Reactivity of Oxotetrachlororhenate(V) with Bidentate and Tetradentate Schiff Bases Containing Oxygen and Nitrogen Donors

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The five-coordinated rhenium(V) $[(C_6H_5)_4As][ReOCl_4]$ compound reacts with bidentate and tetradentate Schiff bases containing oxygen and nitrogen donors to give six-coordinated complexes. With the ligands (LH) (L = N-methylsalicylideneiminate, N-phenylsalicylideneiminate, half N,N'-ethylenebis(salicylideneiminate) and 8-hydroxyquinolinate), the complexes $[(C_6H_5)_4As][ReOCl_4(LH)]$, $[(C_6H_5)_4As][ReOCl_3(L)]$ or $ReOCl(L)_2$ are obtained. The complexes were characterized by elemental analysis and conductivity measurements. Their stereochemistries were postulated on the basis of infrared spectra and X-ray data previously reported for analogous oxo-rhenium(V) compounds.

Introduction

The most important class of rhenium oxohalide compounds includes the $ReOX_3(PR_3)_2$ complexes (X = Cl, Br and PR_3 = tertiary aliphatic or aromatic phosphines). These and the related ethoxo-complexes $ReO(OEt)X_2(PR_3)_2$ have been used as starting materials in the synthesis of complexes of Re^I, Re^{III}, Re^{IV} and Re^{VII}, as well as Re^V [1, 2].

We recently reported [3, 4] that the treatment of $ReOX_3(PPh_3)_2$ (X = Cl, Br) with some bidentate Schiff bases (LH) results in the formation of rhenium(V) complexes of the type $ReOX_2(L)(PPh_3)$ or $ReOX(L)_2$ and that $ReOX_2(L)(PPh_3)$ reacts with dimethylphenylphosphine (PMe_2Ph) to produce the $ReX_2(L)(PMe_2Ph)_2$ complexes through reduction of rhenium(V) to rhenium(III).

Among the other oxohalide compounds, the five-coordinated anion $[ReOX_4]^-$ (X = Cl, Br) raised some interest in its ability in reacting with solvent molecules to form the related six-coordinated complexes $[ReOX_4(solvent)]^-$ [5].

The reactivity of $[(C_6H_5)_4As][ReOCl_4]$ with bidentate and tetradentate Schiff bases of the type LH = N-methylsalicylideneimine (MesalH), N-phenylsalicylideneimine (PhsalH), half N,N'-ethylenebis(salicylideneimine)(sal$_2$en) and 8-hydroxyquinoline (oxine) with the resultant formation of $[ReOCl_4(LH)]^-$, $[ReOCl_3(L)]^-$ and $ReOCl(L)_2$, will be the subject of this paper.

Experimental

Materials

Tetraphenylarsonium tetrachlorooxo-rhenate(V), $[AsPh_4][ReOCl_4]$, was prepared from potassium perrhenate (Alpha-Inorganic) by the method of Lis and Trzebiatowska [6]. N-methylsalicylideneimine, N-phenylsalicylideneimine, N,N'-ethylenebis(salicylideneimine) were synthesized in EtOH from salicylaldehyde and $MeNH_2$, $PhNH_2$ and $H_2N(CH_2)_2NH_2$, respectively. 8-hydroxyquinoline was commercially available (Merck). Other materials were reagent grade chemicals. The solvents were, when necessary, purified and dried by the methods reported in the literature by Perrin *et al.* [7].

Apparatus

The i.r. spectra of solid samples in KBr were recorded on a Perkin-Elmer 577 spectrophotometer.

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TABLE I. Analytical Data.

Compound		M.p.[a] (°C)	Colour	Yield (%)	Analysis: Found (Calc.) (%)			
					C	H	N	Cl
I	$[(C_6H_5)_4As][ReOCl_3(Mesal)]$	209	emerald green	80	46.6 (46.5)	3.4 (3.4)	1.6 (1.7)	12.9 (12.9)
II	$[(C_6H_5)_4As][ReOCl_3(Phsal)]$	207	emerald green	80	50.1 (50.0)	3.3 (3.4)	1.5 (1.6)	12.0 (12.0)
III	$[(C_6H_5)_4As][ReOCl_3(oxine)]$	190 (dec.)	green	85	47.4 (47.4)	3.4 (3.4)	1.7 (1.7)	12.8 (12.7)
IV	$[(C_6H_5)_4As]_2[Re_2O_2Cl_6(sal_2en)]$	180 (dec.)	green	50	46.6 (46.6)	3.5 (3.3)	1.9 (1.7)	12.7 (12.9)
V	$[(C_6H_5)_4As][ReOCl_4(MesalH)]$	86 (dec.)	yellow	85	44.6 (44.5)	3.4 (3.4)	1.7 (1.6)	16.5 (16.4)
VI	$[(C_6H_5)_4As][ReOCl_4(PhsalH)]$	145 (dec.)	yellow	80	48.0 (48.0)	3.4 (3.4)	1.6 (1.5)	15.3 (15.3)
VII	$[(C_6H_5)_4As]_2[Re_2O_2Cl_8(sal_2enH_2)]$	111 (dec.)	yellow	60	44.7 (44.6)	3.3 (3.3)	1.7 (1.6)	17.0 (16.5)

[a] M.p.s were determined in capillaries and are uncorrected.

^1H n.m.r. spectra in $CDCl_3$ were collected on a K.P. 80 MHz Bruker instrument. Electrolytic conductance measurements were carried out using a standard, commercial Wheatstone bridge with a 30 ml cell equipped with platinum electrodes, at 25 °C.

Synthesis of the Complexes

Tetraphenylarsonium tetrachloro (Schiff baseH)-oxo-rhenium(V), $[(C_6H_5)_4As][ReOCl_4(MesalH)]$, $[(C_6H_5)_4As][ReOCl_4(PhsalH)]$ and $[(C_6H_5)_4As]_2[Re_2O_2Cl_8(sal_2enH_2)]$

$[(C_6H_5)_4As][ReOCl_4]$ (0.5 g) was dissolved in the minimum quantity of anhydrous THF at room temperature and a stoichiometric amount of Schiff base was then added. Immediately the precipitation of a powder takes place. After filtration the solid was washed with THF (10 ml), EtOH and pentane. No recrystallization was carried out, owing to the rapid transformation of these compounds to the corresponding monosubstituted chelate complexes in solution.

Tetraphenylarsonium trichloro(Schiff base)oxo-rhenium(V), $[(C_6H_5)_4As][ReOCl_3(Mesal)]$, $[(C_6H_5)_4As][ReOCl_3(Phsal)]$, $[(C_6H_5)_4As][ReOCl_3(oxine)]$ and $[(C_6H_5)_4As]_2[Re_2O_2Cl_6(sal_2en)]$

$[(C_6H_5)_4As][ReOCl_4]$ (0.5 g) was dissolved in boiling EtOH and treated with a stoichiometric amount of the appropriate ligand. The solution was refluxed for 10 minutes under nitrogen atmosphere. The colour changed from yellow to green. The solution was then concentrated to 1/3 of its volume and green plates were obtained. Recrystallization was carried out from CH_2Cl_2/EtOH.

The same compounds can be obtained in THF as solvent, but with longer reaction times (2 h) under reflux. The final products were recovered as solids from the reaction solutions and purified by recrystallization.

Chlorobis(Schiff base)oxo-rhenium(V), $ReOCl(Mesal)_2$, $ReO(Cl(Phsal)_2$, $ReOCl(oxine)_2$, $ReOCl(sal_2en)$

$[(C_6H_5)_4As][ReOCl_4]$ (0.5 g) was mixed with a double stoichiometric quantity of Schiff base in EtOH as in the preceding method. The solution was refluxed for 5 h under nitrogen and then concentrated to small volume. Green crystals were collected and recrystallized from CH_2Cl_2/EtOH.

Results and Discussion

Method of Synthesis

The complex $[(C_6H_5)_4As][ReOCl_4]$ reacts at room temperature or in boiling THF or EtOH with LH = N-methylsalicylideneimine (MesalH), N-phenylsalicylideneimine (PhsalH), half N,N′-ethylenebis(salicylideneimine)(sal$_2$enH$_2$) to give the compounds $[(C_6H_5)_4As][ReOCl_4(LH)]$, $[(C_6H_5)_4As][ReOCl_3(L)]$ and $ReOCl(L)_2$. The general reactions are shown in Scheme 1:

$$[ReOCl_4]^- \xrightarrow[THF]{LH} \underset{(I)}{[ReOCl_4(LH)]^-} \xrightarrow[EtOH]{}$$

$$\underset{(II)}{[ReOCl_3(L)]^-} \xrightarrow[EtOH]{LH} \underset{(III)}{ReOCl(L)_2}$$

TABLE II. Spectroscopic and Conductivity Data.

Compound		IR (cm^{-1}) Nujol mull				Λ_M at 25 °C, ohm^{-1} cm^2	
		ν(Re=O)	ν(C=N)	ν(Re–Cl)	ν(O–H)	In CH_3NO_2 $\sim 10^{-4}$ *M*	In CH_3CN $\sim 10^{-4}$ *M*
I	$[(C_6H_5)_4As][ReOCl_3(Mesal)]$	969vs	1600vs	310s, 300s 270s		98	137
II	$[(C_6H_5)_4As][ReOCl_3(Phsal)]$	963vs	1600vs	310s, 298s 281s		102	130
III	$[(C_6H_5)_4As][ReOCl_3(oxine)]$	965vs	1570s	335s, 300s		109	135
IV	$[(C_6H_5)_4As]_2[Re_2O_2Cl_6(sal_2en)]$	960vs	1600vs	300s		150	254
V	$[(C_6H_5)_4As][ReOCl_4(MesalH)]$	970vs	1660vs	300s	3100m		
VI	$[(C_6H_5)_4As][ReOCl_4(PhsalH)]$	970vs	1630vs	300s	3060m		
VII	$[(C_6H_5)_4As]_2[Re_2O_2Cl_8(sal_2enH_2)]$				3060m		

Complexes of the type (I) are formed readily in THF at room temperature or in EtOH after few minutes of heating. If the reactions are carried out in THF or EtOH at refluxing temperatures, complexes (II) are also obtained. A prolonged heating of (II) in presence of the appropriate ligand gives (III). These compounds can also be prepared from the initial reagents in a 1:2 molar ratio in boiling EtOH. Some differences are observed with oxine, the complex of type (I) not being obtained under the given conditions.

Complexes (III) $ReOCl(Mesal)_2$, $ReOCl(Phsal)_2$, $ReOCl(oxine)_2$ and $ReOCl(sal_2en)$ have already been prepared [3, 8] using $ReOCl_3(PPh_3)_2$ as the starting material. In this case, however, the same complexes were obtained using the lithium salts of the Schiff base or by adding triethylamine to the reaction mixture.

Properties and Probable Structure of the Complexes

The formulation of all the complexes was supported by elemental analysis (Table I). The neutral bisubstituted complexes (III) are described elsewhere [3, 8].

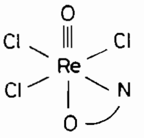
^1H n.m.r. measurements in solution showed that all the complexes are diamagnetic, this result being in agreement with the previous observations on oxorhenium species indicating some distortion from the octahedral configuration [9]. For some complexes, molar conductivity measurements in CH_3NO_2 and CH_3CN solutions gave Λ_M values consistent with a 1:1 or 2:1 electrolyte character (Table II). No measurements in solution were carried out for the complexes (I) because of their rapid transformation to the corresponding monosubstituted chelate complexes (II).

The most important i.r. frequencies for the described complexes are listed in Table II. The band due to the Re=O bond stretching was found in the 960–970 cm^{-1} range, while the corresponding value in the starting compound $[(C_6H_5)_4As][ReOCl_4]$ occurs at 1000 cm^{-1}. This latter band is a superimposed one, resulting from the absorption of the Re=O group as well as of the tetraphenylarsonium cation. After complex formation, the underlying Re=O band was shifted from 1000 cm^{-1} to 960–970 cm^{-1}, the tetraphenylarsonium group vibration being still observable at 1000 cm^{-1}. By X-ray diffraction investigations [6] on rhenium five-coordinated $[ReOCl_4]^-$ ion in the tetraphenylarsonium salt $[(C_6H_5)_4As][ReOCl_4]$, a value of 1.627(24) Å for the Re=O bond length was found, while values of 1.680(4), 1.69(1), 1.685(8) and 1.683(5) Å were found for the rhenium six-coordinated complexes $ReOCl(Mesal)_2$ [10], $ReOCl_2(acac)PPh_3$ [11], $ReOCl_2(Ph(O)CNNCMe_3)PPh_3$ [12] and $ReOBr_2(Phsal)PPh_3$ [13] respectively. In these latter complexes, the ν(Re=O) frequencies fall in the 960–970 cm^{-1} region. Since in general one would expect a 1.63 Å Re=O bond to absorb at higher energy than a 1.68 or 1.69 Å bond, the observed shift from 1000 cm^{-1} to 960–970 cm^{-1} for all the reported complexes is consistent with a lengthening of the Re=O bond on going from five- to six-coordination. Cotton and Lippard [5] did not observe any shift of the Re=O absorption at 1000 cm^{-1} from the five-coordinated $[ReOBr_4]^-$ ion to the six-coordinated $[ReOBr(L)]^-$ (L = CH_3CN, H_2O) derivatives. The unchanged position and intensity of the i.r. Re=O vibration, although the coordination number of the rhenium atom rises from five to six, was interpreted through the formation of a weak rhenium-to-acetonitrile or to-water bond. Indeed, X-ray investigations [14, 15] on these compounds showed that the $[ReOBr_4]^-$ ion consists of a square pyramidal ($ReOBr_4$) grouping as the basic structural unit, with a weakly coordinated solvent molecule attached to its base and with the Re–N (CH_3CN) and

Re–O (H_2O) distances of 2.31 and 2.32 Å respectively.

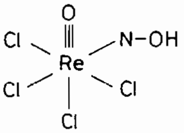
The complexes $[(C_6H_5)_4As][ReOCl_3(L)]$ are air-stable solids, soluble in CH_2Cl_2 and other chlorinated polar solvents such as Me_2CO and CH_3CN, slightly soluble in THF, and insoluble in Et_2O, pentane, EtOH and PhH. Their solutions are not indefinitely stable, the $Re^V{=}O$ group combining with air oxygen to give the most stable $[Re^{VII}O_4]^-$ anion. In addition, repeated treatments with oxygenated solvents such as Et_2O, CH_3NO_2, DMSO, Me_2CO produce decomposition and formation of unknown species.

The $\nu(C{=}N)$ vibrations are in the 1570–1600 cm^{-1} region indicating that the Schiff base ligands are in the chelating form. No definitive information can be deduced from the $\nu(Re{-}Cl)$ stretchings about the *mer* or *fac* configurations of the halogen substituents. The molecular structures of the $ReOCl(Mesal)_2$ [10], $ReOBr_2(Phsal)PPh_3$ [13] and $Re_2O_2Cl_4(sal_2en)(PPh_3)_2$ [17] complexes show an octahedral coordination configuration with the phenolic oxygen of the Schiff base *trans* to the Re=O group. The *trans* $O{=}Re^+{-}O^-R$ (R = alkyl or aryl groups) arrangement can be justified admitting a definite *trans* influence (and therefore a *trans* weakening) by the Re=O bond. This influence increases as a function of the ligand L, in the order $RO^- < Cl^-, Br^- < R_3N$ [10]. It follows that the hard Re=O group would show a higher affinity toward the hardest RO^- species in the above series of substituents. From these facts it is reasonable to assume as the most likely structure for the $[ReOCl_3(L)]^-$ complexes that reported below:



As a consequence of the supposed structure of the complexes, the $[(C_6H_5)_4As]_2[Re_2O_2Cl_6(sal_2en)]$ derivatives can be thought of as formed of two rhenium nuclei in a *mer* halogen octahedral environment joined by an ethylene bridge.

The complexes $[(C_6H_5)_4As][ReOCl_4(LH)]$ are air sensitive solids which slowly decompose if not kept under an inert atmosphere. They are soluble in Me_2CO, $CHCl_3$, CH_2Cl_2, CH_3CN, slightly soluble in THF, and insoluble in Et_2O, EtOH, PhH and pentane. When dissolved they transform rapidly to the corresponding chelates. The i.r. spectra show the $\nu(Re{=}O)$ frequencies in the 960–970 cm^{-1} region. The ligand $\nu(C{=}N)$ stretching appears in the 1620–1660 cm^{-1} range and a band at 3060–3100 cm^{-1} attributed to the $\nu(O{-}H)$ vibration is observed. These i.r. data are characteristic of a neutral monodentate Schiff base and indicate that the ligand is coordinated to the rhenium atom through the aldiminic nitrogen [16]. The supposed configuration for the $[ReOCl_4(LH)]^-$ complexes should contain a chlorine atom *trans* to the Re = O group:



This more reactive chlorine would be substituted by the phenolic oxygen of the ligand with the formation of the more stable $O{=}Re^+{-}O^-R$ arrangement of the chelate complexes (II). The failure to isolate oxine derivatives of type (I) can be ascribed to its high chelation tendency.

A comparison among the rhenium(V) oxohalide compounds reveals a higher reactivity of the $[ReOCl_4]^-$ complex than that exhibited by $ReOCl_3(PPh_3)_2$ with the same Schiff base ligands. The five-coordinated $[ReOCl_4]^-$ reacts with neutral Schiff bases to give rise to the immediate formation of the six-coordinated adducts (I) at room temperature and of the bisubstituted complexes (III) in boiling EtOH. With $ReOCl_3(PPh_3)_2$ as starting material, only the derivative $ReOCl_3(MesalH)PPh_3$ [16] has been obtained in PhH after a long reaction time (about 40 h), while the complexes (III) were produced using the lithium salts of the ligands or by addition of triethylamine to the reaction mixture.

The five-coordination, the absence of stabilizing phosphinic groups and the decrease of charge would be the dominant factors determining the higher reactivity of $[ReOCl_4]^-$ in the formation of complexes (I) and (III) in comparison with the corresponding complexes obtained from $ReOCl_3(PPh_3)_2$.

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