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#### Synopsis

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Structure and properties of the products of pentachloridooxidorhenates(VI) decomposition under air are presented.

## Decomposition of pentachloridooxidorhenates(VI) - a still underinvestigated source of rhenium complexes at different oxidation states

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#### Abstract

Studies on decomposition of pentachloridooxidorhenates(VI) are described. The products are rhenium(V) salts with anions  $[Re^{V}OCl_{4}X]^{-}$  (X = solvent molecule) or  $[Re^{V}OCl_4Re^{VII}O_4]^{2-}$  or, under proper conditions, hexachloridorhenates(IV), as well as salts with  $[ReOCl_5]^{2-}$  or  $[ReOCl_4]^-$  anions. The products are listed and characterized by X-ray diffraction studies, or TGA/IR in the selected cases.

Keywords: rhenium(V), mixed-valent complexes, X-ray diffraction studies, TGA, IR.

#### 1. Introduction

Our recent studies on the system where rhenate(VII) anions react with hydrogen chloride led to the following description [1]:

$$\operatorname{ReO}_{4}^{-\operatorname{HCl}} \xrightarrow{\operatorname{HCl}} \operatorname{ReO}_{3} \operatorname{Cl}_{3}^{2-} \xrightarrow{\operatorname{HCl}} \operatorname{ReO}_{2} \operatorname{Cl}_{4}^{-\operatorname{H}_{2} \operatorname{O}} \xrightarrow{\operatorname{ReO}_{2} \operatorname{Cl}_{4}^{-\operatorname{H}_{2} \operatorname{O}}} \operatorname{ReO}_{2} \operatorname{Cl}_{4}^{-\operatorname{H}_{2} \operatorname{O}} \xrightarrow{\operatorname{HCl}} \operatorname{ReO}_{2} \operatorname{Cl}_{4} \xrightarrow{\operatorname{HCl}} \xrightarrow{\operatorname{HCl}} \operatorname{ReO}_{2} \operatorname{ReO}_{2} \operatorname{Cl}_{4} \xrightarrow{\operatorname{HCl}} \xrightarrow{\operatorname{HCl}} \operatorname{ReO}_{2} \operatorname{ReO}_{2} \operatorname{Cl}_{4} \xrightarrow{\operatorname{HCl}} \xrightarrow{\operatorname{HCl}} \operatorname{ReO}_{2} \operatorname{REO$$

 $2[\text{ReO}_2\text{Cl}_4]^- + 4\text{HCl} = 2\text{ReOCl}_5^- + \text{Cl}_2 + 2\text{H}_2\text{O}$ 

The first stages comprise complexation of the rhenate(VII) anions with hydrogen chloride to yield yellow chloridooxidocomplexes. Subsequently, these transition products are reduced with hydrogen chloride to pentachloridooxidorhenates(VI).

We also managed to obtain remarkably stable rhenium(VI) binuclear complexes utilizing the following reaction [2]:

# $\operatorname{ReOCl}_{5}^{-} + \operatorname{ReO}_{4}^{-} + 4\operatorname{HCl} \rightarrow [\operatorname{ReOCl}_{4}\operatorname{OReOCl}_{4}]^{2-} + \frac{1}{2}\operatorname{Cl}_{2} + 2\operatorname{H}_{2}\operatorname{O}$

The present and the previous [3] studies indicate, that pentachloridooxidorhenates(VI) decompose under air. In this paper we show that this decomposition may lead to a variety of rhenium-containing anions with Re atom at different oxidation states (Scheme 1).

Among the decomposition products, examples of species with alcohol molecule coordinating to  $\text{Re}^{V}$  atom are present. Also, under proper conditions, it is possible to isolate salts of mixed-valent  $[\text{Re}^{V}\text{OCl}_4\text{Re}^{VII}\text{O}_4]^{2^-}$  ions. These results are important as there are related synthetic routes leading to Re(V) potential radiopharmaceuticals [4]. In the first stages of these processes a mixture obtained by bubbling hydrogen chloride and then nitrogen gas through a suspension of tetrabutylammonium rhenate(VII) in methanol is used. It is claimed, that thus solely a  $[\text{ReOCl}_4]^-$  salt is obtained.

The present paper sheds more light on these processes and focuses on listing of the possible products of decomposition of pentachloridooxidorhenates(VI) under air in different solvents. Structural aspects of these compounds are discussed, being of importance for the general coordination chemistry and crystalochemistry of rhenium.

#### 2. Experimental

#### **Preparation descriptions**

#### Caution

The preparations involve irritating and corrosive gaseous hydrogen chloride and should be carried out employing the relevant safety measures.

#### A ([PPh<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>][ReOCl<sub>4</sub>(H<sub>2</sub>O)])

A suspension of 0.3 g ethyltriphenylphosphonium rhenate(VII) in 3.5 ml of isopropanol was prepared and placed in a flow apparatus. Gaseous hydrogen chloride obtained in a reaction of concentrated (96%) sulfuric acid with sodium chloride was bubbled through this suspension. Under a continuous flow of hydrogen chloride, as a result of an exothermal reaction, the solid rhenate(VII) dissolved to form a clear solution, which subsequently underwent colour changes from yellow, through orange to red with precipitation of some red crystals (confirmed previously to contain pentachloridooxidorhenate(VI) salts [1]). The obtained mixture was moved to a separate open vessel. Under air the mixture underwent slow colour changes from red to orange. After about fifteen minutes crystals in form of yellow plates (A) were observed to crystallize from the reaction mixture (the crystals

tend to form hexagonal twins). The crystallization vessel was covered with parafilm and left for slow evaporation overnight. As a result, a mixture of different kind of crystals was obtained, comprising, as evidenced by preliminary X-ray measurements, A, light-green or light-yellow crystals of impure (containing also rhenium(V) complexes) hexachloridorhenate(IV), orange blocks containing trans-tetrachloridooxido(Orhenate(VII))rhenate(V) (probably also with cocrystallizing rhenium(V) impurities, therefore the formally identical **F** salt was obtained by a different method).

IR bands (nujol/NaCl): 666.8 (*m*), 686.5 (*vs*), 695.2 (*s*), 711.4 (*w*), 722.4 (*vs*), 737.9 (*vs*), 754.9 (*m*), 771.7 (*w*), 883.3 (*vw*), 926.1 (*vw*), 999.0 (*vs*), 1012.0 (*vw*), 1034.7 (*vw*), 1113.9 (*vs*), 1165.1 (*vw*), 1189.3 (*w*), 1240.3 (*vw*), 1262.1 (*vw*), 1333.9 (*w*), 1378.1 (*s*), 1436.8 (*vs*), 1458.3 (*vs*), 1585.5 (*w*), 1613.4 (*m*), 1923.4 (*vw*), 1986.0 (*vw*), 2688.4 (*w*), 2854.8 (*vs*), 2924.8 (*vs*), 3314.6 (*m*).

#### B ([PPh<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>3</sub>][ReOCl<sub>4</sub>(CH<sub>3</sub>OH)]<sub>2</sub>)

A suspension of 0.3 g ethane-1,2-bis(triphenylphosphonium) rhenate(VII) in 3.5 ml of methanol was prepared and placed in a flow apparatus. Gaseous hydrogen chloride was bubbled through this suspension. Under continuous flow of hydrogen chloride, as a result of an exothermal reaction, the solid rhenate(VII) dissolved to form a clear solution, which subsequently underwent colour changes from yellow, through orange to red with precipitation of some red crystals (confirmed previously to contain pentachloridooxidorhenate(VI) salts [1]). The obtained mixture was moved to a separate open vessel. Under air the mixture underwent slow colour changes from red to orange. After about fifteen minutes crystals in form of orange blocks ( $\mathbf{B}$ ) were observed to crystallize from the reaction mixture. The crystallization vessel was covered with parafilm and left for slow evaporation overnight. As a result, further crop of crystalline  $\mathbf{B}$  was obtained. The crystals left under air gradually loose methanol.

IR bands (nujol/NaCl): 669.3 (*w*), 688.4 (*vs*), 728.3 (*vs*), 739.7 (*vs*), 749.2 (*m*), 810.5 (*vw*), 871.8 (*vw*), 907.7 (*w*), 918.8 (*w*), 932.8 (*w*), 957.5 (*vw*), 979.8 (*s*), 995.1 (*vs*), 1028.4 (*vw*), 1112.8 (*vs*), 1146.6 (*m*), 1165.9 (*w*), 1192.3 (*w*), 1220.0 (*w*), 1276.8 (*vw*), 1322.4 (*w*), 1338.0 (*w*), 1377.3 (*m*), 1403.3 (*w*), 1437.8 (*vs*), 1462.7 (*s*), 1483.1 (*m*), 1587.1 (*s*), 1824.5 (*vw*), 1905.5 (*vw*), 1976.1 (*vw*), 2854.7 (*vs*), 2928.0 (*vs*), 3053.0 (*s*), 3314.3 (*s*).

#### C ([PPh<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>][ReOCl<sub>4</sub>(C<sub>2</sub>H<sub>5</sub>OH)])

A suspension of 0.3 g ethyltriphenylphosphonium rhenate(VII) in 3.5 ml of methanol was prepared and placed in a flow apparatus. Gaseous hydrogen chloride was bubbled through this suspension. Under continuous flow of hydrogen chloride, as a result of an

exothermal reaction, the solid rhenate(VII) dissolved to form a clear solution, which subsequently underwent colour changes from yellow, through orange to red with precipitation of some red crystals (previously confirmed to contain pentachloridooxidorhenate(VI) salts [1]). The obtained mixture was moved to a separate open vessel. Under air the mixture underwent slow colour changes from red to orange. After about fifteen minutes crystals in form of orange green plates ( $\mathbf{C}$ ) were observed to crystallize from the reaction mixture. The crystallization vessel was covered with parafilm and left for slow evaporation overnight. As a result, further portion of crystalline  $\mathbf{C}$  was obtained. The crystals left under air gradually loose ethanol.

IR bands (nujol/NaCl): 668.9 (w), 690.1 (vs), 696.1 (s), 723.1 (vs), 739.4 (vs), 747.8 (s), 757.8 (s), 777.1 (m), 804.1 (vw), 877.7 (m), 922.1 (vw), 993.2 (vs), 1031.6 (s), 1091.3 (w), 1115.2 (vs), 1166.4 (vw), 1190.9 (vw), 1265.5 (vw), 1340.7 (w), 1378.7 (m), 1417.6 (w), 1438.0 (vs), 1457.3 (s), 1485.0 (w), 1588.2 (w), 1616.0 (vw), 1653.0 (vw), 1684.5 (vw), 1829.3 (vw), 1922.3 (vw), 1977.4 (vw), 2854.1 (vs), 2923.8 (vs), 3042.3 (m), 3059.0 (m), 3084.2 (m), 3508.2 (s).

#### D (2([PPh<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>][ReOCl<sub>4</sub>(<sup>*n*</sup>PrOH)])•<sup>*n*</sup>PrOH)

0.05 g of (4-methylbenzyl)triphenylphosphonium rhenate(VII) was suspended in 0.5 ml of *n*-propanol. A stream of gaseous hydrogen chloride was bubbled through the suspension. An exothermal reaction occurred, as a result of which rhenate(VII) underwent dissolution with formation of a yellow solution, which subsequently turned orange and finally red. The hydrogen chloride stream was stopped at this point. 0.05-0.06 g of solid (4-methylbenzyl)triphenylphosphonium rhenate(VII) was added to the mixture. The reaction vessel was closed and stored in freezer at the temperature of about -10 °C. After 3-4 days the red solution changed its colour to orange and crystals of **D** in form of yellow plates were obtained.

#### E ([PPh<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>][ReOCl<sub>4</sub>('PrOH)])

A suspension of 0.3 g (4-methylbenzyl)triphenylphosphonium rhenate(VII) in 3.5 ml of methanol was prepared and placed in a flow apparatus. Gaseous hydrogen chloride was bubbled through this suspension. Under continuous flow of hydrogen chloride, as a result of an exothermal reaction, the solid rhenate(VII) dissolved to form a clear solution, which subsequently underwent colour changes from yellow, through orange to red with precipitation of some red crystals (previously confirmed to contain pentachloridooxidorhenate(VI) salts [1]). Through thus prepared red reaction mixture gaseous nitrogen was bubbled. As a result,

the reaction mixture changed its colour to orange and subsequently to yellow. On slow evaporation in the nitrogen stream crystals of E in form of yellow plates were obtained.

IR bands (Nujol/NaCl): 687.9 (vs), 705.3 (w), 714.6 (m), 720.2 (s), 739.6 (s), 744.9 (s), 759.1 (w), 809.8 (w), 824.5 (s), 837.2 (m), 848.2 (vw), 909.5 (m), 919.7 (s), 975.7 (vw), 1000.1 (s), 1006.1 (m), 1021.3 (vw), 1089.3 (s), 1109.1 (vs), 1141.0 (vw), 1161.0 (w), 1187.9 (vw), 1288.8 (w), 1318.1 (w), 1339.1 (w), 1375.8 (s), 1437.2 (vs), 1462.0 (vs), 1513.4 (w), 1586.7 (w), 1616.1 (vw), 1684.0 (vw), 1743.2 (vw), 2726.9 (w), 2854.5 (vs), 2925.9 (vs), 3382.4 (m).

#### F ([PPh<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>]<sub>2</sub>[ReOCl<sub>4</sub>ReO<sub>4</sub>])

0.05 g of ethyltriphenylphosphonium rhenate(VII) was suspended in 1 ml of chloroform. A stream of gaseous hydrogen chloride was bubbled through the suspension. An exothermal reaction occurred, as a result of which rhenate(VII) underwent dissolution with formation of a yellow solution, which subsequently turned orange and finally red. The hydrogen chloride stream was stopped at this point. 0.05-0.06 g of solid ethyltriphenylphosphonium rhenate(VII) was added to the mixture. The reaction vessel was closed and stored in freezer at the temperature of about -10 °C. After 3-4 days the red solution changed its colour to violet. Further, the reaction mixture steadily lost the violet colour and became yellow with formation of stable crystals of **D** in form of yellow plates.

IR bands (Nujol/NaCl): 667.5 (*m*), 689.9 (*vs*), 697.1 (*vs*), 712.7 (*m*), 724.2 (*vs*), 736.6 (*vs*), 750.3 (*vs*), 772.7 (*s*), 860.5 (*s*), 882.0 (*vs*), 926.1 (*vs*), 978.0 (*w*), 996.2 (*s*), 1009.9 (*vw*), 1026.8 (*vw*), 1034.9 (*w*), 1074.9 (*vw*), 1114.0 (*vs*), 1161.1 (*w*), 1191.5 (*vw*), 1235.2 (*vw*), 1275.4 (*vw*), 1318.3 (*m*), 1343.4 (*m*), 1380.2 (*m*), 1404.1 (*m*), 1437.9 (*vs*), 1456.2 (*s*), 1481.7 (*m*), 1587.1 (*m*), 1613.5 (*w*), 1904.7 (*w*), 1983.2 (*w*), 2691.4 (*m*), 2854.7 (*vs*), 2922.4 (*vs*), 3041.0 (*s*), 3056.7 (*s*), 3082.1 (*s*).

#### X-ray diffraction measurements

X-ray diffraction data were collected by means of either KM4CCD diffractometer or of Xcalibur PX diffractometer, both equipped with CCD detectors and graphitemonochromatized  $MoK_{\alpha}$  radiation. The measurements were carried out at 100 K or at 120 K (see Table 1 for basic experimental data).

#### Refinement

All structures were solved by direct methods in SHELXS and refined with the aid of SHELXL software [5]. Where possible, H atoms were generated based on known molecular geometry and refined with  $U_{eq}$  at  $nU_{eq}$ (parent atom), where n = 1.5 for methyl groups, 1.2 for phenyl/methylene groups. The treatment of other H atoms was dependent mainly on the

quality of the recorded X-ray diffraction data. For A water H atoms were found on difference Fourier map, refined with a DFIX restraint setting O-H bond lengths at 0.840(2) Å and subsequently their parameters were constrained with  $U_{eq} = 1.5U_{eq}(O \text{ atom})$ . For B/C the coordinated alcohol H atoms were found on a difference Fourier map and refined with DFIX restraint setting O-H bond lengths at 0.840(2) Å as well as  $U_{eq} = 1.5U_{eq}$ (O atom). For **D** the coordinated *n*-propanol H atoms were found on a difference Fourier map, refined with DFIX restraint setting O-H bond lengths at 0.840(2) Å and subsequently their parameters constrained with "AFIX 147 0.8400" constraint and  $U_{eq} = 1.5U_{eq}(O \text{ atom})$ . High difference Fourier peaks in the neighbourhood of the Re1-containing anion indicated it to be disordered or that its site contains impurity with other Re complex. The latter possibility seems to be more probable. Re1 atom and Cl1, Cl4 atoms were split into two components and their occupancies were refined to sum up to unit (the final refined occupancies: 0.88(1) and 0.22(1) for higher- and lower-occupancy components, respectively). It seems, that the impurity anion is also charged mononegatively and containing four Cl ligands with two O-Re-Cl bond angles greater than 90° and two O-Re-Cl bond angles smaller than 90°. Based on our previous studies [6] on the reaction of rhenate(VII) anions with hydrogen chloride the impurity could be trans-tetrachloridooxido(n-propoxido)rhenate(VI) anion. For E the coordinated isopropanol H atoms were found on a difference Fourier map, refined with a DFIX restraint setting O-H bond lengths at 0.840(2) Å and subsequently their parameters were constrained with "AFIX 43 0.8400" constraint and  $U_{eq} = 1.5U_{eq}$  (O atom), assuming an electrostatic mode of coordination of the alcohol molecule to Re central atom.

On the final difference Fourier maps the following maxima/minima were observed: 3.31 e/Å<sup>3</sup> at 0.76 Å from Re2 for **A**, 3.66 e/Å<sup>3</sup> at 1.04 Å from Re2 for **B**, 0.84 e/Å<sup>3</sup> at 0.76 Å from Re1 for **C**, 1.67 e/Å<sup>3</sup> at 0.81 Å from Re2 for **D**, 1.81 e/Å<sup>3</sup> at 0.74 Å from Re2 for **E**, 3.25 e/Å<sup>3</sup> at 0.15 Å from Re2 for **F**.

CCDC reference numbers: 985323-985328.

#### **Other measurements**

Thermogravimetric measurements were carried out on Setsys TG-DTA 16 device under nitrogen atmosphere in Al<sub>2</sub>O<sub>3</sub> crucible for samples of **B** (6.79 mg), **C** (9.95 mg), **E** (12.06 mg), **F** (13.31 mg) with a heating rate of 5 °C/min.

Absorption spectra were collected in the standard IR (500-400 cm<sup>-1</sup>, NaCl window) and FIR (50-650 cm<sup>-1</sup>, polyethylene window) wavelength range on a BRUKER spectrophotometer. The samples were prepared in form of suspensions in nujol mull.

#### 3. Results and discussion

#### Decomposition of pentachloridooxidorhenates(VI) in different solvents

Exposure of the red mixture obtained in the reaction of phosphonium rhenates(VII) with gaseous hydrogen chloride leads not only to contact with atmospheric oxygen, but also to a slow decrease of hydrogen chloride concentration in the reaction mixture.

In case of such solvents as acetone it is possible, that interaction of hydrogen chloride with the solvent itself may be present. This is confirmed by our preliminary GC-MS studies. Furthermore, the rhenium compounds present in the reaction mixture may act as catalysts of the reaction of the corresponding solvent with hydrogen chloride. On the other hand, in e.g. chloroform, such processes should not be relevant. In acetonitrile large quantities of crystalline acetamide chloride (identified based on the unit cell constants crystallographic measurement as [7]) are formed. In the concentrated hydrochloric acid, apparently chlorine formed as a product also of secondary reactions on exposure to air reacts with water to yield an oxidizing agent, making it possible to reverse the reaction and again to obtain crystalline phosphonium rhenate(VII). Such solvents as carbon tetrachloride, aromatic or aliphatic hydrocarbons, do not dissolve very well the products of the reaction of rhenates(VII) with hydrogen chloride, which limits their suitability.

Summary of the possible decomposition products concluded from this study is shown in Scheme 1. Usually the decomposition products include a  $[\text{Re}^{V}\text{OCl}_4]^-$  unit with a solvent molecule (e.g. water, alcohol molecule) coordinated in *trans* position to the short Re-O<sub>terminal</sub> bond. It is also possible to obtain mixed-valence  $[\text{ReOCl}_4\text{ReO}_4]^2^-$  anions, formally comprising a  $[\text{Re}^{V}\text{OCl}_4]^-$  unit with a  $\text{ReO}_4^-$  anion coordinated in *trans* position to the short Re-O<sub>terminal</sub> bond.

#### Structure of the Re(V) products

The investigated system provides new insights into the crystalochemistry of rhenium(V) compounds.

The structure of all Re(V)-containing anions isolated from the investigated system is illustrated on Fig. 1 (a)-(f). Below a detailed description of the anions structural aspects is provided. Different bulky phosphonium cations used as counterions allow to limit the anion disorder affecting the other previously reported structures [3]. The structure of these cations is described in detail in SI.

The *trans*- $[\text{Re}^{V}\text{OCl}_4(\text{H}_2\text{O})]^{-}$  anion (as in **A**, Fig. 1a) structure is known from X-ray diffraction studies performed for its tetraphenylarsonium salt [8], as well as for its dithiobis(formamidinium) chloride monohydrate [9] and (18-crown-6)hydroxonium salts [10].

The corresponding anion geometric parameters are comparable in **A** (there are two symmetryindependent anions) and in the former reports [8, 9, 10] (Table 2). Similar *trans*- $[MOCl_4(H_2O)]^-$  complexes are also known for niobium [11] and molybdenum [12]. In all these complexes the central metal ion is bonded to the terminal oxido ligand to form a short multiple bond, which imposes a *trans* influence on the Re-O(water coordinated in *trans* position) bond. The sum of bond angles around the water atom should be indicative of the degree of covalency in the M-O(water) bond. Although the H atoms position determination in **A** is by no means reliable, it might be expected, that the degree of covalency in Re-O(water) bond is considerable.

The complex anions in **A** form two kinds of hydrogen-bonded pairs (Fig. S1a): Re1containing anion - Re1<sup>i</sup>-containing anion (symmetry code (i) -x+2, -y+1, -z+1); Re2containing anion - Re2<sup>ii</sup>-containing anion (symmetry code (ii) -x+2, -y+2, -z). The anions within each pair interact *via* O-H...Cl hydrogen bonds (Table S1), in which the coordinated water molecules act as donors and the Cl ligands act as acceptors with formation of two  $R^2_2(6)$  and two  $R^2_2(8)$  graph set motifs [13]. The hydrogen-bonded anion pairs are arranged in columns parallel to [100]. The phosphonium cations also form columns along [100], which are further organized in layers parallel to (110) (Fig. S2a).

**B-E** are unprecedented examples of salts containing  $[Re^{V}OCl_{4}(ROH)]^{-}$  anions with different alcohols molecules coordinated *trans* to the terminal oxido ligand in a [Re<sup>V</sup>OCl<sub>4</sub>]<sup>-</sup> unit (B: CH<sub>3</sub>OH, C: C<sub>2</sub>H<sub>5</sub>OH, D: <sup>n</sup>PrOH, E: <sup>i</sup>PrOH, Fig. 1 b-e). The reported X-ray structures of Re complexes with trans-coordinated alcohol molecule are scarce. Data collected for the analogous alkoxidocomplexes are available (e.g. [14-15]). On the other hand, the Mo analogues are known [16-17]. In B-E the bonding of the alcohol molecule to the Re ion seems to be of mainly ion-dipol interaction character. The relevant Re-Otrans bond lengths are comparable in case of C-E (see Table 2). It is interesting to note, that in the case of B this bond is slightly longer and comparable to the Re-O<sub>trans</sub> bond length in the [ReOCl<sub>4</sub>(H<sub>2</sub>O)]<sup>-</sup> anion in A. The variability in the Re- $Cl_{cis}$  bond lengths observed in some particular cases could be attributed to the steric effect of alcohol R moiety presence as well as to involvement in hydrogen bonds. The short terminal Re-O bond length in **B-E** adopts values characteristic for the formally triple Re-O bond [18]. All Re-Cl bond lengths are equivalent (see Table 2). As expected, based on the *trans* effect theory, all Ot-Re-Clcis angles are greater than 90°. All these observations correspond well to the structure of the [ReOCl<sub>4</sub>] moiety in the [ReOCl<sub>5</sub>]<sup>-</sup> and the  $[\text{ReOCl}_5]^{2-}$  anion [1]. The O<sub>t</sub>-Re-O<sub>trans</sub> bond angle is in each case close to 180°. The

[ReOCl<sub>4</sub>(ROH)]<sup>-</sup> anions are capable of participating in hydrogen bonds, which, as illustrated below, leads to the formation of a variety of structural motifs.

In **B** both symmetry-independent anions comprise a [ReOCl<sub>4</sub>] moiety with methanol molecule coordinated *trans* to the short Re-O<sub>t</sub> bond. The Re-Cl<sub>cis</sub> bond lengths within the [ReOCl<sub>4</sub>] moiety differ slightly, which corresponds to their involvement in hydrogen bonds. Within the Re1-containing anion two intramolecular hydrogen bonds are formed (Table S1), however, no participation in intermolecular hydrogen bonds is observed. On the other hand, the Re2-containing anion participates in the formation of similar intermolecular hydrogenbonded structural motifs (Fig. S1b) as in **A**, stabilized by two kinds of O-H...Cl hydrogen bonds involving hydroxyl groups of the coordinated methanol molecules as donors, resulting in a  $R^2_2(8)$  graph set motif presence [13]. Thus defined anion pairs occupy spaces formed between the columns of phosphonium cations extending along [010] (Fig. S2b). Probably the tendency to form hydrogen-bonded anion pairs may be of importance in the field of crystal engineering.

In **C** the complex anion comprises a [ReOCl<sub>4</sub>] moiety with ethanol molecule coordinated *trans* to the triple Re-O<sub>t</sub> bond. The ethyl moiety of the ethanol molecule adopts apparently a low-energy arrangement with respect to the [ReOCl<sub>4</sub>] moiety with C21E-C11E-O1E-Cln (n = 1 to 4) torsion angles of -50.7(2), -93.5(2), -160.2(2) and 155.8(2)°, respectively. The hydroxyl group from the coordinated ethanol molecule is hydrogen-bonded to the O atom from the ethanol molecule of solvation (Table S1). The hydroxyl group from the ethanol molecule of solvation is further involved in a weaker O-H...Cl hydrogen bond to another anion. Thus defined hydrogen-bonded units (Fig. S1c) along with the phosphonium cations form layers parallel to (110) (Fig. S2c).

**D** contains two symmetry-independent anions, comprising a [ReOCl<sub>4</sub>] moiety with *n*propanol molecule coordinated *trans* to the short Re-O<sub>t</sub> bond. One of these anions is affected by disorder described in the Refinement section. The position of the *n*-propyl moiety with respect to the [ReOCl<sub>4</sub>] moiety in the ordered Re2-containing anion is illustrated by the corresponding C-C-C-O and Cl-Re-O-C torsion angles (-175.6(5), 56.3(4), -33.4(4), -122.1(4) and 146.6(4)°, respectively). The ordered Re2-containing anion forms part of an interesting hydrogen-bonded unit comprising two anions and two *n*-propanol molecules of solvation (Fig. S1d). Hydroxyl groups of each of the two *n*-propanol molecules of solvation are donors to bifurcated O-H...Cl hydrogen bonds to the anion Cl22 and Cl32 atoms with formation of  $R^2_1(4)$  motifs. These hydroxyl groups are also acceptors to O-H...O hydrogen bonds involving *n*-propanol molecules coordinated to the interacting anions to close a characteristic

double-decker hydrogen-bonded structure (Fig. S1d). The Re1-containing anion is not involved in any hydrogen bonds, occupying considerable spaces between the columns of phosphonium cations extending along [010] (Fig. S2d). The hydrogen-bonded anionic units described above also occupy these spaces. Further, double layers parallel to (110) could be distinguished, comprising the hydrogen-bonded units surrounded by phosphonium cations columns and the Re1-containing anions in the outer parts. No involvement in specific interactions apparently makes it possible for the other anions to be built into the site occupied by the Re1-anions. Therefore apparently part of the anions is probably substituted with *trans*-tetrachloridooxido(*n*-propoxido)rhenate(VI) anions, which was accounted for during the corresponding crystal structure refinement (see Experimental section).

In **E** there are two symmetry-independent anions with isopropanol molecules coordinated *trans* to the [ReOCl<sub>4</sub>] moiety. The two anions differ slightly by the distribution of the Re-Cl bond lengths, which can be explained in terms of the hydrogen bonding scheme. The two anions interact *via* O-H...Cl hydrogen bonds with the anion-coordinated isopropanol molecule hydroxyl group acting as a hydrogen bond donor (Fig. S1e). Thus an  $R^2_2(8)$  graph set motif is formed. These units form columns along [100], isolated by columns of the analogous phosphonium cations (Fig. S2e).

#### Structure of the mixed-valence Re(V)-Re(VII) products

Mixed-valence Re complexes are rare. Examples include e.g. salts of the arguable  $[\text{Re}_2\text{O}_3\text{Cl}_{10}]^{3-}$  anion [19] or binuclear phosphinotiolate Re(VII)-Re(V) complex [20]. Moreover, coordination of the rhenate(VII) anion to Re atom at different oxidation states (I, II, III, V, VI, VII) is well established, also leading to formally mixed-valence compounds (e.g. [21-39]).

The mixed-valence anion in **F** (Fig. 1f) could formally be regarded as a  $[\text{Re}^{V}\text{OCl}_4]^$ unit with a ReO<sub>4</sub><sup>-</sup> anion coordinated *trans* to the terminal oxido ligand. In the  $[\text{ReOCl}_4]^-$  unit a short, formally triple [18] Re-O bond is present, imposing *trans* influence as shown by the O-Re-Cl<sub>cis</sub> bond angles deformation (Table 2). The Re-Cl bond lengths are comparable to the Re-Cl<sub>cis</sub> bond lengths in the  $[\text{ReOCl}_5]^{2^-}$  anion [40] (Table 2). The ReO<sub>4</sub><sup>-</sup> unit is nearly tetrahedral as in a non-coordinated ReO<sub>4</sub><sup>-</sup> anion [41, 42] (Table 2). The Re2-O12 bond, through which this unit is coordinated to the  $[\text{ReOCl}_4]^-$  unit, is longer than the remaining Re-O bonds of equivalent lengths (Table 2) with order lower than for a formally double Re-O bond (e.g. 1.723(4) Å for KReO<sub>4</sub> [43]). Similar observation could be made in case of other compounds where the ReO<sub>4</sub><sup>-</sup> anion is coordinated to the Re<sup>V</sup> atom (e.g. [44]). The Re<sup>V</sup>-O12(from the coordinated ReO<sub>4</sub><sup>-</sup> unit) is shorter than in the case of Re-O(from water ligand)

bond for **A**, also located in *trans* position to a triple Re-O bond. This shows, that the division into two anionic units within the mixed-valence anion in **F** is only formal and a more correct treatment would be considering the anion as a whole binuclear unit. The Re-O<sub>µ</sub>-Re bond angle value (Table 2) is closer to 180° in **F** than in the reported systems with a ReO<sub>4</sub><sup>-</sup> unit coordinated to the Re<sup>V</sup> atom (e.g. 146.5(4)° for a Re<sup>V</sup> phtalocyaninate complex reported in [44]).

In **F** no specific hydrogen bonds could be distinguished, which results in an increased mobility of the anion (as shown by thermal ellipsoids of O atoms belonging to the  $\text{ReO}_4^-$  unit). The phosphonium cations are arranged in columns parallel to [010] (Fig. S2f). The complex anions occupy spaces between these columns.

#### Thermal decomposition of the selected Re(V) salts

The thermal decomposition studies carried out for samples of phosphonium salts with a [ReOCl<sub>4</sub>(ROH)]<sup>-</sup> anion show, that all these salts apparently decompose following a similar pattern. First step, as easily concluded from the experimental data, is evolution of the alcohol molecule coordinated to the [ReOCl<sub>4</sub>] moiety (along with the alcohol molecules of solvation, if present). This is in accordance with the conclusion from X-ray diffraction studies (see above), that the alcohol molecules are very weakly coordinated to the [ReOCl<sub>4</sub>] moiety and interact with the Re centre mainly via dipole-ion interaction. Then, as a second step, apparently the organic part (the phosphonium cations) is decomposed. As the third step, most of the chlorine/oxygen contents from the remaining part are lost. In the case of **B** the first decomposition step (evolution of the coordinated methanol contents) is endothermal and occurs at 100-150 °C. At 260-270 °C another endothermal process occurs. At 150-350 °C a gradual decomposition of the organic part occurs. The last, clearly resolved decomposition step starts at about 350 °C and leads to the loss of most of the remaining chlorine/oxygen contents. In the case of C only two well resolved decomposition steps visible on the TG curve could be distinguished. The first step, leading to an evolution of the ethanol molecules coordinated to the [ReOCl<sub>4</sub>] moiety, as well as of ethanol of solvation, occurs up to 400 °C (apparently the process is endothermal and gradual, however, at about 103 °C and 123 °C two sharp endothermal peaks are present on the heating curve). From about 400 °C the second decomposition step starts, in fact comprising two poorly resolved process stages: the loss of the organic part and of the chlorine/oxygen contents. A very similar decomposition pattern is observed in the case of  $\mathbf{E}$  (clearly visible evolution of the coordinated isopropanol up to about  $300 \,^{\circ}\text{C}$  with two overlapping sharp endothermal peaks at about 133  $^{\circ}\text{C}$ ; the loss of the organic part and of part of the chlorine/oxygen contents starting from 300 °C). F shows a completely

different decomposition pattern with a sharp endothermal peak on the heating curve at about 148-155 °C, resulting from melting with decomposition, proceeding smoothly from this temperature, apparently leading to pure metallic rhenium as the final product.

#### **IR** spectra

On the recorded IR spectra many bands connected with the presence of the organic cations arise, therefore for their analysis it is helpful to compare them with the analogous IR spectra of the corresponding phosphonium halides. The most characteristic band on these spectra was assigned to the Re-O<sub>t</sub> stretching mode (990.0 cm<sup>-1</sup> for A, 995.1 cm<sup>-1</sup> for B, at 993.2 cm<sup>-1</sup> for C, at 1000.1 cm<sup>-1</sup> for E, at 996.2 cm<sup>-1</sup> for F). On the IR spectrum of F also two broad bands at 882.0 and 926.1 cm<sup>-1</sup> with a smaller band at 860.5 cm<sup>-1</sup> could be clearly distinguished. These bands can be assigned to the  $ReO_4^-$  unit vibrations and correspond well to the experimentally detected two values of the Re-O bond lengths within this unit, resulting in an approximate  $C_{3y}$  symmetry. The band connected with the Re-O<sub>u</sub>-Re stretching mode is observed in a less straightforward manner due to the presence of phosphonium cations at 724.2 cm<sup>-1</sup>. On the IR spectrum recorded for the sake of comparison for ethyltriphenylphosphonium rhenate(VII) a single band at 902.3 cm<sup>-1</sup> could be assigned to the Re-O stretching mode. Further, the recorded data could also be compared with the available literature, e.g. Göldner et al. [22] provide a detailed analysis of the spectroscopic properties of the  $\text{Re}^{V}$ -phtalocyaninate compound with a coordinated  $\text{ReO}_{4}^{-}$  unit. The vibrations of the ReO<sub>4</sub><sup>-</sup> unit are attributable to the IR bands at 937, 832 and 807 cm<sup>-1</sup>, respectively.

#### 4. Conclusions

Secondary reactions occurring when the mixture obtained in a reaction of rhenates(VII) with hydrogen chloride is exposed to air, have been shown to be a rich source of Re(VII), Re(V), Re(IV) complexes. It is essential to be aware of these possibilities when this reaction mixture is used as a reagent in a multi-stage synthesis. The structure aspects of the salts containing [ReOCl<sub>4</sub>(ROH)]<sup>-</sup>, [ReOCl<sub>4</sub>(H<sub>2</sub>O)]<sup>-</sup> and [ReOCl<sub>4</sub>ReO<sub>4</sub>]<sup>2-</sup> anions, have been discussed and brought new insights into the crystalochemistry of rhenium compounds at higher oxidation states. Moreover, IR spectra and thermal decomposition patterns for these salts have been described.

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#### **Supporting Information**

Electronic Supplementary Information (ESI) available: additional tables/figures for crystal structures. X-ray crystallographic data in CIF format: CCDC 985323-985328 contains the supplementary crystallographic data for this paper. Copies of this information can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax. 44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk).

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**Figures and schemes** 











(b)







(e)



(f)

ar hyrr Fig. 1. Structure of the complex anions in A-F (a-f) with atom labeling scheme. Thermal ellipsoids are drawn at 30% probability level. Intramolecular hydrogen bonds are denoted

#### Tables Table 1 Basic X-ray diffraction experimental data for A-F.

	Α	В	С	D	Ε	F
Formula	[PPh <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> ]	[PPh <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> PPh <sub>3</sub> ]	[PPh <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> ]	2([PPh <sub>3</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ]	[PPh <sub>3</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ]	[PPh <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub>
	[ReOCl <sub>4</sub> (H <sub>2</sub> O)]	[ReOCl <sub>4</sub> (CH <sub>3</sub> OH)] <sub>2</sub>	[ReOCl <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> OH)]·	[ReOCl <sub>4</sub> ( <sup>n</sup> PrOH)])· <sup>n</sup> PrOH	[ReOCl <sub>4</sub> ( <sup>i</sup> PrOH)]	[ReOCl <sub>4</sub> ReO <sub>4</sub> ]
			C <sub>2</sub> H <sub>5</sub> OH			
Formula weight	653.35	1304.68	727.47	1603.13	771.52	1176.86
Temperature [K]	100(2)	100(2)	85(2)	100(2)	100(2)	120(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	Pī	Pī	$P2_1/n$	Pī	Pī	$P2_1/c$
a [Å]	10.478(3)	10.116(6)	12.362(3)	10.846(6)	10.314(3)	18.058(4)
b [Å]	13.057(4)	11.856(7)	14.122(4)	14.930(6)	13.327(4)	13.836(3)
c [Å]	18.735(4)	19.663(7)	16.726(4)	21.953(9)	22.598(5)	19.430(4)
α [°]	100.51(3)	96.46(5)		96.66(3)	91.89(3)	
β [°]	94.19(3)	101.01(5)	104.88(3)	102.10(4)	101.30(3)	120.81(3)
γ [°]	111.45(3)	97.61(5)		110.46(4)	101.05(3)	
V [Å <sup>3</sup> ]	2318(2)	2271(2)	2822(2)	3186(3)	2982(2)	4170(2)
Z, $\rho_{calc}$ [g cm <sup>-3</sup> ]	4, 1.872	2, 1.908	4, 1.712	2, 1.671	4, 1.719	4, 1.875
μ [mm <sup>-1</sup> ]	5.79	5.91	4.76	4.23	4.51	6.18
F(000)	1264	1260	1432	1588	1520	2272
Crystal size [mm]	0.23x0.12x0.07	0.38x0.33x0.16	0.30x0.28x0.25	0.26x0.14x0.08	0.20x0.14x0.10	0.20x0.15x0.11
θ range[°]	2.8-35.0	2.9-28.5	4.7-32.5	3.0-32.5	2.8-32.5	4.4-35.0
rflns: total/unique	49106/18738	16971/9804	46974/12215	53261/21548	49972/19532	77211/18320
R(int)	0.046	0.069	0.026	0.063	0.055	0.048
Abs. corr.	analytical	analytical	analytical	analytical	analytical	analytical
Min., max.	0.285, 0.661	0.204, 0.723	0.292, 0.428	0.635, 0.843	0.415, 0.727	0.328, 0.574
transmission factors						
Data/restraints/params	18738/0/505	9804/2/511	12215/0/298	21548/2/722	19532/0/673	18320/0/480
GOF on F <sup>2</sup>	1.02	1.00	1.01	1.03	1.00	0.86
$R_1 [I > 2\sigma(I)]$	0.037	0.056	0.019	0.052	0.046	0.031
wR <sub>2</sub> (all data)	0.061	0.174	0.029	0.098	0.069	0.039
Max., min. $\Delta \rho_{\text{elect}} [e \text{ Å}^{-3}]$	3.31, -1.91	3.66, -2.21	0.84, -0.78	1.67, -1.49	1.81, -1.83	3.25, -2.16
20						

Α			
Re1—011	1.664(2)	Re2—O12	1.665(2)
Re1—O1W	2.265(2)	Re2—O2W	2.261(2)
Re1—Cl11	2.3549(12)	Re2—Cl12	2.3563(12)
Re1—Cl21	2.3563(11)	Re2—Cl42	2.3599(11)
Re1—Cl41	2.3611(11)	Re2—Cl22	2.3627(10)
Re1—Cl31	2.3956(11)	Re2—Cl32	2.3791(11)
O11—Re1—O1W	176.39(10)	O12—Re2—O2W	177.73(10)
O11—Re1—Cl11	98.51(9)	O12—Re2—C112	98.41(11)
O1W—Re1—Cl11	85.09(6)	O2W—Re2—Cl12	83.69(6)
O11—Re1—Cl21	100.76(8)	O12-Re2-Cl42	99.14(10)
O1W—Re1—Cl21	79.06(6)	O2W—Re2—Cl42	80.04(7)
Cl11—Re1—Cl21	88.34(5)	Cl12—Re2—Cl42	88.28(4)
D11—Re1—Cl41	100.03(8)	O12—Re2—Cl22	100.51(10)
O1W—Re1—Cl41	80.20(6)	O2W—Re2—Cl22	80.34(7)
Cl11—Re1—Cl41	88.35(5)	Cl12—Re2—Cl22	88.50(4)
Cl21—Re1—Cl41	159.21(3)	Cl42—Re2—Cl22	160.35(3)
O11—Re1—Cl31	95.28(9)	O12—Re2—Cl32	96.47(11)
O1W—Re1—Cl31	81.11(6)	O2W—Re2—Cl32	81.44(6)
Cl11—Re1—Cl31	166.20(3)	Cl12—Re2—Cl32	165.12(3)
Cl21—Re1—Cl31	88.70(5)	Cl42—Re2—Cl32	89.80(4)
Cl41—Re1—Cl31	89.65(4)	Cl22—Re2—Cl32	88.36(4)
В			
	1.649(7)	Re2-012	1.669(7)
Re1—O1M	2.259(7)	Re2-O2M	2.254(8)
Re1—Cl21	2.350(3)	Re2-Cl22	2.338(3)
Re1—Cl11	2,353(3)	Re2-C142	2 343(3)
Re1—Cl41	2.361(3)	Re2-C112	2.349(3)
Re1—Cl31	2,380(3)	Re2-Cl32	2.371(3)
011—Re1— $01M$	177.2(3)	$\frac{1}{012} = \frac{1}{8} = \frac{1}{2} = $	174 6(3)
$\frac{11 - \text{Re} 1 - \text{C} 121}{1 - \text{Re} 1 - \text{C} 121}$	99 6(2)	012 Re2 $0210$	99 7(3)
$\frac{O1M}{Re1}$	83.0(2)	$0^{2}M_{Re}^{2}$	82 7(2)
011 - Re1 - C111	97 5(3)	012 Re2 Cl42	98 5(3)
$\frac{O1M}{Re1}$	83 4(2)	$\frac{O12}{O2M} = \frac{Re^2}{C^{142}}$	79.0(2)
$\frac{C121}{Re1}$	87 57(10)	$C_{122} = Re^2 = C_{142}$	161 70(12)
$\frac{11}{1} = \frac{1}{1} = 1$	97 7(2)	012 Re2 C112	100.9(3)
$\frac{O1M}{Re1} = \frac{O141}{O1M}$	79.6(2)	$\frac{O2M}{Re^2}$	83 9(2)
$C_{121}$ Re1 $C_{141}$	162 63(9)	$C_{122} = R_{e^2} = C_{112}$	88 37(14)
C121 - RC1 - C141	01.28(10)	C122— $Rc2$ — $C112$	80.37(14)
$\begin{array}{c} \text{CIII}  \text{Rel}  \text{CIII} \\ \text{OIII}  \text{Rel}  \text{CIII} \\ \end{array}$	07 2(2)	$O_{12} P_{2} O_{12} O$	05 2(2)
$\begin{array}{c} 011 \\ \hline \\ 01M \\ \hline \\ Po1 \\ \hline \\ Cl21 \\ \hline \\ Cl21 \\ \hline \\ \end{array}$	97.3(3) 81.8(2)	$\begin{array}{c} 012 \\ \hline 02M \\ 02M \\ \hline 0$	70.0(2)
C121  Po1  C121	80.52(10)	$C_{122}$ $P_{02}$ $C_{132}$	80 16(12)
C121 - Re1 - C131	<u> </u>	C122 - Re2 - C132	89.10(13)
C111 - Re1 - C131	87.17(11)	C142 - Re2 - C132	<u>87.01(14)</u> 162.77(10)
C141—Re1—C151	87.17(11)	CI12—Re2—CI32	103.77(10)
	1 6646(10)	Del Cl4	2 2650(6)
Re1 - OIE	1.0040(10)		2.3039(0)
$\frac{1}{10000000000000000000000000000000000$	2.2033(10)	Rel—Ull Dol_Cl2	2.3008(7)
$\frac{1}{1} = \frac{1}{1} = \frac{1}$	2.3034(0)	Kel—Ul3	2.5/19(7)
DI - KeI - OIE	1/8.02(4)	CI2—Kel—CII	87.59(3)
$\frac{JI-KeI-CI2}{DIE}$	98.14(4)	CI4—KeI—CII	90.25(3)
UIE - KeI - CI2	83.24(3)	UI—KeI—Cl3	90.08(4)
UI—KeI—Cl4	98.19(4)	UIE—KeI—CI3	83.30(3)
UIE—ReI—Cl4	80.43(3)	CI2—ReI—CI3	89.85(3)
CI2—ReI—Cl4	163.66(2)	CI4—ReI—CI3	88.61(3)
UI—KeI—CII	96.35(4)	CII—Rel—CI3	166.95(2)
OIE—Rel—Cll	83.69(3)	1	

<b>2</b> Selected geometric data for the complex anions for A-F [Å, °].

D			
Re1-011	1.640(4)	Re2-012	1.657(3)
Re1—O1P	2.222(4)	Re2—O2P	2.211(3)
Re1—Cl41	2.3521(18)	Re2-Cl42	2.3574(14)
Re1—Cl31	2.3618(19)	Re2—Cl12	2.3599(15)
Re1—Cl21	2.362(2)	Re2—Cl22	2.3786(14)
Re1—Cl11	2.383(3)	Re2—Cl32	2.3808(15)
O11—Re1—O1P	176.21(18)	O12—Re2—O2P	177.35(14)
O11—Re1—Cl41	98.75(15)	O12—Re2—Cl42	97.07(12)
O1P—Re1—Cl41	78.12(12)	O2P—Re2—Cl42	82.58(9)
011—Re1—Cl31	98.15(13)	O12—Re2—C112	100.01(12)
O1P—Re1—Cl31	84.01(11)	O2P—Re2—C112	82.61(10)
Cl41—Re1—Cl31	89.06(7)	Cl42—Re2—Cl12	89.36(5)
011—Re1—Cl21	101.10(16)	O12—Re2—Cl22	97.30(13)
O1P—Re1—Cl21	82.08(14)	O2P—Re2—C122	83.03(9)
Cl41—Re1—Cl21	160.12(12)	Cl42—Re2—Cl22	165.62(4)
Cl31—Re1—Cl21	87.17(8)	Cl12—Re2—Cl22	88.80(5)
011—Re1—Cl11	97.5(2)	012—Re2—Cl32	94.55(12)
OIP—Re1—Cl11	80.38(19)	O2P—Re2—Cl32	82.84(10)
Cl41—Re1—Cl11	89.26(15)	Cl42—Re2—Cl32	90.41(5)
CI31—Re1—Cl11	164.31(18)	Cl12—Re2—Cl32	165.36(4)
Cl21—Re1—Cl11	89.13(16)	Cl22—Re2—Cl32	87.80(5)
<u>E</u>			1 ( ( 2 ( 2 )
Re1-011	1.663(2)	Re2-012	1.663(3)
Rel—OII	2.222(2)	Re2-021	2.212(2)
Rel—CIII	2.3632(11)	Re2-C112	2.3469(12)
Rel—Cl21	2.3642(12)	Re2-C122	2.3530(12)
ReI—Cl3I	2.3/18(11)	Re2-Cl42	2.3698(11)
Rel—Cl41	2.3/49(12)	Re2-Cl32	2.3921(12)
OII—ReI—OII	177.25(10)	012—Re2—021	1/4.50(10)
$\frac{\text{OII}-\text{KeI}-\text{CIII}}{\text{OII}-\text{ReI}-\text{CIII}}$	99.32(9)	012—Re2—C112	99.80(10)
$\frac{\text{OII}-\text{ReI}-\text{CIII}}{\text{OII}-\text{ReI}-\text{CIII}}$	82.01(7)	021—Re2—C112	83.97(7)
$\frac{\text{OII}-\text{KeI}-\text{CI2I}}{\text{OII}-\text{ReI}-\text{CI2I}}$	97.00(9)	O12—Re2—Cl22	99.79(10)
CI11 Pel CI21	84.32(7)	021—Re2—C122	84.31(7)
$\frac{\text{CHI}-\text{ReI}-\text{CI2I}}{\text{O11}-\text{ReI}-\text{CI2I}}$	88.48(4) 06.22(0)	CI12—Re2—CI22	87.34(4)
OII—ReI—CI3I	96.33(9)	O12—Re2—Cl42	90.14(10)
$\frac{\text{OII}-\text{KeI}-\text{CI3I}}{\text{CI11}-\text{ReI}-\text{CI3I}}$	61.75(7)	$C_{112}$ Re2-C142	79.83(7)
$\frac{C121}{C121} = \frac{C121}{C121}$	00.22(4)	C122 Re2 - C142	164.06(2)
$\frac{C121-Rc1-C131}{O11-Rc1-C131}$	96.23(4)	C122 - RC2 - C142	95 57(10)
$\frac{011-Rc1-C141}{011-Rc1-C141}$	<u>90.24(9)</u> 81 79(7)	012 - Rc2 - C132	80.75(7)
$\frac{C111}{Re1}$	88.97(4)	$C112 Re^2 C132$	164.62(4)
$\frac{C121}{Re1}$	166.09(3)	C122 - Rc2 - C132	89 27(4)
C121 Re1 $C141$	88 54(4)	C122 - Rc2 - C132	89.80(4)
F	00.54(4)	CI+2 RC2 CI32	07.00(4)
Re1-01	1 6679(15)	Re1-Cl2	2 3823(9)
Re1-012	2.1588(15)	Re2-032	1.692(2)
Re1-C11	2.3637(8)	Re2-042	1.696(2)
Re1—Cl4	2.3665(8)	Re2-022	1.7048(17)
Re1—Cl3	2.3752(9)	Re2-012	1.7391(15)
01 - Re1 - 012	177.82(7)	012—Re1—C12	82.41(4)
01—Re1—C11	98,29(6)	Cl1—Re1—Cl2	88.96(4)
012—Re1—Cl1	83,55(5)	Cl4—Re1—Cl2	166.80(2)
$\overline{O1-Re1-Cl4}$	96,78(5)	Cl3—Re1—Cl2	89.88(4)
012—Re1—Cl4	84,40(5)	032—Re2—042	109.48(12)
Cl1—Re1—Cl4	89,19(4)	032—Re2—022	108.56(9)
01—Re1—Cl3	97.55(6)	042—Re2—022	107.37(10)
012-Re1-C13	80.62(5)	032—Re2—012	111.68(9)

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C11—Re1—C13 164.14(2) 042—Re2—012 109.86(9)   C14—Re1—C13 88.33(4) 022—Re2—012 109.78(8)   O1—Re1—C12 96.42(5) Re2—O12—Re1 160.67(9)
Cl4Re1Cl3   88.33(4)   O22Re2O12   109.78(8)     O1Re1Cl2   96.42(5)   Re2O12Re1   160.67(9)
01-Re1-Cl2 96.42(5) Re2-O12-Rel 160.67(9)

#### Supplementary material

#### 1. Structure of the phosphonium cations

The ethyltriphenylphosphonium ion present in A is also the counterion of C and F(Fig. S3a). Based on studies on the structure of ethyltriphenylphosphonium rhenate(VII) [S1] it was concluded, that the ethyltriphenylphosphonium cation may adopt different forms depending on the degree of a shift of the ethyl group from the plane of the phenyl ring in trans position. In the case of both symmetry-independent cations in A this shift is not considerable (for the cation with P1 the shift of the methyl C11 atom is of -0.030(8) Å, the shift of the methylene C21 atom is of 0.130(6) Å; for the cation with P2 the shift of the methyl C12 atom is of 0.031(9) Å, the shift of the methylene C22 atom is of 0.164(7) Å; it is interesting to note, that the shift is greater for the methylene moiety than for the methyl group). For the cation with P1 the maximum shift of the P1 atom from the phenyl rings planes is at 0.078(5) Å (from the phenyl ring with the C111 atom). The interplanar angles for the phenyl rings within the -PPh<sub>3</sub> moiety are of 69.1(1), 72.6(1) and  $53.0(1)^{\circ}$ , respectively. For the cation with P2 the maximum shift of the P2 atom from the phenyl rings planes is at 0.082(5) Å (from the phenyl ring with the C132 atom); the interplanar angles for the phenyl rings within the -PPh<sub>3</sub> moiety are of 70.4(2), 73.0(2) and  $62.0(1)^{\circ}$ . In the case of the cation from C the ethyl group is considerably shifted from the plane of the phenyl ring in *trans* position (the shift of the methyl C1 atom is of 0.627(4) Å, the shift of the methylene C2 atom is of 0.442(3) Å). The maximum shift of the P1 atom from the phenyl rings planes is of only 0.050(2) Å (from the phenyl ring with the C11 atom); the interplanar angles for the phenyl rings within the -PPh<sub>3</sub> moiety are of 65.3(1), 66.9(1) and  $53.9(1)^{\circ}$ . The two symmetryindependent cations in F represent two different cases: of not considerable (the shift of the methyl C11 atom is of -0.002(6) Å, the shift of the methylene C21 atom is of -0.033(5) Å) and considerable (the shift of the methyl C12 atom is of 0.434(6) Å, the shift of the methylene C22 atom is of -0.372(5) Å) shift of the ethyl group from the plane of the phenyl ring in *trans* position. For the cation with the P1 the maximum shift of P1 atom from the phenyl rings planes is of -0.159(3) Å (from the phenyl ring with the C111 atom). The interplanar angles for the phenyl rings within the -PPh<sub>3</sub> moiety are of 77.5(1), 67.8(1) and  $66.5(1)^{\circ}$ . For the cation with P2 the maximum shift of the P2 atom from the phenyl rings planes is of -0.114(4) Å (from the phenyl ring with the C122 atom). The interplanar angles for the phenyl rings within the -PPh<sub>3</sub> moiety are of 67.5(1), 75.0(1) and 53.7(1)°.

The phosphonium cation in **B** (Fig. S3b) lies in general position, contrary to the cation in the analogous rhenate(VII) salt [S2], which is centrosymmetric. The P1-C1-C2-P2 torsion angle is of 146.7(6)°. For the -PPh<sub>3</sub> moiety with P1 the maximum shift of the P1 atom from the phenyl rings planes is of -0.13(2) Å (from the phenyl ring with the C111 atom). The interplanar angles for the phenyl rings within this moiety are of 75.6(3), 61.8(4) and 89.9(3)°. For the -PPh<sub>3</sub> moiety with P2 the maximum shift of the P2 atom from the phenyl rings planes is of -0.20(2) Å (from the phenyl ring with the C112 atom). The interplanar angles for the phenyl rings within this moiety are of 80.7(3), 86.4(4) and 58.5(4)°.

The (4-methylphenyl)triphenylphosphonium cation, present as a counterion in **D** and in E (Fig. S3c) has appeared in only one crystal structure report so far, namely for the  $[ZnCl_2(NA)]$  compound (NA = nicotinic acid) [S3]. It seems, that this cation is capable of adopting different conformations. In **D** there are two symmetry-independent cations with the corresponding torsion angles: C131-P1-C111-C111 of -160.0(4)° and C132-P2-C12-C112 of -178.4(4)°. For the cation with P1 the maximum shift of the P1 atom from the phenyl rings planes is of 0.282(6) Å (from the phenyl ring with the C131 atom). The interplanar angles for the phenyl rings within the -PPh<sub>3</sub> moiety are 72.6(2), 73.3(2) and  $69.8(2)^{\circ}$ . For the cation with the P2 the maximum shift of P2 atom from the phenyl rings planes is of 0.074(6) Å (from the phenyl ring with the C142 atom); the interplanar angles for the phenyl rings within the -PPh<sub>3</sub> moiety are of 89.0(2), 83.3(2) and 68.8(2)°. On the other hand, in E the two symmetryindependent cations adopt similar conformations (the C131-P1-C11-C111 torsion angle of - $166.3(4)^{\circ}$ ; the C132-P2-C12-C112 torsion angle of  $166.5(3)^{\circ}$ ). For the cation with P1 the maximum shift of the P1 atom from the phenyl rings planes is of 0.145(5) Å (from the phenyl ring with the C121 atom). The interplanar angles for the phenyl rings within the  $-PPh_3$  moiety are of 88.1(1), 82.4(1) and 56.5(2)°. For the cation with P2 the maximum shift of the P2 atom from the phenyl rings planes is of 0.233(5) Å (from the phenyl ring with the C122 atom). The interplanar angles for the phenyl rings within the -PPh<sub>3</sub> moiety are of 89.2(2), 70.9(1) and 67.4(2)°.

### 2. Figures





(c)





(e)

**Fig. S1.** Anion hydrogen-bonded motifs in **A-E**. Hydrogen bonds are denoted with dashed lines. Symmetry codes: (i) -x+2, -y+1, -z+1; (ii) -x+2, -y+2, -z+2, (iii) -x+2, -y+1, -z+2, (iv) x+1/2, -y+1/2, z+1/2; (v) -x+1, -y, -z+1, (vi) 1.5-x, 0.5+y, 1.5-z.

RCC



(a)



(b)



(c)



(d)



(e)



#### (f)

**Fig. S2** Packing of the cations and anions in **A-F** (see the article Discussion section). Hydrogen bonds (O-H...Cl/O-H...O, see Table S1) are denoted with dashed lines.









(b)





(c) **Fig. S3** Structure of the phosphonium cations in: (a) **A**, **C**, **F** (on the example of **A**); (b) **B**; (c) **D**, **E** (on the example of **D**).

#### 3. Tables

D—H···A	D—H	$H \cdots A$	$D \cdots A$	D—H···A
Α				
O1W—H1W1…Cl41 <sup>i</sup>	0.84	2.75	3.278(2)	122
$O1W$ — $H1W2$ ···Cl $31^{i}$	0.84	2.30	3.141(2)	176
O2W—H2W1…Cl42 <sup>ii</sup>	0.82	2.83	3.241(2)	114
O2W—H2W2····Cl32 <sup>ii</sup>	0.82	2.41	3.204(3)	165
C221—H221…O12 <sup>iii</sup>	0.95	2.68	3.448(4)	139
C22—H22C…O12 <sup>iii</sup>	0.99	2.49	3.362(4)	146
C632—H632…Cl12	0.95	2.80	3.652(3)	150
C231—H231…Cl42 <sup>iii</sup>	0.95	2.66	3.591(4)	168
C21—H21B…O11 <sup>iv</sup>	0.99	2.57	3.392(4)	141
C222—H222····O11 <sup>i</sup>	0.95	2.58	3.308(4)	133

Table S1 Hydrogen bonding data for A-F [Å, °].

C631—H631…Cl11	0.95	2.81	3.655(3)	149
C11—H11A····Cl21 <sup>iv</sup>	0.98	2.87	3.559(3)	129
C232—H232…Cl41 <sup>i</sup>	0.95	2.68	3.613(3)	167
Symmetry codes: (i) -x+	2, -y+1, -z+1; (ii) -x-	+2, -y+2, -z; (iii) -x+1, -	y+1, -z; (iv) -x+1, -y, -z	z+1.
B				
O1M—H1M…Cl11	0.82	2.39	3.070(8)	141
O1M—H1M…Cl41	0.82	2.51	2.960(8)	114
O2M—H2M····Cl32 <sup>i</sup>	0.82	2.52	3.246(8)	148
C2M—H2MB…Cl22	0.98	2.89	3.398(15)	113
C2M—H2MC···Cl12	0.98	2.85	3.338(14)	112
$C1$ — $H1B$ ···· $Cl32^{i}$	0.99	2.64	3.548(10)	152
C611—H611…Cl32 <sup>i</sup>	0.95	2.59	3.461(12)	152
C621—H621…Cl22 <sup>ii</sup>	0.95	2.87	3.575(10)	132
C622—H622…Cl42 <sup>iii</sup>	0.95	2.69	3.332(11)	125
C232—H232…Cl12 <sup>ii</sup>	0.95	2.71	3.559(10)	149
C632—H632…Cl21	0.95	2.96	3.451(10)	114
Symmetry codes: (i) -x+	$\frac{1}{2, -y+1, -z+2; (ii) -x-2}$	+1, -y+1, -z+2; (iii) x, y-	+1, <i>z</i> .	
C			, .	
O3P—H3P…Cl22	0.84	2.51	3.235(4)	145
O3P—H3P…Cl32	0.84	2.80	3.426(4)	132
O2P—H2P····O3P <sup>1</sup>	0.84	1.89	2.641(5)	147
C22E—H22C…C11	0.98	2.83	3,730 (2)	153
$C2-H2B\cdots Cl1^{i}$	0.99	2.79	3,683 (2)	151
C11E—H11B…Cl2	0.99	2.78	3,306 (2)	114
$C_{23}$ H23Cl3 <sup>ii</sup>	0.95	2.81	3,730 (2)	164
C31—H31…Cl4 <sup>iii</sup>	0.95	2.73	3.628 (2)	157
Symmetry codes: (i) -r+	$\frac{1}{2}$ -v+1 -7+2: (ii) -r-	+1/2 $+1/2$ $-7+3/2$ (iii)	) -x+1 -y+1 -z+2	107
D	<u>2</u> , <i>y</i> +1, <i>z</i> +2, (ii) <i>x</i>	(112, y)(112, z)(312, (11))	), , ,	
03P—H3P…Cl22	0.84	2.51	3.235(4)	145
03P—H3P…C132	0.84	2.80	3 426(4)	132
$O2P$ — $H2P$ ··· $O3P^{i}$	0.84	1.89	2.641(5)	132
C12—H12A…C111	0.99	2.67	3.629(7)	163
C12_H12BCl11 <sup>ii</sup>	0.99	2 75	3 669(7)	155
C212_H212Cl11 <sup>ii</sup>	0.95	2.82	3 520(7)	132
C642—H642…C111	0.95	2.73	3.644(8)	162
C11_H11ACl31 <sup>iii</sup>	0.99	2.75	3 690(5)	159
C11_H11BCl42	0.99	2.75	3 538(5)	132
C12_H12AC11A	0.99	2.00	3 73(3)	163
$C12$ H12R $C11A^{ii}$	0.99	2.79	3 72(3)	156
$C_{212}$ H212C11A <sup>ii</sup>	0.95	2.82	3.54(3)	134
C231—H231…Cl2A <sup>iii</sup>	0.95	2.63	3.36(2)	134
C232_H232Cl2A <sup>ii</sup>	0.95	2.63	3.30(2)	116
Symmetry codes: (i) -r+	$\frac{1}{2} - \frac{1}{2} - \frac{1}$	$\frac{2.07}{1}$	5.20(2)	110
E	2, y = 1, z = 2, (11) x	1, y1, 21, (iii) x1	r, y, 2,11.	
011_H11Cl32	0.84	2 50	3 279(3)	156
02LH2ICl/1	0.84	2.50	3 252(3)	165
$C_{432}$ H432012 <sup>i</sup>	0.04	2.73	3 346(5)	103
C11_H11BCl21	0.95	2.70	3.775(4)	164
C322_H322Cl/1 <sup>ii</sup>	0.99	2.02	3.631(4)	146
$C_{322}$ $H_{322}$ $C_{141}$ $C_{142}$	0.95	2.01	3 516(4)	138
Symmetry codes: (i) $r = 1$	$v_{7}$ (ii) $v_{-7}$ $v_{-7}$	2.75 : (iii) _r+1 _v _7±1	5.510(4)	130
<b>F</b>	, y, z, (11) - x, -y, -z + 1	, (III) -171, -y, -2,+1.		
г С631 Ц621 С12 <sup>і</sup>	0.05	2 70	3 704(2)	167
$C_{001} = 0001 \cdots C_{12}^{12}$	0.93	2.19	3.704(2)	102
$\begin{array}{c} C_{222} \\ \hline C_{222} \\ \hline \\ H_{222} \\ \hline \\ C_{222} \\ \hline \\ H_{222} \\ \hline \\ C_{12}^{ll} \\ \hline \end{array}$	0.93	2.13	3.007(3)	131
$C_{622} = H_{622} = O_{11}^{11}$	0.95	2.11	3.430(3)	130
$C_{00} = C_{00} = C$	0.95	2.33	3.204(3)	132
$C_{21}$ —H2IB···· $U_{22}$	0.99	2.50	5.297(5)	13/
C231—H231…O22 <sup>m</sup>	0.95	2.49	3.431(3)	170

C22—H22B····O32 <sup>iv</sup>	0.99	2.23	3.207(3)	171	
C511—H511…O42 <sup>v</sup>	0.95	2.58	3.343(3)	138	
C332—H332…O42 <sup>v</sup>	0.95	2.48	3.120(3)	125	
C631—H631…Cl2 <sup>i</sup>	0.95	2.79	3.704(2)	162	
Symmetry codes: (i) - <i>x</i> +1, <i>y</i> -1/2, - <i>z</i> +1/2; (ii) - <i>x</i> +1, - <i>y</i> +1, - <i>z</i> ; (iii) - <i>x</i> +1, <i>y</i> +1/2, - <i>z</i> +1/2; (iv) <i>x</i> +1, - <i>y</i> +1/2, <i>z</i> +1/2; (v)					
-x+1, -y, -z,					

#### 4. References for ESI

- Acceleration

#### Highlights

Products of the phosphonium pentachloridooxidorhenates(VI) decomposition were crystallized.

J<sup>2</sup> x Salts with  $[\text{Re}^{V}\text{OCl}_{4}X]^{-}$  (X = solvent molecule) or  $[\text{Re}^{V}\text{OCl}_{4}\text{Re}^{VII}\text{O}_{4}]^{2-}$  anions are obtained.