITALY

Halogen-Bridged Rhenium Carbonyl Nitrosyl Complexes and Derivatives

BY FRANCO ZINGALES, ALDO TROVATI, FRANCO CARIATI, AND PAOLO UGUAGLIATI*

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The new carbonyl nitrosyl complex of rhenium $[Re(CO)_2(NO)Cl_2]_2$ is obtained by the reaction of $[Re(CO)_4Cl]_2$ with nitric oxide in the presence of hydrogen chloride. The analogous bromo and iodo derivatives are produced by metathesis of the chloro complex with potassium bromide or iodide. These halide-bridged dimeric compounds undergo facile bridge-splitting reactions by neutral ligands (L) to give monomeric complexes of type $Re(CO)_2(NO)X_2L$ (L = pyridine, 4-picoline, 3,4-lutidine, tributylphosphine, pyridine oxide, triphenylphosphine oxide, tetrahydrothiophene and X = Cl; L = pyridine and X = Br, I). The chloride derivatives can also be obtained by the reaction of $Re(CO)_4ClL$ or $Re(CO)_3ClL_2$ with nitric oxide in the presence of hydrogen chloride. All of these carbonyl nitrosyl complexes display remarkable stability. Infrared spectra are reported. Based on these data, probable structures for these complexes are proposed.

Introduction

Comparably few nitrosyl complexes of group VIIa elements have been reported so far.[1] Most of these are manganese compounds, which can be grouped into three main types: (i) carbonyl nitrosyl complexes such as $Mn(CO)_4(NO)$,[2,3] $Mn(CO)(NO)_3$,[4] $Mn(CO)_3(NO)L$,[5–7] $Mn(CO)_2(NO)L_2$[5–7] (where L is a monodentate ligand such as tertiary phosphine, phosphite, etc.), and $Mn_2(CO)_7(NO)_2$;[2] (ii) simple nitrosyl complexes such as $Mn(NO)_3L$[5,7] and $Mn(NO)_2L_2X$;[5,6] (iii) cyclopentadienyl nitrosyl complexes such as $(C_5H_5)Mn(CO)_2(NO)^+$,[8] $[(C_5H_5)Mn(CO)(NO)]_2$,[9] $(C_5H_5)Mn(OCOCH_3)(CO)(NO)$,[10] and $(C_5H_5)_3Mn_2(NO)_3$.[11]

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[1] For a comprehensive survey on transition metal nitrosyl complexes, see B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966).

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[10] R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.*, **4**, 256 (1965).

[11] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

TABLE I

Complex	Color	Mp,[a] °C	Mol wt Calcd	Mol wt Found	Analyses, % C Calcd	C Found	H Calcd	H Found	N Calcd	N Found	O Calcd	O Found	Halogen Calcd	Halogen Found
$[Re(CO)_2(NO)I_2]_2$	Orange-yellow	230 dec	1052	1052[b]	4.56	4.72	...	...	2.66	2.74	9.12	9.21	48.25	47.92
$[Re(CO)_2(NO)Br_2]_2$	Yellow	280 dec	864	864[b]	5.56	5.68	...	...	3.24	3.39	11.11	11.16	36.99	36.10
$[Re(CO)_2(NO)Cl_2]_2$	Yellow	268 dec	686	686[b]	6.99	7.08	...	...	4.08	4.08	13.98	14.75	20.66	19.78
$Re(CO)_2(NO)I_2(C_5H_5N)$	Yellow	167	605	635[c]	13.89	14.01	0.83	0.97	4.63	4.82	7.93	8.13	41.94	...
$Re(CO)_2(NO)Br_2(C_5H_5N)$	Yellow	196	511	535[c]	16.45	17.47	0.98	1.04	5.48	5.68	9.39	9.46	31.29	...
$Re(CO)_2(NO)Cl_2(C_4H_8S)$	Yellow	66	431	405[c]	16.70	16.10	1.87	1.80	3.25	3.23	11.13	11.51	16.44	...
$Re(CO)_2(NO)Cl_2(C_5H_5N)$	Yellow	184	422	478[c]	19.91	20.06	1.19	1.19	6.63	6.60	11.37	11.37	16.79	16.34
$Re(CO)_2(NO)Cl_2$(4-pic)	Yellow	117	436	481[c]	22.02	22.64	1.62	1.81	6.42	6.40	11.00	10.50	16.25	15.96
$Re(CO)_2(NO)Cl_2$(3,4-lut)	Yellow	148	450	461[c]	24.00	23.40	2.01	1.74	6.22	6.11	10.66	10.71	15.74	15.48
$Re(CO)_2(NO)Cl_2(C_5H_5NO)$	Yellow	150	438	435[c]	19.18	19.40	1.15	1.21	6.39	6.43	14.60	15.44	16.18	...
$Re(CO)_2(NO)Cl_2[(C_6H_5)_3PO]$	Yellow	152	621	604[c]	38.65	38.77	2.43	2.39	2.25	2.45	10.29	10.17	11.41	...

[a] Uncorrected values determined in evacuated tubes. [b] Determined by mass spectra. [c] Determined in chloroform solution using a Mechrolab osmometer, Model 301 A.

As far as rhenium complexes are concerned, the only examples described so far are derivatives of types $Re(NO)_2L_2X_2$, $Re(NO)_2L_2Y$ ($L = P(C_6H_5)_3$, $X = NO_3$, Cl, Br, I; Y = I),[12] and the recently reported $[(C_5H_5)Re(CO)_2(NO)]PF_6$.[13]

In this paper we will report the first halogen-bridged carbonyl nitrosyl complexes of rhenium $[Re(CO)_2(NO)X_2]_2$ (X = Cl, Br, I), and some of their derivatives, $Re(CO)_2(NO)X_2L$, which result from splitting of the halogen bridge by neutral monodentate ligands (L).

Results and Discussion

It is known that manganese carbonyl complexes, such as $Mn(CO)_5I$, $Mn_2(CO)_8(P(C_6H_5)_3)_2$, or $[Mn(CO)_4I]_2$ react with nitric oxide to give $Mn(CO)(NO)_3$[4] or $Mn(CO)_4(NO)$.[3] By contrast, analogous rhenium compounds, such as $[Re(CO)_4X]_2$,[14] do not react with NO. We have now found that nitrosyl chloride or nitric oxide in the presence of hydrogen chloride reacts in benzene with $[Re(CO)_4Cl]_2$ to give the chloride-bridged complex $[Re(CO)_2(NO)Cl_2]_2$ in 70% yield: $[Re(CO)_4Cl]_2 + 2NOCl \rightarrow [Re(CO)_2(NO)Cl_2]_2 + 4CO$. The corresponding bromo and iodo derivatives can be obtained by metathesis of $[Re(CO)_2(NO)Cl_2]_2$ with the appropriate potassium halides in acetone.

These carbonylnitrosyl complexes are obtained as yellow crystals, which are stable in solution even in the presence of air. They are diamagnetic in the solid, nonconductors in nitrobenzene, and sublimable. Elemental analyses, infrared spectra, and other data of the complexes are given in Tables I and II. The dimeric nature of these compounds is shown by molecular weights, based on the appearance of the parent molecular ions in the mass spectra. The position of the NO stretching vibration in the infrared spectrum indicates that nitric oxide is bonded as NO^+ to the central metal in the oxidation state $+1$[14,15] (*vide infra*). It is worth mentioning that $[Mn(CO)_4Cl]_2$ failed to react with nitrosyl chloride under similar conditions to those employed for the preparation of the rhenium nitrosyl compounds.

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]
$[Re(CO)_2(NO)Cl_2]_2$	2106 vs 2047 vs	1803 vs	331 s 287 s 252 m
$[Re(CO)_2(NO)Br_2]_2$[d]	2105 vs 2046 vs	1798 vs	
$[Re(CO)_2(NO)I_2]_2$[d]	2097 vs 2028 vs	1785 vs	
$Re(CO)_2(NO)I_2(C_5H_5N)$	2085 vs 2013 vs	1763 vs	
$Re(CO)_2(NO)Br_2(C_5H_5N)$	2088 vs 2014 vs	1769 vs	
$Re(CO)_2(NO)Cl_2(C_4H_8S)$	2110 vs 2033 vs	1772 vs	317 s 292 s
$Re(CO)_2(NO)Cl_2(C_5H_5N)$	2106 vs 2029 vs	1761 vs	320 s 295 s
$Re(CO)_2(NO)Cl_2$(4-pic)	2106 vs 2028 vs	1763 vs	320 s 291 s
$Re(CO)_2(NO)Cl_2$(3,4-lut)	2106 vs 2028 vs	1765 vs	311 s 288 s
$Re(CO)_2(NO)Cl_2(C_5H_5NO)$	2099 vs 2028 vs	1761 vs	311 s 288 s
$Re(CO)_2(NO)Cl_2[(C_6H_5)_3PO]$	2096 vs 2020 vs	1761 vs	313 s 291 s
$Re(CO)_2(NO)Cl_2[P(n\text{-}C_4H_9)_3]$	2093 vs 2019 vs	1770 vs	319 s 284 s

[a] All spectra recorded using a Perkin-Elmer Model 621 spectrophotometer. [b] Carbon tetrachloride solution. [b] Nujol mull. [d] Chloroform solution.

The carbonyl nitrosyl rhenium halide dimers react in solution with various neutral ligands (L) to give halide bridge splitting products of the type $Re(CO)_2(NO)X_2L$: $[Re(CO)_2(NO)X_2]_2 + 2L \rightarrow 2Re(CO)_2(NO)X_2L$ (L = pyridine, 4-picoline, 3,4-lutidine, tributylphosphine, pyridine oxide, triphenylphosphine oxide,

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(12) M. Freni, D. Giusto, and V. Valenti, *Gazz. Chim. Ital.*, **94**, 797 (1964).

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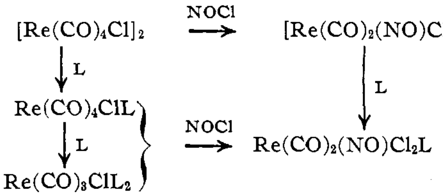
and tetrahydrothiopene). These products can be isolated as crystalline solids which are diamagnetic in the solid, nonconductors in nitrobenzene, air stable, and soluble in common organic solvents in which they are monomeric. Analytical data and infrared spectra are reported in Tables I and II. The compound $Re(CO)_2(NO)Cl_2(P(n\text{-}C_4H_9)_3)$ could not be isolated in a pure state but showed an infrared spectrum similar to those of the other derivatives. The complexes of type $Re(CO)_2(NO)Cl_2L$ can also be obtained by the reaction of $Re(CO)_4ClL$[16a] or $Re(CO)_3ClL_2$[16b] with nitrosyl chloride, as outlined in the reaction scheme



Infrared Spectra. (i) $[\mathbf{Re(CO)_2(NO)X_2]_2}$.—The infrared spectra of $[Re(CO)_2(NO)X_2]_2$ in carbon tetrachloride in the range 2200–1700 cm^{-1} show two strong bands assigned to CO stretching vibrations and one single strong band attributed to ν(NO). The far-infrared spectrum of $[Re(CO)_2(NO)Cl_2]_2$ in the 400–200-cm^{-1} region shows two strong absorptions at 331 and 287 cm^{-1} which can be assigned to terminal ν(Re–Cl)[17] and bridging ν(Re–Cl),[18] respectively. ν(Re–Br) and ν(Re–I) could not be located since they fall beyond the range covered by our instrument. The most probable structures for these complexes, having C_{2h} and C_i symmetries, are drawn in Figure 1. In fact, for these structures the number of infrared-active CO, NO, Re–Cl(terminal), and Re–Cl(bridging) stretching vibrations required by vibrational analysis and reported in Table III are in agreement with those observed experimentally.

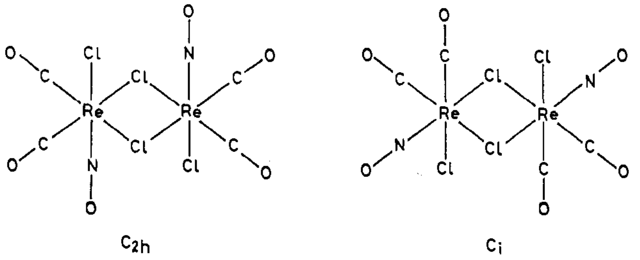


Figure 1.

A choice between these proposed structures is not feasible since the paucity of experimental frequencies prevents one from carrying out a calculation of all stretching and interaction CO force constants.

(ii) $\mathbf{Re(CO)_2(NO)X_2L}$.—The infrared spectra of the complexes in solution in the range 2200–1700 cm^{-1} show two strong bands attributable to carbonyl stretching vibrations and one strong band assigned to the NO stretching absorption. The far-infrared spectra in Nujol in the 400–200-cm^{-1} region for $Re(CO)_2(NO)Cl_2L$ show two strong bands in a position characteristic of Re–Cl stretchings, which are assigned to Re–Cl stretching vibrations involving terminal chlorine atoms. Since the two CO stretchings have nearly the same intensity, as do the Re–Cl stretchings, we propose the following structures as the most probable ones for these complexes (Figure 2).

TABLE III

VIBRATIONAL ANALYSIS FOR $[Re(CO)_2(NO)Cl_2]_2$

C_{2h}	C_i
ν(CO); $A_g(R) + B_g(R) + A_u(ir) + B_u(ir)$	ν(CO); $2A_g(R) + 2A_u(ir)$
ν(NO); $A_g(R) + B_u(ir)$	ν(NO); $A_g(R) + A_u(ir)$
$\nu(Re–Cl)_t$; $A_g(R) + B_u(ir)$	$\nu(Re–Cl)_t$; $A_g(R) + A_u(ir)$
$\nu(Re–Cl)_b$; $2A_g(R) + 2B_u(ir)$	$\nu(Re–Cl)_b$; $2A_g(R) + 2A_u(ir)$

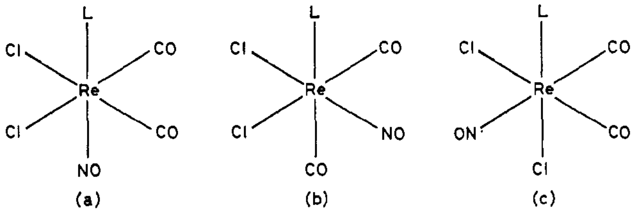


Figure 2.

All of these structures involve *cis*-dichloro-*cis*-dicarbonyl configurations as suggested by the spectra. Since the NO stretching vibration appears to be the most sensitive to changes in the ligand L (see Table II), we are inclined to prefer structure a which has C_s symmetry.

Experimental Section

Materials.—$[Re(CO)_4Cl]_2$ was prepared according to the procedure of the literature.[19] Methods for the synthesis of $Re(CO)_4XL$ and $Re(CO)_3XL_2$ have been described previously.[16]

The ligands tetrahydrothiophene, pyridine, 4-picoline, 3,4-lutidine, tributylphosphine, and pyridine oxide were used as purchased from Fluka A.G. Triphenylphosphine oxide was prepared following a previously reported procedure.[20]

All the solvents were purified by distillation and saturated with nitrogen prior to use.

Preparation of Complexes. $\mathbf{[Re(CO)_2(NO)Cl_2]_2}$.—$[Re(CO)_4Cl]_2$ (0.4 g) was dissolved in 200 ml of thiophene-free benzene heated to reflux. Nitric oxide and hydrogen chloride gas were then bubbled into the boiling solution. The progress of reaction was monitored by infrared spectroscopy and the reaction was found to be complete after 4 days. The deep yellow solution was filtered while warm and taken to dryness under reduced pressure. The crude residue was dissolved in boiling carbon tetrachloride (100 ml) and the resulting solution was filtered and concentrated to half its volume. Addition of 100 ml of *n*-pentane gave $[Re(CO)_2(NO)Cl_2]_2$ as a yellow precipitate. This was filtered off, washed with pentane, and dried *in vacuo* (yield *ca.* 70%). A further purification can be achieved by sublimation under high vacuum (110° (4×10^{-4} mm)). The complex is soluble in acetone, benzene, nitrobenzene, 1,2-dichloroethane, carbon tetrachloride, and chloroform and insoluble in aliphatic hydrocarbons. It is very stable both in the solid and in solution

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[16] (a) F. Zingales, U. Sartorelli, F. Canziani, and M. Raveglia, *Inorg. Chem.*, **6**, 154 (1967); (b) F. Zingales, U. Sartorelli, and A. Trovati, *ibid.*, **6**, 1246 (1967).

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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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