

BRIDGE SPLITTING REACTIONS ON μ -DICHLOROBIS[TETRACARBONYLRHENIUM(I)] WITH LIGANDS HAVING GROUP VI DONOR ATOMS

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SUMMARY

Bridge splitting reactions on μ -dichlorobis[tetracarbonylrhenium(I)] with L ligands bearing oxygen, sulphur, selenium and tellurium as donor atoms give compounds of the type $\text{Re}(\text{CO})_4\text{LCl}$ and $\text{Re}(\text{CO})_3\text{L}_2\text{Cl}$.

The stereochemistries of these new compounds have been established from their IR spectra in the C–O stretching region. The $\nu(\text{CO})$ frequencies indicate that the order of bond strengths is $\text{Re–Se} > \text{Re–Te} \approx \text{Re–S} > \text{Re–O}$.

INTRODUCTION

The μ -dichlorobis[tetracarbonylrhenium(I)], $[\text{Re}(\text{CO})_4\text{Cl}]_2$, and chloropentacarbonylrhenium(I), $\text{Re}(\text{CO})_5\text{Cl}$, have proved convenient source materials for the preparation of other rhenium complexes. The reactions of $[\text{Re}(\text{CO})_4\text{Cl}]_2$ with neutral ligands having nitrogen, phosphorus, arsenic and antimony as donor atoms give complexes of the type $\text{Re}(\text{CO})_4\text{LX}$ and $\text{Re}(\text{CO})_3\text{L}_2\text{X}$ ($\text{X} = \text{halogen}$)^{1–5}. Bridge splitting reactions with ligands bearing oxygen, sulphur, selenium and tellurium as donor atoms are relatively few and some of their gave sulphur-, selenium- and tellurium-bridged complexes^{6,7}.

In this paper, the preparation and properties of the complexes $\text{Re}(\text{CO})_4\text{LCl}$ and $\text{Re}(\text{CO})_3\text{L}_2\text{Cl}$ are reported. They were formed in reactions involving the monodentate ligands pyridine oxide, triphenylphosphine oxide, diethyl sulphide, diethyl selenide, and diethyl telluride with $[\text{Re}(\text{CO})_4\text{Cl}]_2$.

EXPERIMENTAL

μ -Dichlorobis[tetracarbonylrhenium(I)] was prepared as previously described⁸. Diethyl selenide was prepared by Bird's method⁹. Diethyl sulphide, diethyl telluride, pyridine oxide and triphenylphosphine oxide were all reagent grade commercial materials and were used without further purification.

Reactions were followed by the disappearance of the higher frequency carbonyl absorption of $[\text{Re}(\text{CO})_4\text{Cl}]_2$. Spectra were recorded with a Perkin–Elmer Model 457 IR grating spectrophotometer.

cis-Chlorotetracarbonyl(diethyl sulphide)rhenium(I)

Diethyl sulphide (60 mg; 0.76 mmole) was added to a stirred solution of μ -dichlorobis[tetracarbonylrhenium(I)] (250 mg; 0.37 mmole) in carbon tetrachloride (80 ml). After about 5 h the solution was filtered and concentrated to small volume. Addition of petroleum ether (b.p. 40–70°) and cooling to –80° gave a white product, m.p. 132° (decompn.). (Found: C, 22.91; H, 2.54; Cl, 8.42; O, 15.21; S, 7.34. $C_8H_{10}ClO_4ReS$ calcd.: C, 22.66; H, 2.37; Cl, 8.36; O, 15.09; S, 7.56%.)

cis-Chlorotetracarbonyl(diethyl selenide)rhenium(I) and cis-chlorotetracarbonyl(diethyl telluride)rhenium(I)

These compounds (m.p. 102° and 48°) were similarly prepared from the reaction between μ -dichlorobis[tetracarbonylrhenium(I)] (0.37 mmole) and diethyl selenide or diethyl telluride (0.76 mmole). (Found: C, 20.25; H, 2.33; Cl, 7.21; O, 13.12. $C_8H_{10}ClO_4ReSe$ calcd.: C, 20.41; H, 2.14; Cl, 7.53; O, 13.59%.) (Found: C, 18.75; H, 2.04; Cl, 6.58; O, 12.76. $C_8H_{10}ClO_4ReTe$ calcd.: C, 18.49; H, 1.94; Cl, 6.82; O, 12.32%.)

cis-Chlorotricarbonylbis(diethyl sulphide)rhenium(I)

Diethyl sulphide (136 mg; 1.50 mmoles) was added to a stirred solution of μ -dichlorobis(tetracarbonylrhenium(I)) (250 mg; 0.37 mmole) in carbon tetrachloride (80 ml). The solution was heated under reflux for 8 h and was then filtered and concentrated to small volume. A white, air-stable solid, was obtained by adding petroleum ether (b.p. 40–70°) and cooling at –80°. The product was recrystallized from pentane, m.p. 103°. (Found: C, 26.96; H, 4.51; Cl, 7.35; O, 9.76; S, 13.42. $C_{11}H_{20}ClO_3ReS_2$ calcd.: C, 27.18; H, 4.18; Cl, 7.28; O, 9.88; S, 13.21%.)

cis-Chlorotricarbonylbis(diethyl selenide)rhenium(I) and cis-chlorotricarbonylbis(diethyl telluride)rhenium(I)

These complexes (m.p. 112° and 42°) were prepared similarly from the reaction between μ -dichlorobis[tetracarbonylrhenium(I)] (0.37 mmole) and diethyl selenide or diethyl telluride (1.50 mmoles). (Found: C, 23.08; H, 3.54; O, 8.36. $C_{11}H_{20}ClO_3ReSe_2$ calcd.: C, 22.90; H, 3.45; O, 8.21%.) (Found: C, 19.32; H, 3.12; Cl, 5.41. $C_{11}H_{20}ClO_3ReTe_2$ calcd.: C, 19.51; H, 2.97; Cl, 5.23%.)

cis-Chlorotricarbonylbis(triphenylphosphine oxide)rhenium(I)

μ -Dichlorobis[tetracarbonylrhenium(I)] (250 mg; 0.37 mmole) and triphenylphosphine oxide (418 mg; 1.50 mmoles) in carbon tetrachloride (80 ml) was heated under reflux for 2 h. The white product obtained by cooling the solution was washed with carbon tetrachloride and recrystallized from chloroform/petroleum ether, m.p. 223°. (Found: C, 54.12; H, 3.92; Cl, 4.23. $C_{39}H_{30}ClO_5P_2Re$ calcd.: C, 54.32; H, 3.51; Cl, 4.11%.)

cis-Chlorotricarbonylbis(pyridine oxide)rhenium(I)

This complex was similarly prepared from the reaction between μ -dichlorobis[tetracarbonylrhenium(I)] (0.37 mmole) and pyridine oxide (1.50 mmoles), m.p. 156° (decompn.). (Found: C, 31.37; H, 2.16; Cl, 7.28; O, 16.34. $C_{13}H_{10}ClN_2O_5Re$ calcd.: C, 31.48; H, 2.03; Cl, 7.15; O, 16.13%.)

RESULTS AND DISCUSSION

Cleavage of the chloro bridges of the μ -dichlorobis[tetracarbonylrhenium(I)] by ligands L [$L = S(C_2H_5)_2$, $Se(C_2H_5)_2$, $Te(C_2H_5)_2$, C_5H_5NO , $(C_6H_5)_3PO$] leads to the complexes $Re(CO)_3L_2Cl$. With $S(C_2H_5)_2$, $Se(C_2H_5)_2$ and $Te(C_2H_5)_2$ under relatively mild conditions it is possible to prepare the monosubstituted derivatives $Re(CO)_4LCl$. It is not possible to introduce more L ligands.

This is in agreement with electron impact studies on the halopentacarbonylrhenium(I)¹⁰ and with kinetic reactivities of $M(CO)_5X$ ($M = Mn, Re$; $X = \text{halogen}$) compounds in reactions in which M-CO bond rupture is the rate determining step¹¹, which have shown that two M-CO bonds are weaker than the remaining three.

The IR spectra in carbonyl stretching region are shown in Table 1. The M-CO

TABLE I
CO STRETCHING FREQUENCIES

Compound	CO stretching frequencies (cm^{-1})
$Re(CO)_4[S(C_2H_5)_2]Cl$	2102 m, 2006 s, 1992 s, 1920 s ^a
$Re(CO)_4[Se(C_2H_5)_2]Cl$	2104 m, 2012 s, 1996 s, 1922 s ^a
$Re(CO)_4[Te(C_2H_5)_2]Cl$	2100 m, 2010 s, 1995 s, 1918 s ^a
$Re(CO)_3(C_5H_5NO)_2Cl^b$	2010 s, 1890 s, 1946 s ^d
$Re(CO)_3[(C_6H_5)_3PO]_2Cl^b$	2020 s, 1920 s, 1908 s ^d
	2020 s, 1918 s, 1903 s ^c
$Re(CO)_3[S(C_2H_5)_2]_2Cl$	2025 s, 1938 s, 1910 s ^c
$Re(CO)_3[Se(C_2H_5)_2]_2Cl$	2033 s, 1942 s, 1898 s ^c
$Re(CO)_3[Te(C_2H_5)_2]_2Cl$	2022 s, 1937 s, 1898 s ^c

^a Recorded in nujol mull. ^b A different method of preparation is described in ref. 12. ^c Recorded in CCl_4 solution.

bond strength in metal carbonyls is currently thought to be attributable in part to back-bonding from filled non bonding d orbitals on the metal atom to fairly low-lying CO π antibonding orbitals. Because of the geometry of the d orbitals, ligands in *trans* positions compete for the same sets of orbitals. Since the π -bonding tendency of CO is greater than that of Cl, it follows that the CO *trans* to Cl should have a greater degree of Re-C multiple bonding than the four carbonyl groups lying opposite to each other in the central plane.

In the light of this knowledge, the IR spectra in Nujol mulls, which show four bands ($3A' + A''$) in the CO stretching region, indicate a C_s symmetry for the compounds $Re(CO)_3L_2Cl$ (Fig. 1a).

As shown in Fig. 1 (b-d), three stereochemical configurations are possible for

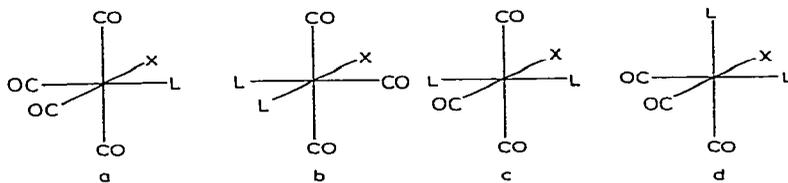


Fig. 1. Possible configurations for complexes of the type $Re(CO)_3L_2Cl$.

molecules of the type $\text{Re}(\text{CO})_3\text{L}_2\text{Cl}$. The configuration illustrated in Fig. 1b may be eliminated because it does not contain a CO ligand *trans* to Cl. Of the two remaining possible configurations, for a complex of the type shown in Fig. 1d (point group C_s) group theory predicts three IR active modes ($A'_a + A'_b + A''$) in the $\nu(\text{CO})$ region, all of similar strong intensity. On the other hand, a complex of the type shown in Fig. 1c (point group C_{2v}) will display three IR active modes of which the highest energy absorption should be weak. The complexes $\text{Re}(\text{CO})_3\text{L}_2\text{Cl}$, here reported, exhibit three strong $\nu(\text{CO})$ absorption bands in their IR spectra. Furthermore, the $\nu(\text{Re}-\text{Cl})$ vibration is in the range $265\text{--}280\text{ cm}^{-1}$ and is insensitive to variation of the ligand L. A structure of C_s symmetry can be assigned to these complexes.

The above analysis has assumed, of course, that the CO stretching frequencies are reliable indicators of the M-C bond strength in octahedral carbonyl derivatives, although this is open to question^{13,14}. The variation of the CO stretching frequency of compounds here reported is consistent with the ability of this ligand to form bonds with fairly strong π character.

In compounds with oxygen as the donor atom, the $\nu(\text{CO})$ stretching frequencies occur at lower frequencies than in analogous compounds involving donor sulphur, selenium, and tellurium ligands. The IR data indicate that the strengths of the bonds between rhenium and Group VI donors fall in the sequence $\text{Re}-\text{Se} > \text{Re}-\text{Te} \approx \text{Re}-\text{S} > \text{Re}-\text{O}$.

Comparison of the IR spectra of our compounds with those of the analogous derivatives having ligands with Group V donor atoms shows that the latter have the greater aptitude for forming bonds of fairly strong π character.

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