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Synthesis and Characterization of Rhenium Complexes with Salicylaldehyde

ADRIANO DUATTI, ROBERTO ROSSI, ANDREA MARCHI

Istituto Chimico, Università di Ferrara, Ferrara, Italy

ANTONIO PASQUETTO

Istituto di Chimica Generale, Università di Padova, Padua, Italy

and ULDERICO MAZZI

Istituto di Chimica e Tecnologia dei Radioelementi CNR, Padua, Italy

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Rhenium complexes with salicylaldehyde were prepared starting from different compounds in which the rhenium atom is in V, III and I oxidation states. $ReOCl_2(sal)PPh_3$, $AsPh_4$, $ReOCl_3(sal)$, $ReOCl_2(CHOsal)(PMe_2Ph)_2$, $ReCl_3(SalH)(PPh_3)_2$ *and* $Re(CO)_2(sal)(PPh_3)_2$ *were collected and characterized by elemental analysis, magnetic susceptibility measurements, and infrared spectroscopy.*

Introduction

Salicylaldehyde (salH) is a common reagent in coordination chemistry and many complexes with this ligand have been reported in the literature [1–8]. Nevertheless, very few salicylaldehyderhenium complexes are known [9]. We report here the reaction with salH of some already known rhenium complexes and the characterization of the resulting products by means of elemental analysis, magnetic measurements, and infrared spectroscopy.

Salicylaldehyde interacts with rhenium complexes in different oxidation states and forms stable chelate compounds when the rhenium atom is in V and I oxidation states, while with the used rhenium(III) complexes only a monodentate compound was defined.

The reactions we have carried out are:

a) $KReO_4 + HCl(exc.) + salH + 2PPh_3 \longrightarrow$

$$ReOCl_2(sal)PPh_3 \qquad (I)$$

b) $ReOCl_3(PPh_3)_2 + salH \longrightarrow$

$$ReOCl_2(sal)PPh_3 \qquad (I)$$

c) $AsPh_4[ReOCl_4] + salH \longrightarrow AsPh_4[ReOCl_3(sal)]$

$$(II)$$

d) $ReOCl_2(sal)PPh_3 + 2PMe_2Ph \longrightarrow$

$$ReOCl_2(CHOsal)(PMe_2Ph)_2 \qquad (III)$$

e) $ReCl_3(MeCN)(PPh_3)_2 + salH \longrightarrow$

$$ReCl_3(salH)(PPh_3)_2 \qquad (IV)$$

f) $ReCl(Co)_3(PPh_3)_2 + salLi \longrightarrow$

$$Re(CO)_2(sal)(PPh_3)_2 \qquad (V)$$

Experimental

Materials

Rhenium complexes used as starting materials were prepared by methods reported in the literature [10]. Other materials were reagent grade chemicals. Solvents were purified and dried by the methods reported by Perrin *et al.* [11] and were distilled under N_2 before use.

Physical Measurements

I.r. spectra of solid samples in KBr or nujol mulls between polyethylene pellets were recorded on a Perkin Elmer 580B spectrophotometer (4000–180 cm^{-1}). The magnetic susceptibility of CH_2Cl_2 solutions was measured at 300 K on a Varian T60 instrument using Evans' method.

Synthesis of the Complexes

Complex (I), $ReOCl_2(sal)PPh_3$, was obtained by two methods. Using method a), $KReO_4$ was treated

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TABLE I. General Properties and Elemental Analysis of Rhenium Salicylaldehyde Complexes.

Complex		M.p.* (°C)	Colour	Yield %	Found (Calcd) %		
					C	H	Cl
(I)	$ReOCl_2(sal)PPh_3$	203	emerald green	75[a] 92[b]	46.0(45.7)	3.1(3.1)	11.0(10.8)
(II)	$[ReOCl_3(sal)]AsPh_4$	219	olive green	42	45.2(45.8)	3.0(3.1)	13.1(13.1)
(III)	$ReOCl_2(CHOsal)(PMe_2Ph)_2$	170(dec.)	green	25	42.6(41.2)	4.2(4.1)	11.3(10.6)
(IV)	$ReCl_3(salH)(PPh_3)_2$	188(dec.)	green	10	53.7(54.9)	3.5(3.9)	12.2(11.3)
(V)	$Re(CO)_2(sal)(PPh_3)_2$	229(dec.)	orange	40	59.9(61.0)	4.0(4.0)	

*M.p.'s. were determined in capillaries and are uncorrected. [a]Method of synthesis a). [b]Method of synthesis b) (see text).

TABLE II. Principal I.r. Stretching Frequencies (cm^{-1}).

Complex		ν(Re=O)	ν(C=O)	ν(C–O)	ν(Re–Cl)	other bands
(I)	$ReOCl_2(sal)PPh_3$	975s	1600s	1280m	295m	–
(II)	$[ReOCl_3(sal)]AsPh_4$	960s	1607s	1297m	315w, 308s, 290w	–
(III)	$ReOCl_2(CHOsal)(PMe_2Ph)_2$	970s	1665s	1275m	292m	–
(IV)	$ReCl_3(salH)(PPh_3)_2$	–	1610s	1275m	315sh, 309m, 300sh	3335 ν(O–H)
(V)	$Re(CO)_2(sal)(PPh_3)_2$	–	1603s	1280m	–	1910s, 1830s ν(CO)

in boiling EtOH with a stoichiometric amount of PPh_3 for 2 h, to undergo reduction in the presence of salH and an excess of HCl. The final product was collected as a green powder from the reaction solution. Through method b) a substitution reaction occurred between $ReOCl_3(PPh_3)_2$ and salH or its lithium salt (salLi), causing the exchange of the Cl^- and PPh_3 groups with the phenolic charged oxygen and the neutral carbonyl one of the ligand respectively. The reaction was carried out in PhH at refluxing (2 h) or room temperature (12 h), the final product being recovered as a solid from the reaction solution. The increase in the ligand concentration gives rise to the formation of reduction products, owing to the reducing properties of the salH ligand. Complex (I) is a crystalline, air-stable solid, soluble in CH_2Cl_2, $CHCl_3$, MeCN, THF and Me_2CO and insoluble in PhH, CCl_4, Et_2O, EtOH and pentane.

Complex (II), $AsPh_4[ReOCl_3(sal)]$, was obtained from $AsPh_4[ReOCl_4]$ and salH (1:1) in refluxing EtOH, after 1 h of reaction. The recovered yellow brown powder was recrystallized from Me_2CO. The compound is a crystalline, air-stable solid, soluble in CH_2Cl_2, $CHCl_3$ and Me_2CO, and insoluble in EtOH, Et_2O and pentane.

Complex (III), $ReOCl_2(CHOsal)(PMe_2Ph)_2$, was obtained by treating complex (I) in refluxing PhH for two hours with a 1:2 stoichiometric ratio of PMe_2Ph. After concentration of the reaction solution under reduced pressure, a green powder was recovered and then crystallized from $CHCl_3$ and EtOH. Complex (III) is a crystalline, air-stable solid, soluble in CH_2Cl_2, $CHCl_3$, Me_2CO and THF, and insoluble in EtOH, Et_2O and pentane. Its solutions are not stable indefinitely.

Complex (IV), $ReCl_3(salH)(PPh_3)_2$, was prepared by reacting $ReCl_3(MeCN)(PPh_3)_2$ in boiling salH as solvent, for 5 min. The final product was precipitated from the reaction medium by addition of EtOH after concentration under low pressure. Recrystallization was obtained from $CHCl_3$ and EtOH. Complex (IV) in an air-stable solid, soluble in CH_2Cl_2, $CHCl_3$, MeCN, THF and Me_2CO, and insoluble in PhH, EtOH, Et_2O and pentane.

Complex (V), $Re(CO)_2(sal)(PPh_3)_2$, was prepared by allowing $ReCl(CO)_3(PPh_3)_2$ to react in boiling PhH with an excess of salLi. After 50 h an orange solid was obtained by slow evaporation of the reaction solution. The long reaction time and the use of the ligand lithium salt greatly improved the purity of the final compounds, this however being always mixed to some extent with the starting complex. Only by chromatographic methods can a satisfactory separation be achieved. Recrystallization was carried out in CH_2Cl_2 and EtOH. Complex (V) is an air-stable solid, soluble in CH_2Cl_2, $CHCl_3$, Me_2CO and THF, and insoluble in EtOH, Et_2O and pentane.

Results and Discussion

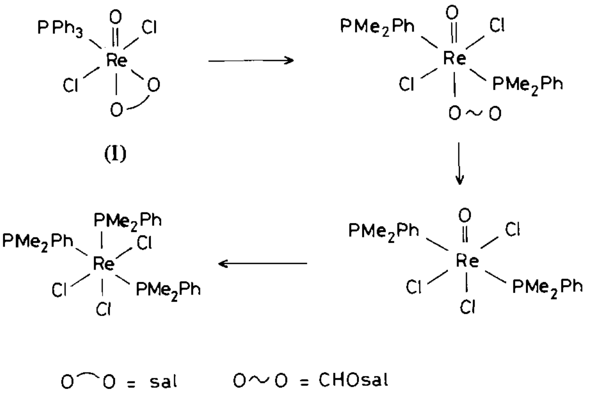
Some general properties of the obtained complexes are reported in Table I, and the i.r. data are given in Table II.

The i.r. spectrum of (I), $ReOCl_2(sal)PPh_3$, shows the characteristic stretching vibration of the Re=O group at 975 cm^{-1}, in agreement with the usual observed range [12–15]. The ν(C=O) and ν(C–O) frequencies, appearing at 1600 and 1280 cm^{-1} respectively, support a coordination of the sal^- ligand as a chelating one, while the ν(Re–Cl) vibration gives rise to a single band at 295 cm^{-1} supporting a *trans* configuration of the two chlorine atoms. The probable configuration of (I) is reported in Scheme 1.

Conductivity measurements on (II), $AsPh_4[ReOCl_3(sal)]$, gave a value of Λ_M = 138 cm^2 ohm^{-1} mol^{-1} in MeCN solutions, assuring the 1:1 electrolyte character of (II). The i.r. spectrum shows the ν(Re=O) at 960 cm^{-1}, the ν(C=O) at 1607 cm^{-1}, while the ν(Re–Cl) stretching gives rise to three bands at 315, 305 and 290 cm^{-1}. By assuming a *trans* position between the phenolic oxygen of the ligand and the triple bonded oxygen, as usually found in oxo-rhenium(V) complexes [13–15], the most probable structure for (II) possesses a *mer* configuration of the three chlorine groups in the molecule. The vibrations attributed to the $AsPh_4^+$ cation are observed at 470, 454, 341 cm^{-1}.

Complex (IV), $ReCl_3(SalH)(PPh_3)_2$, is formed through a substitution of the neutral nitrogen of the MeCN ligand with the neutral carbonyl oxygen of salH. These facts are clearly deduced by inspection of the i.r. spectrum in which the ν(O–H) stretching vibration of the protonated ligand is observed at 3335 cm^{-1} and the ν(C=O) vibration falls at a higher frequency than for the chelate ligand [4]. ν(Re–Cl) appears at 309 cm^{-1}. This implies that the interaction between the starting rhenium complex and the salH ligand is extremely weak. No type (IV) complex can be obtained in refluxing PhH, even with a large excess of salH. In addition the $ReCl_3(salH)(PPh_3)_2$ compound is very ephemeral: its solutions decompose after few hours, or by heating. These facts forced us to look for other preparative routes to synthesize stable rhenium compounds in the III oxidation state, containing salH as ligand. To this goal reaction d) was accomplished in refluxing PhH at two different molar ratios between the initial complex (I) and dimethylphenylphosphine (PMe_2Ph).

When the stoichiometric ratio was for excess PMe_2Ph (1:8), after 1 h of refluxing the reduced complex *mer*-$ReCl_3(PMe_2Ph)_3$ was collected. Starting with a lower stoichiometric ratio (1:2), after two hours of reflux, complex (III), $ReOCl_2(CHOsal)(PMe_2Ph)_2$, was obtained. Going over 2 h of reaction, the *mer*-$ReOCl_3(PMe_2Ph)_2$ blue complex began to form. In (III), the deprotonated sal^- ligand is bonded to the rhenium atom only through the charged phenolic oxygen (CHOsal). The complete route of the reactions is sketched in the following scheme:



Scheme 1

The $CHOsal^-$ ligand leaves the rhenium atom before reduction and no rhenium(III) complex with salH was obtained. The salH ligand therefore is not so strongly bonded to the rhenium center as to avoid substitution with other electron donor ligands.

The i.r. spectrum of complex (III), $ReOCl_2(CHOsal)(PMe_2Ph)_2$, shows a stretching vibration at 1665 cm^{-1}, characteristic of a free, non-bonded aldehydic C=O group: this has to be compared with the lower frequency value of the same group in complex (IV) in which the aldehydic oxygen is bonded to the metal ion. The ν(Re=O) stretching falls in the usual range at 970 cm^{-1}, while ν(Re–Cl) gives rise to a single band at 292 cm^{-1} suggesting a *trans* configuration for the two chlorine groups as showed in the above scheme.

The i.r. spectrum of complex (V), $Re(CO)_2(sal)(PPh_3)_2$, shows two stretching vibrations at 1910 and 1830 cm^{-1} assigned to the two carbonyl groups, while the ν(C=O) and ν(C–O) of the ligand fall at 1600 and 1280 cm^{-1} respectively, suggesting a chelation of the ligand around the rhenium atom.

Magnetic susceptibility measurements in solution by Evans' method of complexes (I), (II), (III) and (V) showed a diamagnetic character, while complex (IV) showed a μ_{eff} = 2.1 B.M., in agreement with values found from similar measurements on other rhenium(III) complexes [16].

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