

Rhenium oxohalides: Synthesis and crystal structures of $\text{ReO}_3\text{Cl}(\text{THF})_2$, $\text{ReOCl}_4(\text{THF})$, $\text{Re}_2\text{O}_3\text{Cl}_6(\text{THF})_2$, and $\text{Re}_2\text{O}_3\text{Cl}_6(\text{H}_2\text{O})_2$

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Received 13th November 2006, Accepted 14th December 2006

First published as an Advance Article on the web 15th January 2007

DOI: 10.1039/b616495a

Convenient methods to prepare solvated rhenium oxochlorides are described; these compounds should serve as useful starting materials for rhenium chemistry. Treatment of perrhenic acid, HReO_4 , with chlorotrimethylsilane or with thionyl chloride, followed by addition of tetrahydrofuran, forms the new oxochloride complexes $\text{ReO}_3\text{Cl}(\text{THF})_2$ and $\text{ReOCl}_4(\text{THF})$, respectively. Small amounts of two dinuclear oxochlorides, which evidently resulted from adventitious hydrolysis, were also isolated: $\text{Re}_2\text{O}_3\text{Cl}_6\text{L}_2$, where $\text{L} = \text{THF}$ or H_2O . All four compounds were characterized by X-ray crystallography. The rhenium(VII) complex $\text{ReO}_3\text{Cl}(\text{THF})_2$ adopts a distorted octahedral geometry in which the three oxo ligands are in a facial arrangement; the rhenium(VI) complex $\text{ReOCl}_4(\text{THF})$ adopts a *trans* octahedral structure. The two dinuclear rhenium(VI) compounds both have a single, nearly linear, bridging oxo group; on each Re center, the three terminal chlorides adopt a *mer* arrangement, and the terminal oxo and the coordinated Lewis base are mutually *trans*. The water ligand in the aqua complex is hydrogen bonded to nearby THF molecules. IR data are given.

Introduction

Rhenium chlorides and oxochlorides—especially ReCl_5 , Re_3Cl_9 , ReO_3Cl , ReOCl_4 , and ReOCl_3L_2 —play an important role in the syntheses of a wide variety of rhenium compounds, particularly in the preparation of organorhenium species.^{1,2} For example, a wide variety of organorhenium complexes can be prepared from these starting materials, including oxorhenium alkyls and aryls such as ReOR_4 ($\text{R} = \text{Me}$,³ CH_2SiMe_3 ,⁴ or $\text{C}_6\text{H}_2\text{Me}_3$);⁵ dinuclear compounds such as $\text{Re}_2(\mu\text{-CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4$ ⁶ and $\text{Re}_2\text{O}_3\text{R}_6$ ($\text{R} = \text{Me}$ or CH_2SiMe_3);⁷ trirhenium clusters such as Re_3R_{12} ($\text{R} = \text{Me}$, CH_2SiMe_3 , or CH_2CMe_3);⁸ $\text{Re}_3\text{Me}_9\text{L}_3$ ($\text{L} = \text{PMe}_2\text{Ph}$ or PEt_2Ph);⁹ and $\text{Re}_3\text{Cl}_3\text{R}_6$ ($\text{R} = \text{CH}_2\text{SiMe}_3$);¹⁰ and other species such as the cyclopentadienyl complex Cp_2ReH ^{11,12} and the hydride $\text{ReH}(\text{PMe}_3)$.¹³

Many synthetic methods have been developed to prepare rhenium chlorides and oxochlorides,¹⁴ the most common method beginning with the high-temperature chlorination of rhenium powder in a quartz tube to produce ReCl_5 .¹⁵ Thermolysis of ReCl_5 produces Re_3Cl_9 , and burning these materials in dry oxygen produces ReOCl_4 and ReO_3Cl , respectively.¹⁶ Although these methods proceed in high yield, they are somewhat inconvenient because they require specialized apparatus and are somewhat hazardous.

In this paper, we describe simple solution preparations of several solvated rhenium oxochlorides in the +7 and +6 oxidation states.

Results and discussion

Syntheses

Perrhenic acid, HReO_4 , which is easily prepared by dissolving rhenium metal in aqueous hydrogen peroxide,^{17,18} is a convenient

starting material for rhenium chemistry. We find that treatment of perrhenic acid with chlorotrimethylsilane at room temperature affords the rhenium(VII) oxochloride ReO_3Cl , which can easily be isolated in 67% yield as its tetrahydrofuran adduct $\text{ReO}_3\text{Cl}(\text{THF})_2$ (**1**). Violet **1** hydrolyzes readily in air and reacts with silicone grease;¹⁹ it is stable for months at -20°C but decomposes over a few days at room temperature. The IR spectrum contains strong, sharp $\text{Re}=\text{O}$ stretching bands at 952, 967, and 987 cm^{-1} that are comparable to the 948, 963, and 983 cm^{-1} frequencies for $\text{ReO}_3\text{Cl}(\text{SO}_2\text{Cl}_2)$.²⁰ In comparison, the $\text{Re}=\text{O}$ stretch for the parent compound ReO_3Cl appears at 960 cm^{-1} ,²¹ whereas adducts of ReO_3Cl with strong donors have lower $\text{Re}=\text{O}$ stretching frequencies: $900\text{--}950\text{ cm}^{-1}$ for $\text{ReO}_3\text{Cl}(\text{dmsO})_2$,²² and 912, 923, and 947 cm^{-1} for $\text{ReO}_3\text{Cl}(\text{bipy})$ and $\text{ReO}_3\text{Cl}[4,4'-(t\text{-Bu})_2\text{bipy}]$.^{23–26} Bands due to coordinated THF appear in the IR spectrum of **1** at 674, 840, 1011, 1039, 1072, 1169, 1244, 1317, and 1341 cm^{-1} . Coordinated THF ligands generally show multiple bands in the IR spectrum, the most diagnostic being the asym and sym $\nu(\text{C}-\text{O}-\text{C})$ bands, which generally appear as strong features near 1010–1040 and 840 cm^{-1} respectively.^{27,28}

Treatment of perrhenic acid in refluxing thionyl chloride affords the rhenium(VI) oxochloride ReOCl_4 , which again can be easily isolated in 80% yield as its tetrahydrofuran adduct $\text{ReOCl}_4(\text{THF})$ (**2**). Purple **2** hydrolyzes readily in air. The IR spectrum shows a strong, sharp band in the $\text{Re}=\text{O}$ stretching region at 1015 cm^{-1} . For comparison, the $\text{Re}=\text{O}$ stretching frequency for ReOCl_4 varies between 1016 and 1033 cm^{-1} depending on the medium,^{20,29–33} and the $\text{Re}=\text{O}$ bands in $\text{ReOCl}_4(\text{H}_2\text{O})$ ³⁴ and $\text{ReOCl}_4(\text{MeCN})$ ³³ appear at 1000 and 1016 cm^{-1} , respectively. Broad, reasonably strong bands due to coordinated THF are seen at 846, 922, 956, 993, 1044, 1118, 1169, 1250, 1308, and 1348 cm^{-1} .

Under certain circumstances, pentane/THF solutions of **1** stored at low temperature slowly deposit crystals of a new complex, which was subsequently identified (see below) as the oxo-bridged dirhenium(VI) complex $\text{Re}_2\text{O}_3\text{Cl}_6(\text{THF})_2$ (**3**). Under

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slightly different conditions, a similar oxo-bridged rhenium(vi) compound, identified as $\text{Re}_2\text{O}_3\text{Cl}_6(\text{H}_2\text{O})_2 \cdot 4\text{THF}$ (**4**), could be isolated. Neither of these dinuclear complexes could be prepared reproducibly; both are the result of adventitious hydrolysis. Several attempts to reproduce the syntheses of **3** and **4** by treating **1** with H_2O were unsuccessful. The IR spectrum of **4** contains a band at 668 cm^{-1} that is assigned to the Re–O–Re stretch; for comparison, IR features due to this vibration appear at 624 and 649 cm^{-1} in $\text{Re}_2\text{O}_5\text{Me}_4(\text{py})_2$,³⁴ at 850 cm^{-1} in $\text{Re}_2\text{O}_3\text{Me}_6$,⁷ at about 730 cm^{-1} in $[\text{Re}_2\text{O}_3\text{Cl}_8]^{2-}$,³² and at 675 – 710 cm^{-1} in $\text{Re}_2\text{O}_3\text{Cl}_4(\text{py})_4$.³⁵

We also investigated the reaction of HReO_4 with other chlorinating reagents. Treatment of perrhenic acid in refluxing hexachloropropene^{36,37} resulted in the formation of a dark insoluble powder that exhibited a featureless IR spectrum. Microanalytical data suggested that the powder was largely ReO_3 ,^{38,39} it was generated in 89% yield.

Crystallographic investigations

Single crystals of $\text{ReO}_3\text{Cl}(\text{THF})_2$ (**1**) were grown from THF/pentane at $-20\text{ }^\circ\text{C}$. The molecular structure of **1** is shown in Fig. 1; crystallographic data and important bond distances and angles are given in Tables 1 and 2. The six ligands about the rhenium center describe a distorted octahedral coordination sphere. The three oxo ligands are in a facial arrangement; most likely, this arrangement is adopted to prevent the strongly π -bonding and *trans*-directing oxo ligands from being *trans* to one another.⁴⁰ The Re=O double bond distances average $1.713(4)\text{ \AA}$, the Re–O single bonds to the THF ligands average $2.263(3)\text{ \AA}$,

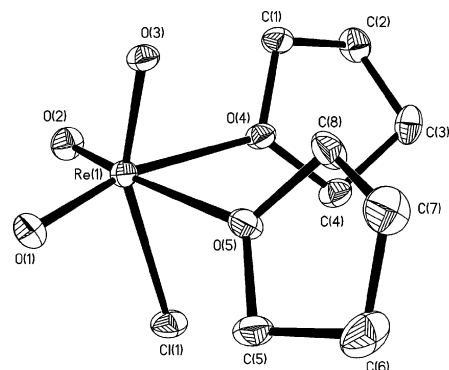


Fig. 1 Molecular structure of $\text{ReO}_3\text{Cl}(\text{THF})_2$ (**1**). The 30% probability density surfaces are shown. Hydrogen atoms are omitted for clarity.

and the Re–Cl bond distance is $2.427(1)\text{ \AA}$. The O–Re–O angles lie between $102.2(2)$ and $103.7(2)^\circ$. For comparison, in the compound $\text{ReO}_3\text{Me}(\text{phen})$ the Re=O bond distances are $1.717(2)$ – $1.767(3)\text{ \AA}$ and the O–Re–O angles are $105.3(1)$ – $107.1(1)^\circ$.⁴⁰ The larger Re–O–Re angles in the latter complex reflect the reduced steric demand of its bidentate Lewis base relative to the two THF molecules in **1**.

Single crystals of $\text{ReOCl}_4(\text{THF})$ (**2**) were grown from THF/pentane at $-20\text{ }^\circ\text{C}$. The molecular structure of **2** is shown in Fig. 2, crystallographic data are given in Table 1, and bond distances and angles are given in Table 3. The rhenium center in **2** adopts a *trans*-octahedral geometry in which the Re=O distance is $1.662(5)\text{ \AA}$ and the Re–Cl bond distances are all essentially equal at $2.302(2)\text{ \AA}$. For comparison, the parent molecule ReOCl_4 adopts

Table 1 Crystal data and structure refinement for $\text{ReO}_3\text{Cl}(\text{THF})_2$, **1**, $\text{ReOCl}_4(\text{THF})$, **2**, $\text{Re}_2\text{O}_3\text{Cl}_6(\text{THF})_2$, **3**, and $\text{Re}_2\text{O}_3\text{Cl}_6(\text{H}_2\text{O})_2 \cdot 4\text{THF}$, **4**

	1	2	3	4
Formula	$\text{C}_8\text{H}_{16}\text{ClO}_5\text{Re}$	$\text{C}_4\text{H}_8\text{Cl}_4\text{O}_2\text{Re}$	$\text{C}_8\text{H}_{16}\text{Cl}_6\text{O}_5\text{Re}_2$	$\text{C}_{16}\text{H}_{36}\text{Cl}_6\text{O}_9\text{Re}_2$
Formula weight	413.86	416.10	777.31	957.55
<i>T</i> /K	193(2)	193(2)	193(2)	193(2)
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$I2/a$	$P\bar{1}$	$P\bar{1}$
<i>a</i> /Å	7.724(2)	15.220(4)	8.285(2)	8.528(5)
<i>b</i> /Å	12.795(3)	7.996(2)	9.252(3)	10.051(5)
<i>c</i> /Å	12.204(3)	16.717(7)	12.070(3)	10.707(6)
$\alpha/^\circ$	90	90	91.525(4)	66.006
$\beta/^\circ$	98.412(4)	91.089(3)	90.116(4)	67.762
$\gamma/^\circ$	90	90	92.490(4)	67.683
<i>V</i> /Å ³	1193.0(5)	2034.0(11)	924.0(4)	747.9(7)
<i>Z</i> , $\rho_{\text{calc}}/\text{g cm}^{-3}$	4, 2.304	8, 2.718	2, 2.794	1, 2.126
μ/mm^{-1}	10.408	12.951	13.967	8.660
<i>F</i> (000)	784	1528	712	456
Crystal size/mm	0.12 × 0.18 × 0.20	0.40 × 0.14 × 0.03	0.18 × 0.16 × 0.08	0.16 × 0.08 × 0.04
θ range/ $^\circ$	2.32–28.33	2.44–25.35	1.69–25.36	2.63–25.38
rfins: total/unique	10983/2919	6260/1850	6759/3341	7745/2741
<i>R</i> (int)	0.0815	0.1150	0.0754	0.1201
Abs. corr.	ellipsoidal	face-indexed	face-indexed	ellipsoidal
Max., min. transm. factors.	0.125, 0.057	0.675, 0.156	0.346, 0.125	0.757, 0.400
Data/restraints/params	2919/0/137	1850/0/101	3341/0/190	2741/2/157
GOF on <i>F</i> ²	0.956	1.015	0.945	0.991
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0297	0.0361	0.0364	0.0388
<i>wR</i> ₂ (all data)	0.0749	0.0789	0.0862	0.0655
ext. coeff.	0.0041(3)	0.00043(6)	NA	NA
Max., min. Δρ _{elect} /e.Å ⁻³	1.008, −1.284	1.518, −2.130	1.728, −1.855	1.234, −1.638

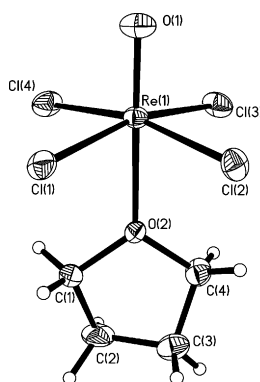
$$R_1 = \frac{\sum \|F_o\| - \sum \|F_c\|}{\sum \|F_o\|}, wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

Table 2 Selected bond distances and angles for $\text{ReO}_3\text{Cl}(\text{THF})_2$, **1**

Distances/Å			
Re(1)–O(1)	1.711(4)	Re(1)–O(2)	1.708(4)
Re(1)–O(3)	1.719(3)	Re(1)–O(4)	2.264(4)
Re(1)–O(5)	2.262(3)	Re(1)–Cl(1)	2.4269(13)
Angles/°			
O(2)–Re(1)–O(1)	103.66(18)	O(2)–Re(1)–O(3)	102.17(18)
O(1)–Re(1)–O(3)	103.68(18)	O(2)–Re(1)–O(5)	165.49(16)
O(1)–Re(1)–O(5)	88.91(16)	O(3)–Re(1)–O(5)	81.44(15)
O(2)–Re(1)–O(4)	89.78(16)	O(1)–Re(1)–O(4)	164.00(16)
O(3)–Re(1)–O(4)	81.46(15)	O(5)–Re(1)–O(4)	76.77(13)
O(2)–Re(1)–Cl(1)	92.15(13)	O(1)–Re(1)–Cl(1)	91.23(13)
O(3)–Re(1)–Cl(1)	156.04(12)	O(5)–Re(1)–Cl(1)	80.19(9)
O(4)–Re(1)–Cl(1)	79.47(9)		

Table 3 Selected bond distances and angles for $\text{ReOCl}_4(\text{THF})_2$, **2**

Distances/Å			
Re(1)–O(1)	1.662(5)	Re(1)–O(2)	2.224(4)
Re(1)–Cl(1)	2.302(2)	Re(1)–Cl(2)	2.303(2)
Re(1)–Cl(3)	2.3034(18)	Re(1)–Cl(4)	2.303(2)
Angles/°			
O(1)–Re(1)–O(2)	179.0(2)	O(1)–Re(1)–Cl(1)	98.34(19)
O(2)–Re(1)–Cl(1)	82.62(13)	O(1)–Re(1)–Cl(4)	96.6(2)
O(2)–Re(1)–Cl(4)	83.72(13)	Cl(1)–Re(1)–Cl(4)	88.69(7)
O(1)–Re(1)–Cl(2)	97.2(2)	O(2)–Re(1)–Cl(2)	82.50(13)
Cl(1)–Re(1)–Cl(2)	88.64(7)	Cl(4)–Re(1)–Cl(2)	166.19(8)
O(1)–Re(1)–Cl(3)	96.28(19)	O(2)–Re(1)–Cl(3)	82.76(13)
Cl(1)–Re(1)–Cl(3)	165.38(6)	Cl(4)–Re(1)–Cl(3)	89.59(7)
Cl(2)–Re(1)–Cl(3)	89.58(7)		

**Fig. 2** Molecular structure of $\text{ReOCl}_4 \cdot \text{THF}$ (**2**). The 30% probability density surfaces are shown, except for hydrogen atoms, which are depicted as arbitrarily-sized spheres.

a square pyramidal structure in which the mean $\text{Re}=\text{O}$ distance is 1.63 Å and the mean $\text{Re}-\text{Cl}$ bond length is 2.26 Å.⁴¹ The slightly shorter metal–ligand distances in the parent molecule reflect the lower coordination number and reduced steric crowding. The steric effects are also manifested in the interligand bond angles: the $\text{O}-\text{Re}-\text{Cl}$ angles in **2** range from 96.3(2) to 98.3(2)°, vs. 103.9 to 105.2° for ReOCl_4 .

Crystallographic data for $\text{Re}_2\text{O}_3\text{Cl}_6(\text{THF})_2$ (**3**) and $\text{Re}_2\text{O}_3\text{Cl}_6(\text{H}_2\text{O})_2 \cdot 4\text{THF}$ (**4**) are summarized in Table 1, and important bond distances and angles are given in Tables 4 and 5. Their structures are very similar to one another, except for the identity of the coordinated Lewis base (Figs. 3 and 4). These dinuclear molecules each contain a single oxo bridge. Each rhenium center is six-coordinate, with three chloride ligands in a

Table 4 Selected bond distances and angles for $\text{Re}_2\text{O}_3\text{Cl}_6(\text{THF})_2$, **3**

Distances/Å			
Re(1)–O(1)	1.860(6)	Re(1)–O(2)	1.667(7)
Re(1)–O(3)	2.247(6)	Re(1)–Cl(1)	2.326(3)
Re(1)–Cl(2)	2.320(3)	Re(1)–Cl(3)	2.309(3)
Re(2)–O(1)	1.849(7)	Re(2)–O(4)	1.654(7)
Re(2)–O(5)	2.253(6)	Re(2)–Cl(4)	2.328(3)
Re(2)–Cl(5)	2.304(3)	Re(2)–Cl(6)	2.311(3)
Angles/°			
O(2)–Re(1)–O(1)	98.3(3)	O(2)–Re(1)–O(3)	178.7(3)
O(1)–Re(1)–O(3)	80.7(3)	O(2)–Re(1)–Cl(3)	98.2(3)
O(1)–Re(1)–Cl(3)	92.41(19)	O(3)–Re(1)–Cl(3)	81.09(19)
O(2)–Re(1)–Cl(2)	96.5(3)	O(1)–Re(1)–Cl(2)	165.2(2)
O(3)–Re(1)–Cl(2)	84.48(18)	Cl(3)–Re(1)–Cl(2)	85.54(11)
O(2)–Re(1)–Cl(1)	99.2(3)	O(1)–Re(1)–Cl(1)	90.79(19)
O(3)–Re(1)–Cl(1)	81.66(18)	Cl(3)–Re(1)–Cl(1)	161.70(12)
Cl(2)–Re(1)–Cl(1)	86.77(10)	O(4)–Re(2)–O(1)	99.8(3)
O(4)–Re(2)–O(5)	178.3(3)	O(1)–Re(2)–O(5)	80.9(2)
O(4)–Re(2)–Cl(5)	96.5(3)	O(1)–Re(2)–Cl(5)	163.7(2)
O(5)–Re(2)–Cl(5)	82.85(18)	O(4)–Re(2)–Cl(6)	98.5(3)
O(1)–Re(2)–Cl(6)	90.2(2)	O(5)–Re(2)–Cl(6)	82.99(17)
Cl(5)–Re(2)–Cl(6)	86.43(11)	O(4)–Re(2)–Cl(4)	96.1(3)
O(1)–Re(2)–Cl(4)	91.91(19)	O(5)–Re(2)–Cl(4)	82.34(17)
Cl(5)–Re(2)–Cl(4)	87.32(11)	Cl(6)–Re(2)–Cl(4)	164.67(11)
Re(2)–O(1)–Re(1)	168.0(4)		

Table 5 Selected bond distances and angles for $\text{Re}_2\text{O}_3\text{Cl}_6(\text{H}_2\text{O})_2$, **4**^a

Distances/Å			
Re(1)–O(1)	1.8434(7)	Re(1)–O(2)	1.662(5)
Re(1)–O(3)	2.125(6)	Re(1)–Cl(1)	2.3189(19)
Re(1)–Cl(2)	2.314(2)	Re(1)–Cl(3)	2.321(2)
Angles/°			
O(2)–Re(1)–O(1)	98.1(2)	O(2)–Re(1)–O(3)	179.2(2)
O(1)–Re(1)–O(3)	81.99(14)	O(2)–Re(1)–Cl(2)	96.1(2)
O(1)–Re(1)–Cl(2)	165.76(6)	O(3)–Re(1)–Cl(2)	83.77(15)
O(2)–Re(1)–Cl(1)	97.92(17)	O(1)–Re(1)–Cl(1)	90.99(6)
O(3)–Re(1)–Cl(1)	81.32(14)	Cl(2)–Re(1)–Cl(1)	86.64(8)
O(2)–Re(1)–Cl(3)	97.71(18)	O(1)–Re(1)–Cl(3)	90.64(6)
O(3)–Re(1)–Cl(3)	83.04(14)	Cl(2)–Re(1)–Cl(3)	87.85(8)
Cl(1)–Re(1)–Cl(3)	163.89(8)	Re(1)–O(1)–Re(1)	180.000

^a Primed atoms are related to the unprimed atoms by the transformation $-x, -y, -z$.

mer arrangement. On each metal center, the terminal oxo ligand and the Lewis base are mutually *trans*. In both **3** and **4**, the ligands on each rhenium center are disposed in such a way as to give each molecule idealized inversion symmetry. Interestingly, the $\text{Re}-\text{O}-\text{Re}$ unit in **3** is bent (168°) whereas in **4** it is rigorously linear (180°) owing to the crystallographic symmetry. The $\text{O}-\text{Re}-\text{Re}-\text{O}$ torsion angle involving the two terminal oxo ligands is 154.6° in **3** but 180° in **4**. Otherwise, the bond distances in **3** and **4** are fairly comparable: the average $\text{Re}=\text{O}$ distances are 1.661(2) Å in **3** vs. 1.662(5) Å in **4**, the average $\text{Re}-\text{O}$ distance to the bridging oxo atom is 1.855(2) Å in **3** vs. 1.8434(7) Å in **4**, and the $\text{Re}-\text{Cl}$ distances range from 2.309(3) to 2.328(3) Å in **3** vs. 2.314(2) to 2.321(2) Å in **4**. The interligand angles are also similar: the average $\text{O}=\text{Re}-\text{Cl}$ angle is 97.5(3)° in **3** vs. 97.2(5)° in **4**; and the $\text{O}=\text{Re}-\text{O}$ angles are 98.1(2)° in **3** vs. 99.0(8)° in **4**.

Unlike the above dinuclear Re^{VI} complexes, in dinuclear Re^{V} complexes such as $\text{Re}_2\text{O}_3\text{Cl}_6(\text{pyridine})_4$ ⁴² and $\text{Re}_2\text{O}_3\text{Cl}_6(\text{pyrazine})_4$,⁴³ the $\text{O}=\text{Re}-\text{O}-\text{Re}=\text{O}$ unit is linear and the metal–ligand bond distances are slightly longer than those of **3** and **4**, as expected for the lower oxidation state. Specifically, the

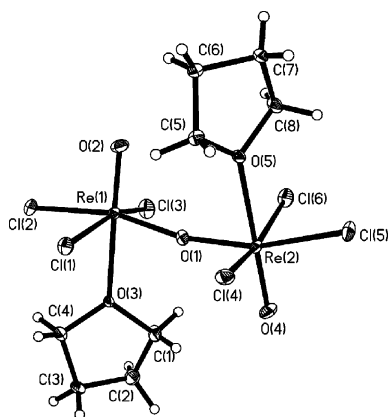


Fig. 3 Molecular structure of $\text{Re}_2\text{O}_3\text{Cl}_6(\text{THF})_2$ (**3**). The 30% probability density surfaces are shown, except for hydrogen atoms, which are depicted as arbitrarily sized spheres.

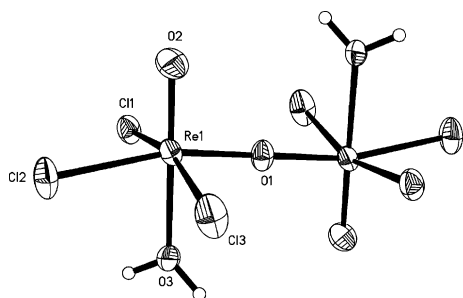


Fig. 4 Molecular structure of $\text{Re}_2\text{O}_3\text{Cl}_6(\text{H}_2\text{O})_2 \cdot 4\text{THF}$ (**4**). The 30% probability density surfaces are shown, except for hydrogen atoms, which are depicted as arbitrarily sized spheres.

$\text{Re}=\text{O}$ distances in the Re^{V} compounds range from 1.69 to 1.76 Å (vs. 1.66 Å for **3** and **4**), the $\text{Re}-\text{O}$ distances range from 1.90 to 1.94 Å (vs. 1.85 Å in **3** and **4**), and the $\text{Re}-\text{Cl}$ distances range from 2.35 to 2.39 Å (vs. 2.31 Å in **3** and **4**).

One interesting structural feature of the aqua complex **4** is that each hydrogen atom in the Re-bound water molecule is involved in a hydrogen bonding interaction with a different nearby non-coordinated THF molecule. The $\text{O} \cdots \text{H}$ distances to the oxygen atoms of these THF molecules are 1.71(5) Å, vs. 0.88(5) Å for the $\text{O}-\text{H}$ bonds within each water molecule.

Experimental

All syntheses were carried out under an argon atmosphere, using a glove box and Schlenk techniques. Solvents were dried over Na/benzophenone and distilled under nitrogen immediately before use. Rhenium powder (325 mesh, Alfa Aesar) and the starting materials SiMe_3Cl , SOCl_2 , and 30% H_2O_2 (Aldrich) were used as received. IR spectra were recorded on a Nicolet Impact 410 spectrometer as Nujol mulls between KBr plates. Melting points were measured on a Thomas Hoover capillary melting point apparatus. X-Ray diffraction data were collected on a Siemens Smart CCD instrument in the X-ray Diffraction Laboratory, and elemental analyses were performed by the Microanalysis

Laboratory; the latter facilities all are operated by the School of Chemical Sciences at the University of Illinois at Urbana-Champaign.

In all of the following preparations, the HReO_4 was prepared from Re powder (either 0.5 g = 0.003 mol or 2.0 g = 0.011 mol) by a literature method and used without further purification.^{17,18}

Caution. These reactions evolve chlorine and HCl gases. Chlorine gas is poisonous and a respiratory irritant, and HCl gas is highly corrosive. The reactions should be carried out in a well-ventilated fume cupboard.

Chlorotrioxobis(tetrahydrofuran)rhenium(vii), $\text{ReO}_3\text{Cl}(\text{THF})_2$ (**1**)

To HReO_4 (0.011 mol) was added chlorotrimethylsilane (20 mL, 0.16 mol) and the mixture was stirred at room temperature. The solution color darkened and a pale yellow gas evolved. After 24 h, the pale red solution was filtered from a small amount of black solid, and the filtrate was transferred into a flask containing tetrahydrofuran (10 mL) at -78°C . The mixture was stirred for 30 min and warmed to room temperature to afford a green precipitate and a red solution. The precipitate was collected by filtration and dried under vacuum. As it dried, its color changed from green to violet. Yield of crude product: 2.96 g (67%). Crystalline material can be obtained by dissolving the crude product in THF (10 mL), diluting with pentane (40 mL), and cooling to -20°C , but with some loss in yield. Mp: $\sim 38^\circ\text{C}$. Anal. Calcd for $\text{C}_8\text{H}_{18}\text{ClO}_5\text{Re}$: C, 23.2; H, 3.9; Cl, 8.6; Re, 45.0. Found: C, 22.2; H, 3.7; Cl, 8.5; Re, 44.2. IR (cm^{-1}): 1341(s), 1317(m), 1244(m), 1169(m), 1072(w), 1039(s), 1011(s), 987(s), 967(s), 952(vs), 840(vs), 674(s).

(Tetrachloro)oxo(tetrahydrofuran)rhenium(vi), $\text{ReOCl}_4(\text{THF})_{1,1}$ (**2**)

To HReO_4 (0.011 mol) was added thionyl chloride (10 mL, 0.14 mol) and the mixture was heated to reflux. The solution color darkened and a pale yellow gas evolved. After 24 h, the dark red solution was filtered and the filtrate was transferred to a flask containing tetrahydrofuran (10 mL) at -78°C . The mixture was stirred for 30 min and warmed to room temperature. The solvent was removed under vacuum to give a red solid. Yield: crude product 3.57 g (80%). Crystalline material can be obtained by dissolving the crude product in THF (10 mL), diluting with pentane (40 mL), and cooling to -20°C , but with some loss in yield. Anal. Calcd for $\text{C}_{4,4}\text{H}_{8,8}\text{Cl}_4\text{O}_{2,1}\text{Re}$: C, 12.5; H, 2.10; Cl, 33.6; Re, 44.1. Found: C, 12.0; H, 2.07; Cl, 31.3; Re, 44.0. Mp: $\sim 128^\circ\text{C}$. IR (cm^{-1}): 1348(s), 1308(m), 1250(m), 1169(m), 1118(m), 1044(w), 1015(s), 993(m), 956(m), 922(m), 846(s).

(μ -Oxo)bis[(trichloro)oxo(tetrahydrofuran)rhenium(vi)], $[\text{ReOCl}_3(\text{THF})_2(\mu\text{-O})]$ (**3**)

To HReO_4 (0.011 mol) was added chlorotrimethylsilane (20 mL, 0.16 mol) and the mixture was heated to reflux. The solution color darkened and a pale yellow gas evolved. After 24 h, the red-black solution was filtered from a small amount of black solid. The filtrate was transferred into a flask containing tetrahydrofuran (10 mL) at -78°C . The mixture was warmed to -30°C and concentrated under reduced pressure. Addition of pentane (40 mL)

resulted in formation of dark purple crystals at $-20\text{ }^{\circ}\text{C}$. IR (cm^{-1}): $\nu(\text{Re}-\text{O}-\text{Re})$ 668 (w).

(μ -Oxo)bis[(trichloro)oxo(aquo)rhenium(vi)] Tetrakis-(tetrahydrofuran) Solvate, $[\text{ReOCl}_3(\text{H}_2\text{O})_2(\mu-\text{O})\cdot 4\text{THF}]$ (4)

To HReO_4 (0.011 mol) was added chlorotrimethylsilane (20 mL, 0.16 mol) and the mixture was heated to reflux. The solution color darkened and a pale yellow gas evolved. After 24 hr, the reaction mixture was distilled and exposed to air, affording a bright red-purple solution. The solution was concentrated at $-30\text{ }^{\circ}\text{C}$, affording a small amount of a black precipitate and a purple solution. Pentane (40 mL) was added, and the solution was filtered and cooled to $-20\text{ }^{\circ}\text{C}$ for 12 h to afford black-red crystals.

Rhenium Trioxide, ReO_3 (5)

To HReO_4 (0.003 mol) was added hexachloropropene (3.8 mL, 0.03 mol) and the mixture was heated to reflux. The solution color darkened and a gas evolved. After 24 h, a dark brown solution and a dark purple solid resulted. The solid was separated by filtration, washed with CH_2Cl_2 ($2 \times 30\text{ mL}$), and dried in vacuum. Yield: 0.56 g (89.0%). Anal. Calcd for ReO_3 : C, 0.0; H, 0.0; Cl, 0.0; Re, 79.5. Found: C, 0.88; H, 0.49; Cl, 3.27; Re, 75.1.

Crystallographic Studies⁴⁴

Suitable crystals were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to $-75\text{ }^{\circ}\text{C}$ in a cold nitrogen gas stream on the diffractometer. Data were collected on a Bruker-Nonius SMART Apex diffractometer using graphite-monochromated Mo-K α radiation. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, scan speed, and Lorentz and polarization effects. No correction for crystal decay was necessary, but the data were corrected for absorption. Systematically absent reflections were deleted, symmetry equivalent reflections were averaged, and statistical outliers were deleted to yield the set of unique data used in the least squares refinement. The structures were solved by direct methods. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms. Methylene hydrogen atoms were placed in "idealized" positions with $\text{C}-\text{H} = 0.99\text{ \AA}$, and the hydrogen atoms on the water molecule in compound 4 were restrained to have equal $\text{O}-\text{H}$ and equal $\text{O}\cdots\text{H}$ distances. Hydrogen atom displacement parameters were set equal to 1.2 times U_{eq} for the attached carbon or oxygen atom. Final refinement parameters are given in Table 1. The largest peaks in the final Fourier difference maps were $1.01\text{ e}\text{\AA}^{-3}$ located 0.01 \AA from Re1 (compound 1), $1.52\text{ e}\text{\AA}^{-3}$ located 0.79 \AA from Re1 (compound 2), $1.73\text{ e}\text{\AA}^{-3}$ located 0.93 \AA from Re2 (compound 3), and $1.23\text{ e}\text{\AA}^{-3}$ located 0.83 \AA from Re1 (compound 4).

CCDC reference numbers 626967–626970.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616495a

Acknowledgements

We thank the National Science Foundation for support of this research under grant numbers DMR03-54060 and DMR04-

20768, and Scott R. Wilson and Teresa Prussak-Wieckowska for collecting the X-ray crystallographic data.

References

- 1 D. M. Hoffman, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, New York, 1995, vol. 6, ch. 10.
- 2 U. Abram, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Pergamon Press, New York, 2005, vol. 5, ch. 5.3.
- 3 L. L. Morris, A. J. Downs, J. C. Green, T. M. Greene, S. J. Teat and S. Parsons, *J. Chem. Soc., Dalton Trans.*, 2002, 3142–3152.
- 4 K. Mertis, D. H. Williamson and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1975, 607–611.
- 5 P. Stravopoulos, P. G. Edwards, T. Behling and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1987, 169–175.
- 6 M. Bochmann, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 1797–1799.
- 7 P. Stavropoulos, P. G. Edwards and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1985, 2167–2175.
- 8 A. F. Masters, K. Mertis, J. F. Gibson and G. Wilkinson, *Nouv. J. Chim.*, 1977, 1, 389–395.
- 9 P. Edwards, K. Mertis, G. Wilkinson, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 334–344.
- 10 M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1978, 1334–1337.
- 11 G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, 1955, 77, 3421–3422.
- 12 D. M. Heinekey and G. L. Gould, *Organometallics*, 1991, 10, 2977–2979.
- 13 V. C. Gibson, C. E. Graimann, P. M. Hare and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1985, 2025–2035.
- 14 J. H. Canterford and R. Colton, *Halides of the Second and Third Row Transition Metals*, Wiley, New York, 1968.
- 15 R. Lincoln and G. Wilkinson, *Inorg. Synth.*, 1980, 20, 41–43.
- 16 P. G. Edwards, G. Wilkinson, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 2467–2475.
- 17 N. P. Johnson, C. J. L. Lock and G. Wilkinson, *Inorg. Synth.*, 1967, 9, 145–148.
- 18 G. W. Watt and R. J. Thompson, *Inorg. Synth.*, 1963, 7, 189–192.
- 19 Although many Lewis base adducts of ReO_3Cl are light-colored, others have darker colors; for example $\text{ReO}_3\text{Cl}(\text{SO}_2\text{Cl}_2)$ is red.²⁰ If the dark color of our sample of $\text{ReO}_3\text{Cl}(\text{THF})_2$ is not intrinsic but due instead to the presence of $\text{ReOCl}_4(\text{THF})$ or ReO_3 , the amounts of these contaminants must be small in view of the excellent microanalytical data.
- 20 K. W. Bagnall, D. Brown and R. Colton, *J. Chem. Soc.*, 1964, 3017–3020.
- 21 C. J. Wolf, A. F. Clifford and W. H. Johnston, *J. Am. Chem. Soc.*, 1957, 79, 4257–4258.
- 22 H. A. Lehmann and C. Ringel, *Z. Anorg. Allg. Chem.*, 1969, 366, 73–81.
- 23 W. A. Herrmann, F. E. Kühn, C. C. Romao, M. Kleine and J. Mink, *Chem. Ber.*, 1994, 127, 47–54.
- 24 A. Davison, A. G. Jones and M. J. Abrams, *Inorg. Chem.*, 1981, 20, 4300–4302.
- 25 W. A. Herrmann, W. R. Thiel and E. Herdtweck, *Chem. Ber.*, 1990, 123, 271–276.
- 26 F. E. Kühn, J. J. Haider, E. Herdtweck, W. A. Herrmann, A. D. Lopes, M. Pillinger and C. C. Romao, *Inorg. Chim. Acta*, 1998, 279, 44–50.
- 27 B. E. Bridgland, G. W. A. Fowles and R. A. Walton, *J. Inorg. Nucl. Chem.*, 1965, 27, 383–389.
- 28 E. A. Allen, N. P. Johnson, D. T. Rosevear and W. Wilkinson, *J. Chem. Soc. A*, 1969, 788–791.
- 29 C. G. Barraclough and D. J. Kew, *Aust. J. Chem.*, 1972, 25, 27–35.
- 30 D. A. Edwards, *J. Chem. Soc. A*, 1966, 91–92.
- 31 C. Calvo, P. W. Fraiss and C. J. L. Lock, *Can. J. Chem.*, 1972, 50, 3607–3618.
- 32 B. J. Brisdon and D. A. Edwards, *Inorg. Chem.*, 1968, 7, 1898–1903.
- 33 D. A. Edwards and R. T. Ward, *J. Chem. Soc., Dalton Trans.*, 1972, 89–91.

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- 34 P. W. Fraiss and C. J. L. Lock, *Can. J. Chem.*, 1972, **50**, 1811–1818.
- 35 F. A. Cotton, W. R. Robinson and R. A. Walton, *Inorg. Chem.*, 1967, **6**, 223–228.
- 36 J. A. Hermann and J. F. Suttle, *Inorg. Synth.*, 1957, **5**, 143–145.
- 37 W. W. Porterfield and S. Y. Tyree, Jr., *Inorg. Synth.*, 1967, **9**, 133–136.
- 38 K. Meisel, *Z. Anorg. Allg. Chem.*, 1932, **207**, 121–128.
- 39 H. Nechamkin and C. F. Hiskey, *Inorg. Synth.*, 1950, **3**, 186–188.
- 40 P. Ferreira, W. Xue, E. Bencze, E. Herdtweck and F. E. Kühn, *Inorg. Chem.*, 2001, **40**, 5834–5841.
- 41 A. J. Edwards, *J. Chem. Soc., Dalton Trans.*, 1972, 582–584.
- 42 C. J. L. Lock and G. Turner, *Can. J. Chem.*, 1978, **56**, 179–188.
- 43 E. Iengo, E. Zangrando, S. Mestroni, G. Fronzoni, M. Stener and E. Alessio, *J. Chem. Soc., Dalton Trans.*, 2001, 1338–1346.
- 44 For details of crystallographic methods and programs used, see J. L. Brumaghim, J. G. Priepot and G. S. Girolami, G. S., *Organometallics*, 1999, **18**, 2139–2144.