

Preparation and reactions of rhenium(VII) trioxo hydrogendiolato complexes and rhenium(VI) oxo bis(diolato) complexes

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Received 1st May 1998, Accepted 24th July 1998

The compound Re_2O_7 , $\text{Re}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ or $[\text{ReO}_3(\text{OSiMe}_3)]$ reacted with H_2diol to form complexes having the general formula $[\text{ReO}_3(\text{Hdiol})]$ where $\text{H}_2\text{diol} = 2,3\text{-dimethylbutane-2,3-diol (H}_2\text{pin)}$ or $1,1'\text{-bicyclohexane-1,1'-diol (H}_2\text{bicy)}$. In the case of H_2pin the complex $[\text{ReO}_3(\text{Hpin})] \cdot \text{H}_2\text{pin}$ is formed initially in the reaction of rhenium(VII) oxides with an excess of pinacol. The hydrogen bonded free pinacol molecule can be removed by sublimation. The monomethyl derivative of pinacol, HMepin , reacts in a similar way to form the complex $[\text{ReO}_3(\text{Mepin})]$. In the rhenium(VII) compounds the Re atom has a distorted trigonal bipyramidal co-ordination geometry. Pale yellow solutions of $[\text{ReO}_3(\text{Hdiol})]$ in CH_2Cl_2 slowly become orange and red crystals having the formula $[\text{ReO}(\text{diol})_2]$ may be isolated. The reaction of rhenium(VII) oxides with H_2diol and PPh_3 in the presence of drying agents in CH_2Cl_2 produced the same compounds in high yield. The crystal structures of the rhenium(VI) complexes reveal that the rhenium(VI) cations have square pyramidal co-ordination geometries. The rhenium(VI) oxo bis(diolato) complexes are thermally stable and do not readily undergo oxidation in dry air.

Introduction

High-valent rhenium oxides¹ have been extensively investigated, particularly because some representatives of this class of compounds exhibit catalytic properties; organorhenium oxides, e.g. methyltrioxorhenium, catalyse a wide range of transformations of organic compounds.² Simple oxides such as Re_2O_7 and ReO_3 have been found to catalyse alkene epoxidations.³ Trioxo-(trifluoroacetato)rhenium(VII)⁴ performs a tandem oxidative cyclization reaction of hydroxypolyenes.⁵ The further development of high valent rhenium oxides for catalytic purposes and stoichiometric reactions is of current interest.

Since earlier reports indicate that rhenium(VII) alkoxide trioxides,⁴ e.g. $\text{ReO}_3(\text{OR})$, $\text{R} = \text{Me}$ or CMe_3 , are accessible, we have chosen to extend our study to diolato complexes of Re^{VII} prepared from the commonly available rhenium(VII) precursors HReO_4 , Re_2O_7 and the hydrocarbon soluble $\text{ReO}_3(\text{OSiMe}_3)$ first used for this purpose by Edwards and Wilkinson.⁴ Following submission of this work we became aware of the work of Herrmann *et al.* in this field. They have also used $\text{ReO}_3\text{-}(\text{OSiMe}_3)$ and silylated derivatives of pinacol (H_2pin) ligands as starting compounds and prepared two pinacolato complexes with the formulae $[\text{ReO}_3(\text{Xpin})]$ ($\text{X} = \text{H}$ or Me).⁶

Reduction of rhenium(VII) oxides by phosphines normally leads to rhenium(V) compounds, e.g. reduction of Re_2O_7 with PMe_3 produces the *trans*-dioxo complex $[\text{ReO}_2(\text{PMe}_3)_4] \cdot [\text{ReO}_4]^-$ and with PEt_3 in the presence of pyridine yields the related compound $[\text{ReO}_2(\text{py})_4][\text{ReO}_4]^-$.⁸ The spontaneous reduction of rhenium(VII) in the formation of red $[\text{ReO}(\text{pin})_2]$ prompted us to study reductions of $[\text{ReO}_3(\text{Hdiol})]$ with tertiary phosphines.

There are few reported examples of the preparation and characterization of rhenium(VI) alkoxo complexes. The first rhenium(VI) alkoxide oxide complexes were reported by Wilkinson and co-workers⁹ and include the compounds $[\text{Re}_2\text{O}_3(\text{OMe})_6]$, $[\text{ReO}(\text{OPr}^i)_3]^-$ and $[\text{ReO}(\text{OBu}^t)_4]$; in each case these were synthesized from ReOCl_4 . Hexamethoxorhenium(VI) $\text{Re}(\text{OMe})_6$, prepared from ReF_6 , has been reported by Jacob.¹⁰ Mononuclear tris(3,5-di-*tert*-butylcatecholato)rhenium(VI) seems to be the first tris(diolato) complex of rhenium(VI).¹¹ The

dinuclear methyl diolato complexes $[\text{Re}_2\text{O}_3\text{Me}_2(\text{eg})_2(\text{py})_2]$ and $[\text{Re}_2\text{O}_3\text{Me}_2(\text{pin})_2]$ ($\text{H}_2\text{eg} = 1,2\text{-dihydroxyethane}$) have been reported by Herrmann *et al.*¹²

In this paper we discuss the syntheses, reactions and crystal structures of two mononuclear rhenium(VII) oxo diolato complexes with the formulae $[\text{ReO}_3(\text{Hpin})] \cdot \text{H}_2\text{pin}$ **1a** and $[\text{ReO}_3\text{-}(\text{Hbicy})]$ **2** ($\text{H}_2\text{bicy} = 1,1'\text{-bicyclohexane-1,1'-diol}$). We also report reactions of rhenium(VII) oxides with diols in the presence of PPh_3 including the syntheses, reactions and crystal structures of two mononuclear rhenium(VI) oxo diolato complexes with the formulae $[\text{ReO}(\text{diol})_2]$ ($\text{diol} = \text{pin}$ **3** or bicy **4**).

Discussion

Reactions of diols with rhenium(VII) oxides

One of the general synthetic methods for the preparation of metal alkoxides is by the use of a metal oxide as a metal source. It was found that both Re_2O_7 and concentrated aqueous HReO_4 ($\text{Re}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) dissolve in CH_2Cl_2 in the presence of an excess of pinacol. When the molar ratio $\text{H}_2\text{pin} : \text{Re}$ was less than 2 : 1, a deep green insoluble and presumably polymeric material was formed, probably due to reduction of Re^{VII} . When the molar ratio was 2 : 1 or more, evaporation of the solvent produced a colourless pinacolato complex **1a** for which analytical data indicate the formula $[\text{ReO}_3(\text{Hpin})] \cdot \text{H}_2\text{pin}$. When the reactions were performed in co-ordinating solvents such as thf, pinacolato complexes could not be isolated. A complex of analytical composition $[\text{ReO}_3(\text{Hpin})]$ **1b** was formed when pinacol was removed from **1a** by sublimation *in vacuo*. The behaviour of ditertiary alcohols is significantly different to that of disecundary and diprimary alcohols in this context since reactions of Re_2O_7 with secondary (butane-2,3-diol) and primary (ethane-1,2-diol) diols yield dark violet solutions in which Re^{VII} is reduced and diol is oxidized.

In the solid state compound **1a** decomposes slowly under air to afford an intractable dark green material. Compound **1a** is insoluble in hexane and petroleum ethers, soluble in toluene, Et_2O , chlorinated solvents and thf. Solutions of **1a** in dry non-co-ordinating solvents (e.g. halogenocarbons) are stable under

air for several days at room temperature, and for weeks at $-18\text{ }^{\circ}\text{C}$. Pale yellow CH_2Cl_2 and ethanol solutions become colourless upon addition of water due to hydrolysis. Under an inert atmosphere at room temperature, CH_2Cl_2 solutions of **1a** slowly become orange due to the formation of $[\text{ReO}(\text{pin})_2]$. Above $30\text{ }^{\circ}\text{C}$ this reaction is more rapid being complete in several hours.

The monomethylated-oxygen derivative of pinacol (HMepin) could be prepared by a reaction of the mono-sodium salt of H_2pin and MeI in thf or by an acid catalysed ring opening reaction of tetramethyloxirane by methanol. The derivative HMepin reacts with the rhenium(vii) precursors Re_2O_7 or concentrated HReO_4 in a manner similar to that with H_2pin and produces the compound $[\text{ReO}_3(\text{Mepin})]$.⁶ An X-ray diffraction study of the latter at room temperature gave the following unit cell parameters: $a = 8.350(3)$, $b = 10.996(4)$, $c = 23.260(4)$ Å. These values are similar to those reported by Herrmann *et al.*,⁶ where the structure determination was performed at $-80\text{ }^{\circ}\text{C}$.

The compound Re_2O_7 or concentrated HReO_4 reacts with an excess of 1,1'-bicyclohexane-1,1'-diol in CH_2Cl_2 to form $[\text{ReO}_3(\text{Hbicy})]$ **2**. The product prepared this way was difficult to separate from free diol and started to decompose during a few hours to give a pink-violet material, which subsequently turned into a brown-green insoluble solid. Similar changes were observed for solutions of **2** prepared from Re_2O_7 . When $[\text{ReO}_3(\text{OSiMe}_3)]$ reacted with a stoichiometric amount of H_2bicy in light petroleum, an analytically pure white product precipitated which was indefinitely stable in the solid state under nitrogen at room temperature. Solutions of **2** prepared this way slowly changed from colourless to pink and finally violet during 1–2 d at room temperature. When the solutions were stored at $-18\text{ }^{\circ}\text{C}$ only a slight pink coloration was observed during several weeks. Crystals suitable for X-ray crystallography were grown from dilute Et_2O –light petroleum solutions. Compound **2** is insoluble in hexane and petroleum ethers, slightly soluble in toluene and Et_2O and soluble in chlorinated solvents and thf .

Compounds **1a**, **1b** and **2** react with alkylating agents LiR ($\text{R} = \text{Me}$ or CH_2SiMe_3), MgMeI and AlMe_3 to produce presumably mixtures of lower oxidation state organorhenium compounds. When these reaction solutions were filtered and evaporated to dryness the residues did not appear to contain alkoxide ligands (by IR and NMR). Reactions of complexes **1a**, **1b** and **2** with ZnR_2 ($\text{R} = \text{Me}$ or Et) produce colourless or light yellow solutions indicating the presence of rhenium(vii) products. No pure products were isolated although ^1H NMR data of the mixtures of ZnMe_2 and rhenium(vii) diolates (ZnMe_2 : $\text{Re} = 1:2$) indicated the formation of ReMeO_3 .

Formation and reactions of $[\text{ReO}(\text{diol})_2]$ compounds

The bis(diolato)rhenium(vi) complex $[\text{ReO}(\text{pin})_2]$ **3** was first isolated from a CH_2Cl_2 solution of rhenium(vii) oxide and pinacol. Alternatively, **3** was obtained when $[\text{ReO}_3(\text{Hpin})]\cdot\text{H}_2\text{pin}$ was treated with PPh_3 in a molar ratio of 2 to 1 in the presence of a drying agent (*e.g.* molecular sieves). At the beginning of the reaction the pale yellow solution of $[\text{ReO}_3(\text{Hpin})]\cdot\text{H}_2\text{pin}$ changed to dark blue, before finally changing to bright orange-red and **3** was formed in high yield (84%). Compound **3** may be recrystallized from light petroleum or hexane solutions as large red needles. It was also obtained when solutions of Re_2O_7 or concentrated HReO_4 in CH_2Cl_2 were treated with H_2pin and PPh_3 in the molar ratio $\text{Re}:\text{diol}:\text{PPh}_3 = 1:2:0.5$ in the presence of molecular sieves which forces the condensation to completion. The reaction between ReOCl_4 and pinacol in the presence of a tertiary amine as a base also produces the same product, but the yield is significantly lower (*ca.* 30%).

In dry air compound **3** decomposes above $70\text{ }^{\circ}\text{C}$ but it appears indefinitely stable at room temperature. It decomposes

slowly during 24 h in moist air. Under an inert atmosphere, solutions of **3** are stable in hydrocarbons (*e.g.* toluene) to $110\text{ }^{\circ}\text{C}$ without noticeable decomposition. In acetone or EtOH **3** becomes colourless upon addition of water, however solid **3** does not dissolve in water and is stable to water in the solid state for several hours. Thus **3** is significantly more stable than other known rhenium(vi) alkoxide oxide complexes, whereas for example $[\text{ReO}(\text{O}^t\text{Bu})_4]$ decomposes above $0\text{ }^{\circ}\text{C}$ under an inert atmosphere resulting in the elimination of unsaturated hydrocarbons and the formation of an insoluble residue.⁹

When solutions of compound **3** in Et_2O were treated with an excess of pyridine a deep green colour developed. When these solutions were evaporated slowly or held at $-18\text{ }^{\circ}\text{C}$ a green solid could be isolated, however it rapidly returned to red *in vacuo* or during *ca.* 30 min under ambient conditions. This may be explained by the reversible formation of a six-co-ordinate pyridine adduct of **3**.

Compound **3** reacted with alkylating agents such as MgMeI , MgMe_2 , LiMe and AlMe_3 to form thermally unstable mixtures. Removal of the volatile materials from these reaction mixtures *in vacuo* led to the isolation of $\text{ReMe}_4\text{O}^{13}$ (cold trap, $-196\text{ }^{\circ}\text{C}$). When **3** was treated with an excess of methylating agent (especially with AlMe_3) at $-80\text{ }^{\circ}\text{C}$ deep green solutions of ReMe_6 were observed (and which is known to be thermally unstable¹⁴). Following warming and evaporating to dryness, the IR and NMR spectra showed the absence of pinacolato ligands clearly indicating their facile substitution by these alkylating agents under these conditions. Reactions of **3** with ZnR_2 ($\text{R} = \text{Me}$ or CH_2SiMe_3) also resulted in decomposition, as did the reaction with AlCl_3 in toluene unlike similar reactions of the analogous $[\text{OsO}(\text{pin})_2]$ where the compounds $[\text{OsOX}_2(\text{pin})]^{15}$ ($\text{X} = \text{Cl}$ or Br) were isolated.

Attempts to prepare a complex of formula $[\text{Re}_2\text{O}_4(\text{pin})_2]$, in a similar manner to its osmium analogue $[\text{Os}_2\text{O}_4(\text{pin})_2]$, were unsuccessful. The reaction of $[\text{ReO}_3(\text{Hpin})]$ with 0.5 mol equivalent of PPh_3 in the presence of molecular sieves yielded a dark brown-violet insoluble and uncharacterized material along with **3** in about 30–40% yield.

The reaction of Re_2O_7 or concentrated HReO_4 with H_2bicy and PPh_3 in molar ratio $\text{Re}:\text{diol}:\text{PPh}_3 = 1:2:0.5$ in CH_2Cl_2 in the presence of molecular sieves produces a red solution of $[\text{ReO}(\text{bicy})_2]$ **4** and OPPh_3 . Evaporation of the solvent and extraction with light petroleum, followed by purification by column chromatography on Florisil with toluene as an eluent, yielded pure **4**, which could then be crystallized from light petroleum. The chemical properties of **4** are similar to those of **3**.

Reactions of Re_2O_7 with disecundary (butane-2,3-diol) and diprimary (ethane-1,2-diol) diols or their silylated derivatives in the presence of PPh_3 yielded orange-red solutions, which became dark brown-violet when the solvent was evaporated to small volume. Dark brown oils were obtained when the solvent (CH_2Cl_2 or thf) was completely removed *in vacuo*; pure compounds could not be isolated from these mixtures. On addition of pyridine these solutions changed to deep blue-violet; again pure products were not isolable.

Spectroscopic characterization

The IR spectra of the rhenium(vii) compounds **1a** and **2** show bands for co-ordinated diolate ligands. Bands at 941 and 910 cm^{-1} for **1a** and 982, 949, 934 and 915 cm^{-1} for **2** are in the region expected for $\nu(\text{Re}=\text{O})$ bands (*cf.* $\nu(\text{Re}=\text{O})$ 998, 959 and 946 cm^{-1} for ReMeO_3 ¹⁶). Differences between **1a** and **1b** are observed in the OH stretching region of their solid state spectra where ν_{OH} for $[\text{ReO}_3(\text{Hpin})]$ **1b** (3200 cm^{-1}) appears at a significantly lower frequency than for **1a** (at 3473 and 3410 cm^{-1}). A crystallographic study (see below) confirms that the hydrogen-bonded framework in **1a** is more complex than that in **1b**. The lower frequency ν_{OH} vibration of **1a** is partially

obscured by $\nu(\text{C-H})$. Compound **2** has a broad OH stretching band (3215 cm^{-1}) close to that observed for **1b**.

The IR spectra of the rhenium(vi) compounds **3** and **4** show bands for co-ordinated diolates and the absence of $\nu(\text{O-H})$ bands. The $\text{Re}=\text{O}$ stretches appear at 980 and 984 cm^{-1} for **3** and **4**, respectively and are located at a similar position to that observed for the osmium analogue $[\text{OsO}(\text{pin})_2]$ ¹⁷ [$\nu(\text{Os}=\text{O})$ 978 cm^{-1}].

The ^1H NMR spectrum (CDCl_3) of compound **1a** shows three signals attributable to methyl hydrogens at δ 1.24 (assigned to non-co-ordinated pinacol) and at δ 1.31 and 1.40 (co-ordinated pinacol) in an intensity ratio of 2:1:1 respectively. The OH hydrogens of both **1a** and **1b** give two broad signals at δ 2.1 and ≈ 6 and 1.41 and 5.3 respectively. These values may be compared to those observed in the ^1H NMR spectrum of free pinacol [δ 1.26 (CCH_3) and 2.10 (OH)].¹⁸ The ^1H NMR spectrum of **2** exhibits a pattern of overlapping signals for the CH_2 hydrogens between δ 1.06 and 2.08 and a signal for the OH hydrogen at $\delta \approx 5$.

In the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of compound **1a** there are three clearly distinguishable signals in the methyl carbon region at δ 22.8 and 23.5 (assigned to co-ordinated pinacol, Hpin) and at 24.5 (non-co-ordinated pinacol, H_2pin). In the spectrum of **2** resonances observed at δ 20.4 and 20.7 are assigned to CH_2 carbons at positions 3 and 5 in the cyclohexane rings by comparison to the free diol. Similarly, carbons at position 4 resonate at δ 24.0 and 24.2 and those assigned to carbons 2 and 6 appear at δ 29.0 and 30.6. The multiplicity of these resonances is due to the presence of inequivalent cyclohexyl groups arising in the monodeprotonated diolate ligand as is expected. The quaternary carbons of **1a** assigned to the COH and CORe carbons give three sharp resonances at δ 75.2 (COH, H_2pin), 77.4 (COH, Hpin) and 93.1 (CORe, Hpin). In the spectrum of **2**, resonances assigned to COH and CORe were located at δ 79.3 and 96.4 respectively.

The mass spectra of compounds **3** and **4** show the molecular ions $\{\text{M}^+, m/z = 433, 435 \text{ and } 593, 595 \text{ respectively; calculated for } [\text{ReO}(\text{pin})_2] m/z = 434.51 \text{ and for } [\text{ReO}(\text{bicy})_2] m/z = 594.78\}$ with the expected rhenium isotope pattern. Solid state magnetic susceptibilities [$\mu_{\text{eff}} = 1.72$ (**3**) and $1.69\ \mu_{\text{B}}$ (**4**)] indicate that the compounds have paramagnetic d^1 -metal centres consistent with Re^{VI} .

Structural studies

Rhenium(vii) compounds. The structures of compounds **1a** and **2** (Figs. 1 and 2) reveal that the rhenium(vii) centres are bonded to one bidentate hydrogendiolate ligand and to three terminal oxo ligands resulting in a distorted trigonal bipyramidal arrangement around Re^{VII} with O(3) and O(4) as axial atoms. As a result, each diolate ligand co-ordinates both axial and equatorial sites, an arrangement which is consistent with the solution NMR data and which presumably arises from the restriction of the chelate bite angle. The core rhenium(vii) units of compounds **1a** and **2** have the same basic structure with similar structural parameters (Table 1). Similar geometries are also found in $[\text{ReO}_3(\text{Rpin})]$ ($\text{R} = \text{H}$ or Me),⁶ $[\text{ReMeO}_2(\text{pin})]$ ¹² and trioxo(3-piperidinopropyl)rhenium(vii).²⁰

In compounds **1a**, **2** and $[\text{ReO}_3(\text{Rpin})]$ ($\text{R} = \text{H}$ or Me)⁶ all $\text{Re}^{\text{VII}}=\text{O}$ distances are very similar (*ca.* $1.70\ \text{\AA}$), although the axial oxide ligand *trans* to the $\text{Re}-\text{O}$ (alcohol or ether) bond tends to form the longest $\text{Re}=\text{O}$ bond. In structurally characterized compounds containing $\text{Re}=\text{O}$ bonds the average $\text{Re}=\text{O}$ distance is $1.700(64)\ \text{\AA}$.²¹ The $\text{Re}-\text{O}$ (alkoxo) distances in **1a**, **1b** and **2** are also similar [$1.866(6)$, $1.865(5)$ and $1.850(3)\ \text{\AA}$ respectively] (this value and all mentioned below for **1b** are values from our X-ray work) at room temperature. The $\text{Re}-\text{O}$ (alcohol) distances however vary between compounds **1a**, **1b** and **2** [$2.277(8)$, $2.319(5)$ and $2.384(3)\ \text{\AA}$ respectively].

Comparison of the trigonal bipyramidal geometries in com-

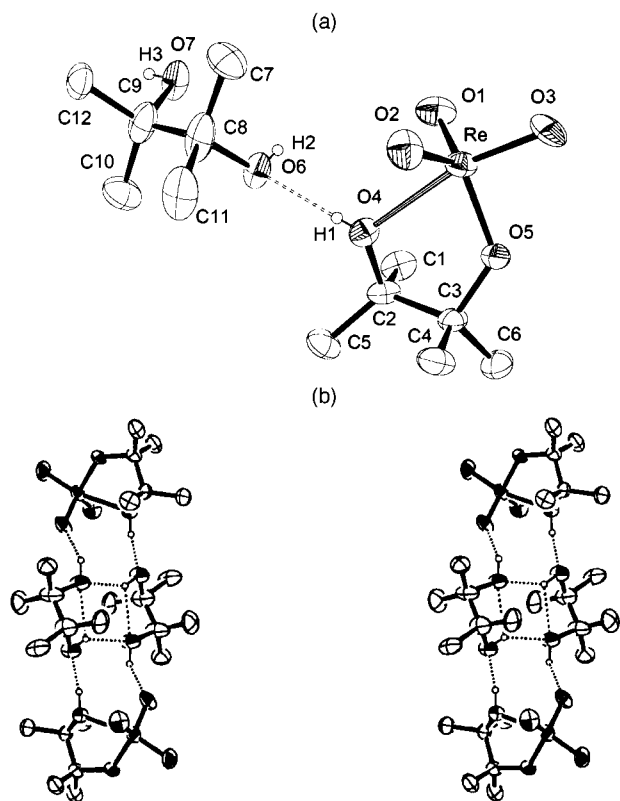


Fig. 1 (a) An ORTEP¹⁹ view of compound **1a** with 30% thermal ellipsoids showing the atom labelling system of the heavy atoms and HO hydrogens. (b) A stereoview of **1a** showing the hydrogen bonding scheme.

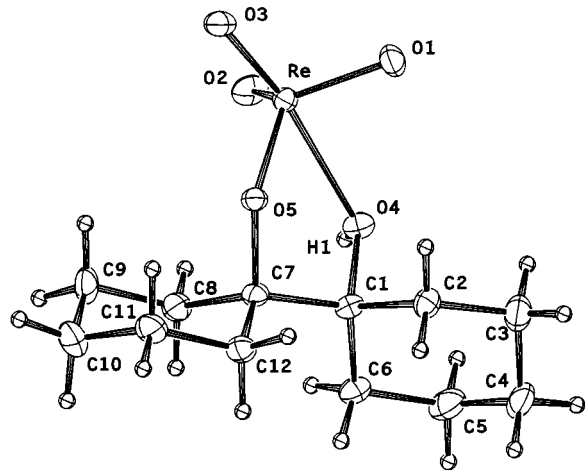


Fig. 2 An ORTEP view of compound **2** with 30% thermal ellipsoids showing the atom labelling system (CH hydrogens are not labelled for clarity).

pounds **1a**, **1b** and **2** to the similar structure in trioxo(3-piperidinopropyl)rhenium(vii),²⁰ $[\text{ReO}_3(\text{pipro})]$, with the $\text{Re}^{\text{VII}}\text{O}_3\text{CN}$ chromophore reveals significant differences. For example, the chelate angles around the five-coordinated Re^{VII} are $72.5(3)$ (for **1a**), $71.8(2)$ (for **1b**), $72.0(2)$ (for **2**) and $74.6(2)^\circ$ for $[\text{ReO}_3(\text{pipro})]$. In **1a**, **1b** and **2** the largest angles around Re^{VII} are $166.8(4)$, $168.3(2)$ and $168.6(3)^\circ$, respectively. The relevant angle for $[\text{ReO}_3(\text{pipro})]$ is $162.4(2)^\circ$.

In compound **1a** the co-ordinated (Hpin) and unco-ordinated pinacol (H_2pin) adopt a *gauche* conformation with $\text{O}(4)-\text{C}(2)-\text{C}(3)-\text{O}(5)$ and $\text{O}(6)-\text{C}(8)-\text{C}(9)-\text{O}(7)$ torsion angles of $44(1)$ and $58.6(13)^\circ$, respectively. The $\text{O}(4)-\text{C}(2)-\text{C}(3)-\text{O}(5)$ torsion angle in **1b** is $45.9(7)^\circ$. In the complexes $[\text{M}_2\text{O}_3(\text{pin})_2(\text{Hpin})_2]$, where $\text{M} = \text{Mo}^{\text{VI}}$ ²² the torsion angle $\text{O}-\text{C}-\text{C}-\text{O}$ in Hpin is $37(2)^\circ$ and for $\text{M} = \text{W}^{\text{VI}}$ ²³ the related angle is $34(1)^\circ$. In these

Table 1 Selected bond distances (Å) and angles (°) for compounds **1a** and **2**

	1a	2
Re–O(1)	1.692(8)	1.703(4)
Re–O(2)	1.694(7)	1.697(4)
Re–O(3)	1.713(7)	1.715(4)
Re–O(4)	2.277(8)	2.384(4)
Re–O(5)	1.866(6)	1.850(3)
O(1)–Re–O(2)	111.0(4)	111.5(2)
O(1)–Re–O(3)	103.7(4)	104.8(2)
O(1)–Re–O(4)	85.2(3)	83.3(2)
O(1)–Re–O(5)	117.8(3)	116.4(2)
O(2)–Re–O(3)	104.3(4)	104.4(2)
O(2)–Re–O(4)	81.2(3)	79.8(2)
O(2)–Re–O(5)	121.2(4)	119.8(2)
O(3)–Re–O(4)	166.6(3)	168.3(2)
O(3)–Re–O(5)	94.3(3)	96.7(2)
O(4)–Re–O(5)	72.5(3)	72.0(2)
Re–O(4)–C	114.5(6)	112.3(3)
Re–O(5)–C	127.1(6)	127.5(3)

complexes there are two strong intramolecular hydrogen bonds. The formation of intra- or inter-molecular hydrogen bonds appears then to have a significant influence upon the Hpin ligand conformation in these compounds in the solid state.

The co-ordination sphere of Re^{VII} in compound **1a** is not significantly affected by the proton of the co-ordinated OH group being hydrogen bonded to an unco-ordinated pinacol in the lattice. The H atoms of the OH groups were located from the Fourier-difference and their coordinates refined. The O(4)⋯O(6) distance is 2.585(10) Å indicating a strong intermolecular O–H⋯O bond. A similar strong hydrogen bond has been found in [W₂O₃(pin)₂(Hpin)₂] where the O⋯O distance is 2.63(3) Å. The HO hydrogens of unco-ordinated pinacol appear to bond to O(7^I) and O(1^I) (I 2 – x, –y, 1 – z). This is indicated by the O(6)⋯O(7^I) and O(7)⋯O(1^I) distances of 2.79(1) and 2.90(1) Å, respectively. Pinacol molecules form dimeric units with possible intramolecular hydrogen bonds. The hydrogen bonds are depicted in Fig. 1(b). Weak hydrogen bonds are also indicated by the bands at 3473 and 3410 cm⁻¹ in the IR spectrum of **1a**. The IR frequency of the O–H stretch related to the O(4)–H(1)⋯O(6) bond was not identified and is presumed to be coincident with the C–H stretches, as is the case in [W₂O₃(pin)₂(Hpin)₂]. By comparison, in **1b** the O(4)⋯O(1) distance is 2.716(7) Å and the observed ν_{OH} is at 3200 cm⁻¹.

The O(4)–C(1)–C(7)–O(5) torsion angle is 44.4(5)° in compound **2** in which the hydrogen bonded framework is defined by O(4)–H(1)⋯O(3^{II}) (II 1 – x, ½ – y, 1½ – z) with O(4)–H(1), H(1)⋯O(3^{II}) and O(4)⋯O(3^{II}) distances of 0.79(5), 2.05(5) and 2.843(5) Å, respectively. The O(4)–H(1)⋯O(3^{II}) angle is 177(6) Å. In this case the hydrogen bond gives rise to ν_{OH} in the IR spectrum at 3215 cm⁻¹.

Rhenium(VI) compounds. The molecular structures of the bis(diolato-*O,O'*)oxorhenium(VI) compounds **3** and **4** are in Figs. 3(b) and 4; relevant bond distances and angles are collected in Table 2. The bond parameters are of poor accuracy for **3** due to a positional disorder discussed below. Compound **3** has a tetragonal unit cell with *a* = *b* = 10.315(2) and *c* = 7.270(1) Å and is isostructural with [OsO(pin)₂] [*a* = *b* = 10.256(1) and *c* = 7.278(3) Å].²⁴ As a result of disorder, the structure of [OsO(pin)₂] could not be completely solved.²⁴ The structure solution presented here shows clearly that in [ReO(pin)₂] the rhenium(VI) cation is bonded to one oxide ligand and to two deprotonated pinacol ligands forming a distorted square pyramid. The oxide ligand is at the apex of the pyramid.

Problems in the structure solution and refinement of compound **3** arise from a molecular disorder in which the [ReO-

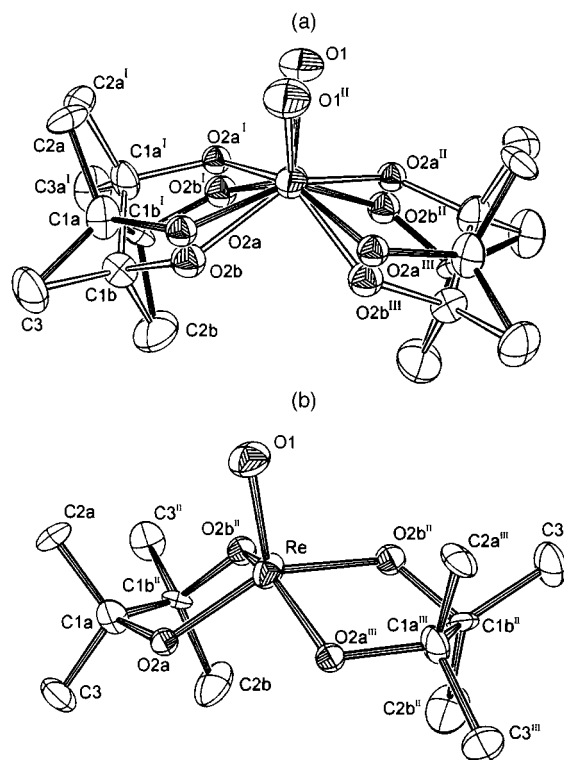


Fig. 3 (a) An ORTEP view of compound **3** in the disordered position with 30% thermal ellipsoids showing the atom labelling scheme. Hydrogen atoms are not included and one half of all atoms and symmetry-related oxygens are labelled. Symmetry operations: I 1 – y, 1 – x, z; II 1 – x, 1 – y, z; III y, x, z. (b) An ORTEP view of **3** with 30% thermal ellipsoids showing the atom labelling system. Hydrogen atoms are not shown.

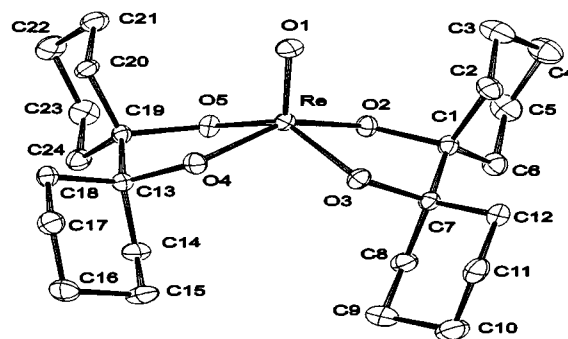


Fig. 4 An ORTEP view of compound **4** with 30% thermal ellipsoids showing the heavy atom labelling system.

(pin)₂] molecule can reside in the crystal having either the orientation **A** or **B**. These orientations are related by rotation of 180° around the average Re=O axis. The overall result of this disorder is shown in Fig. 3(a) in which the molecule having orientation **A** is described by those atoms connected by solid bonds, those atoms connected by unfilled bonds describe orientation **B**. The carbon atoms C2b and C3 are at the same position in both orientations. A view of an individual molecule with C_s symmetry is presented in Fig. 3(b).

In both orientations the opposing diolato chelates adopt both λ and δ conformations simultaneously; the terminal oxygen O(1) also resides in two positions. The overall effect is that the sum of these two superimposed orientations results in two mutually perpendicular mirror planes. The atom labelling in Fig. 3(a) illustrates the situation. The λ conformation of the chelate ring is displayed by atoms O2a, C1a, C1b^I and O2b^I [torsion angle = –42(2)°], and the δ conformation of the chelate ring is defined by the atoms O2b, C1b, C1a^I and O2a^I [torsion angle = 42(2)°]. The atoms of the transoid diolate ligand

Table 2 Selected bond distances (Å) and angles (°) for compounds **3** and **4**

	3	4
Re–O(1)	1.699(10)*	1.690(4)
Re–O(2)	1.845(8)	1.900(3)
Re–O(3)	1.904(9)	1.892(3)
Re–O(4)		1.907(3)
Re–O(5)		1.886(3)
O(1)–Re–O(2)	114.6(8)	107.4(2)
O(1)–Re–O(3)	100.7(10)	111.7(2)
O(1)–Re–O(4)		105.3(2)
O(1)–Re–O(5)		112.5(2)
O(2)–Re–O(3)	79.4(5)	80.9(1)
O(2)–Re–O(4)	143.1(10)	147.1(1)
O(2)–Re–O(5)	94.6(11)	84.7(1)
O(3)–Re–O(4)	84.0(13)	89.2(1)
O(3)–Re–O(5)		135.8(1)
O(4)–Re–O(5)		80.8(1)

* Nearest relevant bond parameters listed. Atoms O2, O3, O4 and O5 in compound **4** are related to O2a, O2bⁱ, O2bⁱⁱ and O2aⁱⁱⁱ in **3**.

connected by the solid (filled in) bonds [Fig. 3(a)] also define a δ conformation. One of two [ReO(pin)₂] molecules with a $\lambda\delta$ conformation pair is represented in Fig. 3(b).

The structure of complex **4** is also composed of distorted square pyramidal rhenium(vi) units similar to those in **3**. The structure solution of **4** supports the result obtained for **3**. However the structure of the rhenium(vi) centre in **4** is more distorted towards trigonal bipyramidal than that in **3** as the largest O–Re–O angles in **4** are 147.1(1) and 135.8(1)° and in **3** there are two O–Re–O angles with the value of 142.7(10)°. In **4** the diolate ligands in the asymmetric unit adopt $\lambda\delta$ conformations with torsion angles of –41.7(4) and 37.0(5)°. A pseudo-mirror passes through Re, O1 and the midpoints of the O2–O5 and O3–O4 vectors. The co-ordination sphere of the central metal atom in **3** and **4** is also comparable to that of the related osmium(vi) oxo diolates [OsO(eg)₂]²⁵ and [Os₂O₄(pin)₂]¹⁷. However in [OsO(eg)₂]²⁵ the molecule has C₂ symmetry indicating that the ligand conformations around Os^{VI} are either $\lambda\lambda$ or $\delta\delta$.

Conclusion

This work has shown that tertiary 1,2-diols readily form five-coordinated, distorted trigonal bipyramidal trioxorhenium(vii) complexes in their reactions with rhenium(vii) oxides and in which the co-ordinated diol is singly deprotonated. These alkoxide oxide complexes readily hydrogen bond to an additional diol molecule and they are relatively stable in air. The synthetic method by which these compounds may be prepared is simple and efficient; yields are high even from rhenium-metal. Diols may be used without protection of the hydroxyl group and water removal is unnecessary when the preparation is performed in CH₂Cl₂.

The reduction of rhenium(vii) trioxo hydrogendiolato complexes by PPh₃ yields paramagnetic rhenium(vi) compounds with the general formula [ReO(diol)₂]. In these compounds, the co-ordination geometry is distorted square pyramidal. They are thermally stable and are not oxidized by dry air. Thus the stabilities of these rhenium(vi) diolato complexes are significantly greater than those observed for complexes of monodentate alkoxide ligands. Reactivity studies indicate that these compounds may be valuable starting materials for organometallic compounds and are a stable, general source for exploring the chemistry of Re^{VI}.

Experimental

All reactions were carried out in a dry nitrogen atmosphere using standard Schlenk techniques. All solvents were distilled

over standard drying agents under nitrogen; light petroleum had bp 40–60 °C. The compounds Re₂O₇,²⁶ [ReO₃(OSiMe₃)]²⁷ and 1,1'-bicyclohexane-1,1'-diol²⁸ were prepared by literature methods. Pinacol (2,3-dimethylbutane-2,3-diol) and rhenium metal powder were obtained from Aldrich Chemical Company. Solutions of pinacol were dried over 4 Å molecular sieves. Infrared spectra were recorded in Nujol on a Nicolet 510 FT-IR spectrometer, NMR spectra on a Bruker W360 instrument operating at 360.13 (¹H) or 90.53 MHz (¹³C) and are referenced to SiMe₄ (δ 0). All chemical shifts δ are in ppm. Microanalyses were obtained from the Microanalysis Group from the University of Turku using a Perkin-Elmer CHNS-Analyzer 2400.

Preparations

[ReO₃(Hpin)]·H₂pin 1a. (a) From Re₂O₇. To a suspension of Re₂O₇ (0.23 g, 0.5 mmol) in CH₂Cl₂ (7 cm³) was added H₂pin (0.34 g, 2.9 mmol) in CH₂Cl₂ (8 cm³). The colourless solution was stirred for 30 min at room temperature, then filtered and evaporated to dryness *in vacuo*. The white residue was washed with light petroleum (3 × 5 cm³). The colourless product (0.28 g, 62%) was crystallized from Et₂O solution (2 cm³) by slow addition of light petroleum (5 cm³), mp 74–76 °C with decomposition under nitrogen (Found: C, 29.5; H, 5.69. C₁₂H₂₇O₇Re requires C, 30.7; H, 5.80%). IR (Nujol mull, cm⁻¹): 3473m (br), 3410m, 2719w, 2617w, 2535w (br), 1231w, 1203m, 1150s, 1130m, 1117m, 1014w, 941s, 910s, 853m, 830m, 670w, 648w, 617m, 578w, 547w, 527m, 510m and 469m. NMR: ¹H (CDCl₃), δ 1.24 (s, 4 H, CCH₃ H₂pin), 1.31 (s, 2 H, CCH₃ Hpin), 1.40 (s, 2 H, CCH₃ Hpin), 2.11–2.17 (br, OH) and \approx 6 (br, OH); ¹³C-{¹H}, (C₆D₆), δ 22.8 (CH₃ Hpin), 23.5 (CH₃ Hpin), 24.5 (CH₃ H₂pin), 75.2 (COH H₂pin), 77.4 (COH Hpin) and 93.1 (CORe).

(b) From HReO₄. Rhenium metal powder (0.25 g, 1.3 mmol) was dissolved in 70% HNO₃ (1 cm³) with gentle heating. The colourless solution was evaporated in an open flask by careful heating (water-bath) until a pale yellow oily residue remained. The residue was diluted with water (1 cm³) and the solution evaporated as before; this procedure was repeated twice more to ensure evaporation of all the nitric acid. The yellow-green HReO₄ residue was placed under a nitrogen atmosphere and H₂pin (0.40 g, 3.4 mmol) in CH₂Cl₂ (25 cm³) added. The HReO₄ dissolved to give a colourless solution during 20 min; this solution was stirred at room temperature for 1 h and subsequently filtered and evaporated to dryness. The white residue was washed with light petroleum (3 × 5 cm³) to give a white microcrystalline crude product (0.52 g, 85%) which was recrystallized as above. It was identical to that obtained from Re₂O₇ (IR and NMR).

[ReO₃(Hpin)] 1b. From Re₂O₇. To a suspension of Re₂O₇ (0.23 g, 0.5 mmol) in CH₂Cl₂ (7 cm³) was added H₂pin (0.34 g, 2.9 mmol) in CH₂Cl₂ (8 cm³). The Re₂O₇ dissolved to give a colourless solution, which was stirred for 30 min at room temperature. The solution was filtered, evaporated to dryness *in vacuo* and the residue washed with light petroleum (3 × 5 cm³). The white residue was heated to 40 °C *in vacuo* and free H₂pin removed by sublimation. The residue was dissolved in Et₂O (2 cm³) and colourless crystals were obtained by slow addition of light petroleum (5 cm³). The moisture sensitive crystals (0.21 g, 64%) were filtered off, washed with light petroleum (2 × 5 cm³) and dried *in vacuo*. The compound decomposes at 73–75 °C under nitrogen (Found: C, 20.6; H, 3.80. C₆H₁₃O₃Re requires C, 20.5; H, 3.74%). IR (Nujol mull, cm⁻¹): 3200m (br), 2707w, 2594w, 2488w, 1232w, 1195w, 1160m, 1137s, 1012w, 983m, 950s, 910s, 888s, 850m, 679m, 617m, 562m, 523w, 498m and 465m. NMR (CDCl₃): ¹H, δ 1.41 (br, CCH₃) and 5.3 (OH); ¹³C-{¹H}, δ 23.30–24.03 (m, CH₃), 78.50 (COH) and 94.94 (CORe).

The crystal structure of a single crystal of [ReO₃(Hpin)] was determined: $a = 12.363(1)$, $b = 11.013(2)$, $c = 14.541(4)$ Å,

Table 3 Crystal data and experimental details for compounds **1a** to **4**

	1a	2	3	4
Formula	C ₁₂ H ₂₇ O ₇ Re	C ₁₂ H ₂₁ O ₅ Re	C ₁₂ H ₂₄ O ₅ Re	C ₂₄ H ₄₀ O ₅ Re
<i>M</i>	469.55	431.50	434.51	594.78
Crystal system	Monoclinic	Monoclinic	Tetragonal	Monoclinic
Space group (no.)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 4 ₂ <i>mm</i> (102)	<i>P</i> 2 ₁ / <i>c</i> (14)
<i>a</i> /Å	12.184(8)	8.623(1)	10.315(2)	9.491(2)
<i>b</i> /Å	11.217(7)	9.917(2)	10.315(2)	16.732(1)
<i>c</i> /Å	13.864(9)	16.373(2)	7.270(1)	15.763(1)
β /°	111.35(5)	91.57(1)		104.49(1)
<i>U</i> /Å ³	1765(2)	1399.6(6)	773.5(2)	2423.6(9)
<i>Z</i>	4	4	2	4
μ (Mo-K α)/cm ⁻¹	69.09	88.09	78.64	51.10
Reflections measured	3276	2809	743	4733
Observed reflections	3122	2023	403	3317
[<i>I</i> > 3.0 σ (<i>I</i>)]				
Parameters/restraints	190/6	167	62/11	271
<i>R</i> ^a	0.097 (0.043) ^b	0.021	0.053 (0.031)	0.024
<i>R</i> '	0.111 (0.081)	0.021	0.072 (0.065)	0.024

^a Calculations for compounds **1a** and **3** with SHELXL 97 and refinements based on F^2 . $R = R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]$ and $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (2F_c + F_o)/3$. ^b For reflections with $I > 2.0\sigma(I)$.

$\beta = 90.18(2)^\circ$, space group *C*2/*c* (no. 15). The structural data are similar to those obtained by Herrmann *et al.*⁶ In our case, however, the hydrogen atom bonded to pinacol was located from the Fourier map and its positional parameters were refined.

[ReO₃(Hbicy)] 2. To a solution of H₂bicy (0.137 g, 0.73 mmol) in light petroleum (10 cm³) was added [ReO₃(OSiMe₃)] (0.235 g, 0.73 mmol) in light petroleum (20 cm³). A white precipitate formed immediately and the reaction mixture was stirred at room temperature for 2 h. The solution was filtered and the analytically pure white microcrystalline precipitate (0.17 g, 63%) washed with light petroleum (3 × 5 cm³). Crystals suitable for single crystal X-ray diffractometry were obtained from mixed Et₂O–light petroleum solutions held at –18 °C. The product decomposed above 90 °C (Found: C, 33.7; H, 4.57. C₁₂H₂₁O₅Re requires C, 33.4; H, 4.91%). IR (Nujol mull, cm⁻¹): 3215m (br), 1313w, 1289w, 1254m, 1225w, 1181m, 1152m, 1078w, 1061w, 1038w, 1019w, 982w (sh), 949s, 934s, 915s, 900s, 867s, 752m, 723m, 687w, 670w, 588m, 534m, 516w, 498w and 479w. NMR (CDCl₃): ¹H, δ 1.06 (d, br, CH₂), 1.31 (d, br, CH₂), 1.41–1.52 (m, br, CH₂), 1.62 (m, br, CH₂), 1.71 (d, br, CH₂), 1.83 (d, br, CH₂), 2.03–2.08 (m, br, CH₂) and \approx 5 (br, OH); ¹³C-{¹H}, δ 20.4 (CH₂), 20.7 (CH₂), 24.0 (CH₂), 24.2 (CH₂), 29.0 (CH₂), 30.6 (CH₂), 79.3 (COH) and 96.4 (CORE).

[ReO(pin)₂] 3. To a solution of compound **1** (0.59 g, 1.3 mmol) in Et₂O (20 cm³) over 4 Å molecular sieves was added a solution of PPh₃ (0.17 g, 0.65 mmol) in Et₂O (20 cm³). The reaction solution changed immediately from colourless to dark blue. It was stirred for 3 h at room temperature during which time it turned to bright orange-red and some white precipitate formed. The solution was evaporated to dryness *in vacuo* and the orange residue extracted with light petroleum (2 × 15 cm³). The combined extracts were slowly evaporated to dryness. Compound **3** crystallized as small red needles during evaporation. The crude product (0.47 g, 84%) was purified by extraction with warm (40 °C) light petroleum (5 cm³). Large red needles (0.38 g, 68%) were formed when the solution was allowed to cool slowly to room temperature, filtered off and dried *in vacuo*. The compound decomposed above 120 °C under N₂ (Found: C, 33.2; H, 5.53. C₁₂H₂₄O₅Re requires C, 33.2; H, 5.58%). IR (KBr, cm⁻¹): 2981s, 2938m, 1461m, 1448m, 1387m, 1367s, 1262m, 1199m, 1164m, 1129s, 1020w, 1000w, 980s, 948s, 885m, 856s, 816m, 746w, 722s, 674s, 638w, 625m, 555w, 484m and 443w. *m/z* 435 (M⁺) and 433 (M⁺). μ_{eff} 1.72 μ_{B} .

[ReO(bicy)₂] 4. To a HReO₄ residue (from 0.106 g Re powder, 0.569 mmol prepared as described above) was added a solution

of H₂bicy (0.229 g, 1.15 mmol) in CH₂Cl₂ (20 cm³) and stirred for 30 min at room temperature. During this time the HReO₄ residue dissolved and formed a pale yellow solution. This was filtered directly into a Schlenk flask containing PPh₃ (0.075 g, 0.286 mmol) in CH₂Cl₂ (5 cm³) and 4 Å molecular sieves. The reaction mixture changed immediately to dark orange-brown and was stirred for 20 h at room temperature. During this time it turned bright orange-red. The solution was filtered and evaporated to dryness *in vacuo* and the orange residue extracted with light petroleum (3 × 5 cm³). The light petroleum solution was evaporated slowly to dryness. The orange-red microcrystalline crude product (0.25 g, 74%) was purified by chromatography on silica gel using toluene as an eluent. The red-orange fraction was collected and evaporated to dryness *in vacuo*. The residue was dissolved in warm light petroleum (3 cm³, 40 °C). Large red needles (0.20 g, 59%) were formed when the solution was allowed to cool slowly to room temperature and then held at –18 °C for 2 d. The crystals were filtered off and dried *in vacuo*. The compound decomposed at 166 °C (Found C: 48.7; H, 7.08. C₂₄H₄₀O₅Re requires C, 48.5; H, 6.79%). IR (KBr, cm⁻¹): 2935s, 2857s, 1448s, 1364m, 1352m, 1341m, 1279m, 1250m, 1199w, 1147m, 1121s, 1062m, 1036m, 1023m, 984s, 953s, 941s, 923s, 908s, 855s, 841s, 750s, 740s, 635s, 582s, 535m, 518w, 502m, 465m and 406m cm⁻¹. *m/z* 595 (M⁺) and 593 (M⁺). μ_{eff} 1.69 μ_{B} .

Crystallography

Crystal data for compounds **1a–4** and other experimental details are summarized in Table 3. The unit cell parameters were determined by least-squares refinements from 25 carefully centred high-angle reflections measured at ambient temperature on a Rigaku AFC5S diffractometer using Mo-K α radiation ($\lambda = 0.71069$ Å). The data obtained were corrected for Lorentz-polarization effects. Absorption (ψ -scan)²⁹ corrections were also applied. The intensity variations of three check reflections showed a decay of 6.8% for **1a** and 0.5% for **4** during the data collection. These effects were corrected using linear correction factors. Secondary extinction was also taken into account for **2** and **3**.³⁰

The structures of compounds **1a–4** were solved by direct methods and subsequent Fourier syntheses. Least-squares refinements minimized the function $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]$ for **2** and **4**, where $w = [\sigma^2(F_o)]^{-1}$. For **1a** and **3** refinements were against F^2 . The heavy atoms were refined anisotropically, and the CH hydrogen atoms were included in calculated positions with fixed thermal parameters. The OH hydrogens of **1a** and **2** were refined isotropically. Calculations

for **2** and **4** were performed using the TEXSAN³¹ crystallographic software. The structures of **1a** and **3** were refined on F^2 with SHELXL 97.³² Figures were drawn with ORTEP II¹⁹ and ORTEP 3 for Windows.³³

In compound **3** atoms C1a, C1b, C2a, C2b, O2a and O2b of the disordered pinacol molecule were given the population parameter 0.5 and for O1 the population parameter was 0.25. Hydrogen atoms were not included in calculations. Atoms O2a and O2b were refined with isotropic displacement factors and the rest with anisotropic ones. Restraints were used for the Re–O, C–O and C–C distances.

CCDC reference number 186/1108.

See <http://www.rsc.org/suppdata/dt/1998/3287/> for crystallographic files in .cif format.

Acknowledgements

We thank the Neste Foundation for financial support, and Dr. Raikko Kivekäs for his valuable help in the structure solution of compound **3**.

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Paper 8/03301C