Multiple Bonds Between Main Group Elements and Transition Metals. 151.[1] Trioxorhenium(VII) Alkoxide Complexes

Wolfgang A. Herrmann,* William A. Wojtczak,[†] Georg R. J. Artus, Fritz E. Kühn,[‡] and Mike R. Mattner[§]

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4,
D-85747 Garching, Germany

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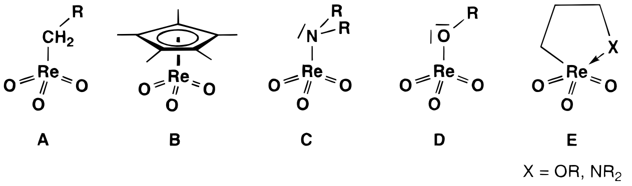
The reaction of $Me_3SiOReO_3$ with trimethylsilyl ethers Me_3SiOR (R = Me, CMe_2CMe_2OMe, CMe_2CMe_2OH, $CMe_2CMe_2OSiMe_3$) yields the trioxorhenium(VII) alkoxide complexes $[ReO_3(OMe)(MeOH)]_2$ (**1**), $ReO_3(OCMe_2CMe_2OMe)$ (**2**), $ReO_3(OCMe_2CMe_2OH)$ (**3**), and the glycolate complex $(Me_3SiO)ReO_2(OCMe_2CMe_2O)$ (**4**), respectively. The alkoxides **1**−**4** have fluxional structures at room temperature in solution on the ^{17}O NMR time scale. The trigonal bipyramidal structure of **2**, in the crystal, is static in solution only at −90 °C. The protic hydrogen of **3** can be abstracted by lithium 2,2,6,6-tetramethylpiperidinate to give the ionic complex $Li[ReO_3(OCMe_2CMe_2O)]$ (**5**). $[ReO_3(OMe)(MeOH)]_2$ (**1**) crystallizes from dichloromethane in the space group $P\bar{1}$ with unit cell dimensions $a = 6.276(3)$ Å, $b = 6.720(3)$ Å, $c = 8.005(4)$ Å, $\alpha = 109.39(3)°$, $\beta = 99.48(3)°$, $\gamma = 110.31(2)°$, $V = 238.3$ Å^3, and $Z = 1$; the structure was refined to $R = 0.050$ and $R_w = 0.056$. $ReO_3(OCMe_2CMe_2OMe)$ (**2**) crystallizes from toluene in the space group *Pbca* with unit cell dimensions $a = 8.263(2)$ Å, $b = 10.884(3)$ Å, $c = 22.963(5)$ Å, $V = 2065$ Å^3, and $Z = 8$; the structure was refined to $R = 0.044$ and $R_w = 0.028$. $ReO_3(OCMe_2CMe_2OH)$ (**3**) crystallizes from dichloromethane in the space group $C2/c$ with unit cell dimensions $a = 12.327(5)$ Å, $b = 10.973(3)$ Å, $c = 14.491(6)$ Å, $\beta = 90.22(2)°$, $V = 1960$ Å^3, and $Z = 8$; the structure was refined to $R = 0.047$ and $R_w = 0.030$. $(Me_3SiO)ReO_2(OCMe_2CMe_2O)$ (**4**) crystallizes from *n*-pentane in the space group $P2_1/c$ with unit cell dimensions $a = 12.042(8)$ Å, $b = 10.782(2)$ Å, $c = 12.485(9)$ Å, $\beta = 117.44(3)°$, $V = 1439$ Å^3, and $Z = 4$; the structure was refined to $R = 0.044$ and $R_w = 0.044$. The edge-sharing bioctahedral complex **1** has bridging methoxy and terminal methanol ligands *trans* to rhenium−oxygen double bonds. The rhenium centers in compounds **2** and **3** are pentacoordinated and located in a distorted trigonal bipyramidal geometry. The alkoxy function of the alkoxy ligand $-OCMe_2CMe_2OR$ (R = H, Me) is located in the equatorial plane, and the Lewis base (−OMe, −OH) is bonded *trans* to an oxygen atom in an axial coordination site. $(Me_3SiO)ReO_2(OCMe_2CMe_2O)$ (**4**) has a similar geometry to **2** and **3** with a trimethylsiloxy ligand *trans* to an alkoxy function in an axial position.

Introduction

Although the organometallic chemistry of the ReO_3 group has experienced considerable growth over the last decade, with the most notable examples being CH_3ReO_3 and Cp^*ReO_3 of types **A** and **B**,[2,3] comparatively little is known about the inorganic chemistry of the ReO_3 moiety.[4] Some organometallic rhenium oxides have useful catalytic applications.[5] A more thorough understanding of the chemistry of inorganic rhenium oxides should help in determining whether this class of compounds is suitable in catalytic reactions, too. New types of inorganic rhenium oxides may also prove important as starting materials in synthesizing new organorhenium oxides.



While hardly anything is known about the amides of type **C**,[4,6] the alkoxides of type **D** have sporadically appeared in the literature.[7,8] They have been proposed as intermediates in specific organic functional group transformations.[7] To date, only a few compounds of general composition $ROReO_3$ and

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[†] Alexander von Humboldt Foundation Fellow, 1993/94. Current address: ACS Inc., 510 Alder Drive, Milpitas, CA 95035.

[‡] Hermann Schlosser Foundation Fellow, 1992−1994.

[§] Fonds der Chemischen Industrie Fellow, 1994−1996.

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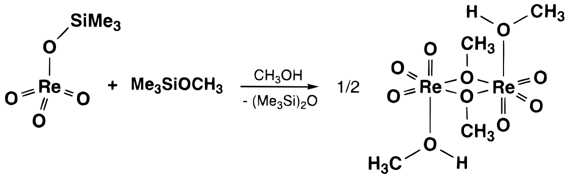
$ROReO_3{\cdot}L_2$ (R = Me, *t*-Bu, or $SiMe_3$) are known.[4a,8] The work of Wilkinson *et al.* on these compounds has shown that the tetracoordinate species are unstable at room temperature, whereas the higher coordinated compounds $ROReO_3{\cdot}L_2$ are thermally stable.[4a] To better understand the properties of alkoxides containing the ReO_3 group, we prepared pentacoordinate alkoxide compounds that would exhibit greater thermal stability but also retain the attributes of coordinative unsaturation and metal acidity that are typical of efficient ReO_3-type catalysts.[9] Previous reports have described organorhenium oxides $R{-}ReO_3$ containing chelating ligands of the types $-(CH_2)_3NR_2$[5g,9c] and $-(CH_2)_2CH(R)OR$ (type **E**).[9c] We now report on trioxorhenium compounds with related alkoxide ligands.

Results and Discussion

(Methoxy)trioxorhenium(VII)—A Dinuclear Solvate Complex. (Methoxy)trioxorhenium(VII) (**9**) was prepared by a method similar to that described by Wilkinson and Edwards for $[ReO_3(OMe)]_n$ and $ReO_3(O\text{-}t\text{-}Bu)$,[4a] namely, by reaction of $Me_3SiOReO_3$ with the trimethylsilyl ether, Me_3SiOMe, and a stoichiometric amount of methanol (eq 1).



(1)

The resulting compound $[ReO_3(OMe)(MeOH)]_2$ (**1**) is moisture sensitive, but unlike $[ReO_3(OMe)]_n$, it is thermally stable at room temperature. The solvating methanol ligands are easily removed under reduced pressure to give $[ReO_3(OMe)]_n$. We were only able to observe the IR band of the OH group (3160 cm^{-1}) of **1** in $CDCl_3$ solution. This band is about 200 cm^{-1} lower in energy than that of methanol, probably due to both metal coordination and hydrogen bonding (see also crystallographic section).[10] After **1** was dried under oil-pump vacuum for a few minutes, the peaks in the IR (Nujol) and ^1H NMR spectrum compare closely to those reported for $[ReO_3(OMe)]_n$. Furthermore, the ν(OH) stretching band is no longer visible.

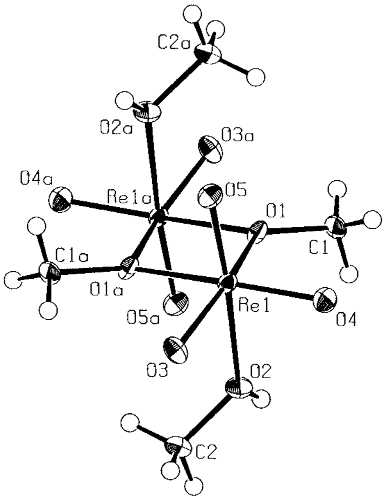


Figure 1. PLATON view[16d] of the solid state structure of the Re(VII) methoxide $[ReO_3(OMe)(MeOH)]_2$ (**1**). Atoms are represented by their thermal ellipsoids at the 50% probability level. Atoms labeled "a" are produced by an inversion center ($-x$, $-y$, $-z$).

The solution behavior of compound **1** is more complex, with a number of exchange mechanisms possible. The ^1H NMR spectrum at room temperature ($CDCl_3$) exhibits peaks at δ = 3.94 and 1.87 ppm. The downfield peak is broad, apparently representing an exchange-averaged position for the methanol and methoxy ligands. The upfield peak is also broadened and is assigned to the proton of the coordinated methanol. Lowering the temperature does not lead to a significant change of the chemical shifts. Unfortunately, the decreasing solubility of complex **1** does not allow measurements below −25 °C. At higher temperatures, both peaks broaden further, and the high-field peak disappears at ca. 40 °C. This might result from a higher exchange velocity at this temperature. The ^{17}O NMR spectrum shows only one peak for the terminal oxygen atoms ($\delta(^{17}O) = 750$ ppm), and this peak does not split over the temperature range from +20 to −20 °C.

The solid state structure of **1** consists of two ReO_3 units bridged by two methoxy groups. The distorted octahedral coordination sphere at both rhenium centers is completed by an additional methanol ligand per rhenium atom located in an axial position *trans* to an oxo ligand. The central $Re{-}O{-}Re'{-}O'$ ring and the remaining oxo ligands define the equatorial plane of the molecule. Both octahedrons share one edge on a crystallographic inversion center. The solid state structure of **1** is shown in Figure 1. Selected bond lengths and angles are given in Table 1.

Replacement of the bridging methoxy groups by bridging hydroxy groups and the methanol ligands by 1,4-dioxane molecules leads to the structurally similar compound $Re_2O_6(OH)_2{\cdot}3(1,4\text{-dioxane})$.[11] The interior angles of the central four-membered ring are almost equal. The distances from rhenium to the bridging oxygen atoms are shorter in the case of hydroxy groups (2.070(4) *vs* 2.091(7), 2.114(7) Å in **1**). This might be a consequence of the strong hydrogen bonding between the hydroxy groups and the neighboring dioxane molecules in $Re_2O_6(OH)_2{\cdot}3(1,4\text{-dioxane})$. The rhenium to methanol oxygen atom distance in **1** is 2.278(8) Å, whereas the long rhenium−

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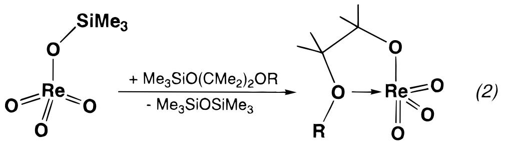
Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[ReO_3(OMe)(MeOH)]_2$, **1**[a]

Re1−O1	2.091(7)	O3−Re1−O2	81.1(3)
Re1−O1a	2.114(7)	O4−Re1−O1	89.9(3)
Re1−O2	2.278(8)	O4−Re1−O1a	154.4(4)
Re1−O3	1.729(7)	O4−Re1−O2	83.9(3)
Re1−O4	1.712(7)	O4−Re1−O3	106.2(4)
Re1−O5	1.725(8)	O5−Re1−O1	95.8(3)
O1−C1	1.43(1)	O5−Re1−O1a	92.3(3)
O2−C2	1.44(2)	O5−Re1−O2	169.9(4)
O1−Re1−O1a	68.0(3)	O5−Re1−O3	103.4(3)
O2−Re1−O1	76.8(3)	O5−Re1−O4	103.1(4)
O2−Re1−O1a	78.7(3)	Re1−O1−Re1a	112.0(3)
O3−Re1−O1	151.1(3)	C1−O1−Re1	124.4(7)
O3−Re1−O1a	89.6(3)	C1−O1−Re1a	121.7(7)

[a] Atoms marked "a" are produced by an inversion center (−*x*, −*y*, −*z*).

dioxane interactions in $Re_2O_6(OH)_2 \cdot 3(1,4\text{-dioxane})$ of 2.486(5) and 2.469(5) Å must be considered as very weak. The methanol proton in **1** could not be found by difference Fourier techniques, but the short intermolecular distance O2−O5′ of 2.77 Å strongly suggests the presence of an intermolecular hydrogen bond. While in **1** two hydrogen bridges link two molecules, in $Re_2O_6(OH)_2 \cdot 3(1,4\text{-dioxane})$, only one hydrogen bridge connects two of the oxo complexes. Nevertheless, both compounds form similar indefinite chains in the crystal.

Alkoxyrhenium(VII) Oxides with Intramolecular O Donor Stabilization. Treatment of $Me_3SiOReO_3$ with the bifunctional ligands $Me_3SiOCMe_2CMe_2OMe$ and $Me_3SiOCMe_2CMe_2OH$ yields the alkoxy complexes **2** and **3**, respectively (eq 2). Both compounds are water sensitive but thermally stable at room temperature.



(2)

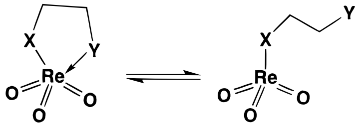
2: R = CH_3
3: R = H

The IR spectrum of **2** shows characteristic ν(ReO) bands at 1007 and 934 cm^{-1} indicating pentacoordination of the Re center.[2h,6] Compound **3** has similar bands plus a band at 3182 cm^{-1} that is assigned to the O−H stretching mode. In comparison with the IR spectrum of the free ligand $Me_3SiOCMe_2CMe_2OH$, the band for the coordinated OH group in **3** is shifted to lower energy by 300 cm^{-1} (probably a consequence of both metal coordination and hydrogen bonding).[10]

Table 2. Temperature-Dependent ^{17}O NMR Data of the Alkoxy Rhenium Complexes **2** and **3** (Terminal O Ligands) in $CDCl_3$

temp (°C)	$ReO_3(OCMe_2CMe_2OMe)$ (**2**)		$ReO_3(OCMe_2CMe_2OH)$ (**3**)	
	δ (ppm)	$\nu_{1/2}$ (Hz)	δ (ppm)	$\nu_{1/2}$ (Hz)
+35	745	25	748	30
+20	744	30	747	40
−20	743	90	745	80
−50	741	400	744	210
−70	760	300	743	450
	730	600		
−90	764	230	738	850
	730	220		

Scheme 1



X = CH_2, O; Y = NR_2, OR

The ^1H NMR spectra of **2** and **3** in $CDCl_3$ contain two upfield singlets between $\delta = 1.2$ and 1.5 ppm (glycolate $-CH_3$ groups). In addition, **2** has a singlet at $\delta = 3.61$ ppm for the ether $-CH_3$ group, and **3** has a peak for the alcohol proton at $\delta = 5.38$ ppm. The low-field shifts of the OCH_3 protons and the O−H proton in **2** and **3**, as compared to the positions of these peaks in the starting materials, indicate the strong electron withdrawing effect of the Re(VII) center. The $^{13}C\{^1H\}$ NMR spectra of **2** and **3** in $CDCl_3$ contain two peaks downfield at $\delta = 82.9$, 93.4 ppm and 78.5, 95.0 ppm, respectively, and two peaks upfield at $\delta = 18.6$, 24.1 ppm and 23.3, 24.0 ppm, respectively. The downfield peaks can be assigned to the quarternary carbon atoms and the upfield peaks can be assigned to the methyl carbon atoms of the glycolate ligand. Compound **2** also has a peak at $\delta = 52.0$ ppm for the carbon atom of the methyl ether group. The ^1H NMR spectrum of **3** in THF-d_8 shows only one broad peak at 1.31 ppm, whereas the $^{13}C\{^1H\}$ NMR spectrum still contains two types of methyl and quarternary carbon atoms. It appears that the protons of the methyl carbon atoms resonate coincidentally in THF, and the singlet probably does not arise from exchange averaging due to proton mobility. The fact that the ^1H NMR spectrum of **2** exhibits the same effect, when recorded in THF-d_8, supports this explanation. For **2**, the backbone methyl protons show up at 1.34 ppm and the $O-CH_3$ singlet is broadened but not shifted significantly ($\delta = 3.54$ ppm) from its position in $CDCl_3$.

^{17}O NMR data of compounds **2** and **3** are given in Table 2 for comparison. This table shows that in the case of **2**, the rigid solid state trigonal bipyramidal geometry occurs in solution only at very low temperature. Cooling a solution of **2** to −90 °C results in splitting up of the peak at $\delta = 744$ ppm, first visible at −70 °C, into two peaks (ca. 1:2 ratio) at 764 and 730 ppm. This gives rise to chemically distinct equatorial and axial oxygen atoms with different chemical shifts. The weak donor capability of the −OMe and −OH functional groups results in the equilibration of these three terminal oxygen atoms, according to Scheme 1, at higher temperature, when the opening and closing of the alkoxy ligand is quick on the ^{17}O NMR time scale. In compound **3**, even at −90 °C the geometry is not rigid but the signal broadens significantly. This broadening phenomenon is not due to the higher viscosity of the solvent at lower temperatures, as can be shown by comparison to ^{17}O NMR data of related compounds.[7b] The broadening of the signal for the terminal oxygen atoms in **3** suggests a similar process is occurring as that in **2**. However, the poor solubility of **3** precludes lower temperature measurements to observe the splitting of the Re═O signal. The recently reported compound $O_3Re(CH_3)_2O-CH_3$ exhibits very similar fluxional behavior above −80 °C.[9c] It has been shown for this and related compounds that the temperature dependent appearance of the NMR spectra is due to intramolecular fluxionality and not to pseudorotation (Scheme 1).[9c]

Compounds **2** and **3** are illustrated in Figures 2 and 3, respectively. Selected bond lengths and angles are given in Tables 3 and 4. Both molecules show similar structural properties, with the core geometry being strongly distorted trigonal bipyramidal. This coordination geometry is also found for compounds of the type $O_3ReCH_2CH_2CH_2NR_2$.[5g,9c] The donating oxygen function and one oxo ligand occupy the axial positions, while an alkoxy function and the two remaining oxo ligands are located in the equatorial plane. The ReO_3 fragment has pseudotetrahedral geometry. The angles O═Re═O vary from 103.4(4)° to 110.3(4)°. As a consequence, the "bite angles" O4−Re1−O5 = 71.6(2)° in **2** and O1−Re1−O2 = 71.9(2)° in **3** are rather acute. This distortion can also be viewed

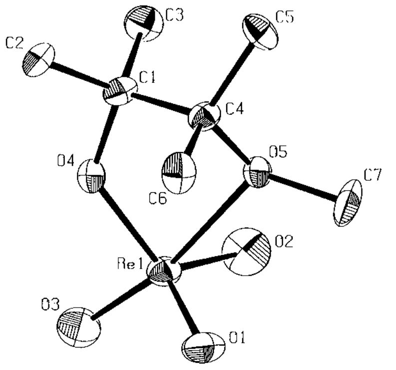


Figure 2. PLATON view[16d] of the solid state structure of the Re(VII) alkoxy ether complex $ReO_3(OCMe_2CMe_2OMe)$ (**2**). Atoms are represented by their thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

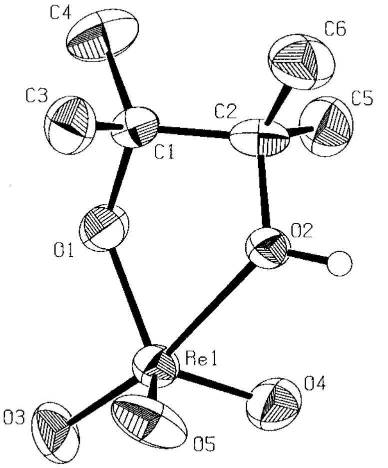


Figure 3. PLATON view[16d] of the solid state structure of the Re(VII) alkoxy alcohol complex $ReO_3(OCMe_2CMe_2OH)$ (**3**). Atoms are represented by their thermal ellipsoids at the 50% probability level. Methyl hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Intramolecularly Stabilized Alkoxy Rhenium Complex **2**

Re1−O1	1.694(5)	O4−Re1−O1	117.6(2)
Re1−O2	1.703(5)	O4−Re1−O2	120.1(2)
Re1−O3	1.708(6)	O4−Re1−O3	96.7(2)
Re1−O4	1.859(5)	O5−Re1−O1	82.7(2)
Re1−O5	2.323(5)	O5−Re1−O2	81.0(2)
O2−Re1−O1	110.0(3)	O5−Re1−O3	168.2(2)
O3−Re1−O1	104.9(3)	O5−Re1−O4	71.6(2)
O3−Re1−O2	104.2(3)		

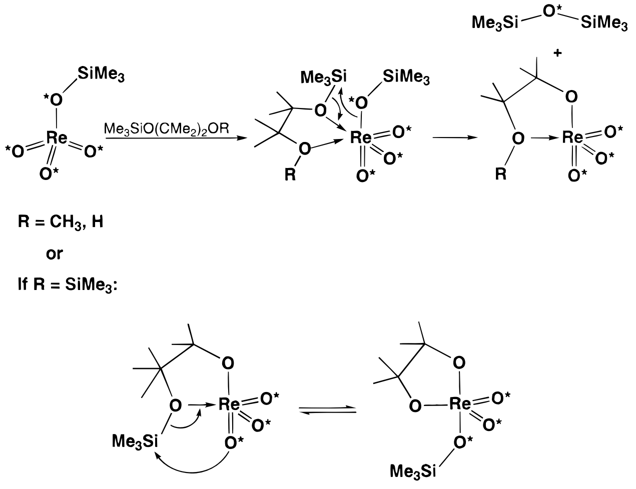
Table 4. Selected Bond Lengths (Å) and Angles (deg) for the Intramolecularly Stabilized Alkoxy Rhenium Complex **3**

Re1−O1	1.854(6)	O4−Re1−O1	118.2(3)
Re1−O2	2.302(5)	O4−Re1−O2	83.6(3)
Re1−O3	1.709(6)	O4−Re1−O3	104.4(3)
Re1−O4	1.709(7)	O5−Re1−O1	120.0(3)
Re1−O5	1.693(7)	O5−Re1−O2	81.0(3)
O2−Re1−O1	71.9(2)	O5−Re1−O3	103.4(4)
O3−Re1−O1	96.9(3)	O5−Re1−O4	110.3(4)
O3−Re1−O2	168.5(3)		

as a shift of the central positively polarized rhenium atom from the center of an undistorted trigonal bipyramid toward the polyhedral face comprised of the three negatively polarized oxo ligands.

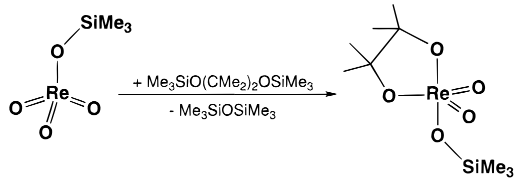
The bond distances from the rhenium atoms to the donating oxygen atoms (i.e., Re−OMe and Re−OH, respectively) in **2** and **3** are longer than the bond distances between the rhenium atoms and the methanol ligands in **1**, indicating a weaker interaction. One might have expected the reverse relationship since the metal centers in **2** and **3** should be sterically and electronically less saturated than in **1**. The bond length Re1−O5 = 2.323(5) Å in **2** is slightly longer than its counterpart Re1−O2 = 2.302(5) Å in **3**. This can be interpreted as a consequence of hydrogen bonding in **3**. The proton at O2 in **3** could not be found by difference Fourier techniques. However, the short intermolecular distance O2−O4′ of 2.70 Å strongly suggests the presence of a hydrogen bond at this position. In the crystal, two molecules of **3** would then be connected by two intermolecular hydrogen bonds to form dimers.

Scheme 2



4a **4b**

A Siloxyrhenium(VII) Oxide. The disilyl ether $Me_3SiOCMe_2CMe_2OSiMe_3$ has the ability to form a glycolate complex with $Me_3SiOReO_3$ by transfer of two trimethylsilyl groups and elimination of $Me_3SiOSiMe_3$. The siloxyrhenium(VII) oxide **4** resulting from the reaction shown in eq 3 represents a base-free glycolate compound of Re(VII). Glycolate compounds are of general interest since they frequently alkylate much cleaner than other precursors (e.g., lithium and zinc alkyls, Grignard compounds).[12] Compound **4** is stable at room temperature, thermally labile just above room temperature, and air and moisture sensitive.



4 (3)

The ^1H NMR spectrum of **4** exhibits singlets at $\delta = 0.22$ (glycolate CH_3) and 1.37 ppm ($SiMe_3$) with the appropriate 4:3 integration. The ^{13}C NMR spectrum shows three peaks, one for the $Si-CH_3$ group ($\delta(^{13}C) = 0.3$ ppm), one for the carbon atoms of ligand backbone ($\delta(^{13}C) = 96.0$ ppm), and one for the ligand CH_3 groups ($\delta(^{13}C) = 24.7$ ppm). The NMR signals are very broad. These results suggest some fluxionality of the complex in solution. The ^{17}O NMR spectrum exhibits two low-field ($\delta(^{17}O) = 755$ and 731 ppm) and three high-field peaks ($\delta(^{17}O) = 199$, 186, and 59 ppm). One possible explanation for the appearance of the ^1H, ^{13}C, and ^{17}O NMR spectra might be an ongoing exchange of the Me_3Si- group in solution, as suggested in Scheme 2 (if $R = SiMe_3$). ^{17}O labeling of the precursor compound shows that the peaks at 199 ($Re-O-C(CH_3)_2C(CH_3)_2$) and at 59 ppm ($Me_3Si-O-C(CH_3)_2C(CH_3)_2O-Re$) can be assigned to the oxygen atoms of the ligand.

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(12) Herrmann, W. A.; Watzlowik, P.; Kiprof, P. *Chem. Ber.* **1991**, *124*, 1101.

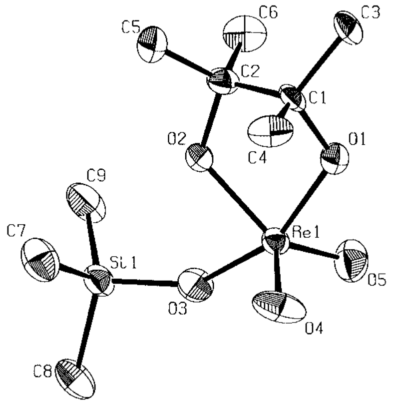


Figure 4. PLATON view[16d] of the solid state structure of $(Me_3SiO)ReO_2(OCMe_2CMe_2O)$ (**4**). Atoms are represented by their thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

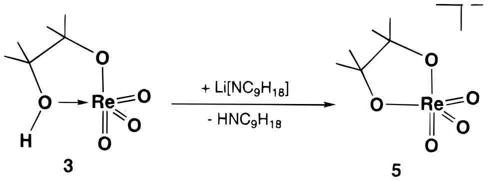
Table 5. Selected Bond Lengths (Å) and Angles (deg) for the Pinakolato Rhenium Complex **4**

Re1−O1	1.904(5)	O4−Re1−O1	98.5(2)
Re1−O2	1.923(6)	O4−Re1−O2	117.2(3)
Re1−O3	1.836(5)	O4−Re1−O3	99.6(3)
Re1−O4	1.699(5)	O5−Re1−O1	90.9(2)
Re1−O5	1.681(6)	O5−Re1−O2	134.2(3)
Si1−O3	1.674(6)	O5−Re1−O3	98.0(3)
O2−Re1−O1	76.8(2)	O5−Re1−O4	108.1(4)
O3−Re1−O1	156.2(2)	Si1−O3−Re1	145.5(3)
O3−Re1−O2	81.3(2)		

The latter signal is significantly smaller than the signal at 199 ppm. The signals at 755 (see Scheme 2) and 731 ppm are in a region associated with $Re^{VII}{=}O$ groups and may represent the terminal oxygen atoms of two interconverting species, namely **4a** and **4b**. The relatively large signal at 186 ppm may be assigned to the Re−*O**−$SiMe_3$ oxygen atom of **4b**. Unfortunately, the solubility of this complex decreases rapidly below −20 °C, and it decomposes quite quickly in solution at higher temperatures, so that a completely satisfying temperature dependence study could not be performed.

The solid state structure of **4** is illustrated in Figure 4. Selected bond lengths and angles are given in Table 5. Replacement of the axial oxo ligand in **3** by a trimethylsiloxy ligand and deprotonating the alcohol function does not drastically alter the distorted trigonal bipyramidal geometry. However, the bite angle O1−Re1−O2 = 76.8(2)° of the pinacolato ligand of **4** is widened as compared with that of **2** and **3** (71.6(2)° and 71.9(2)°, respectively). The angle is similar to the corresponding angle of 77.5(1)° found in (pinacolato-*O,O′*)-methyldioxorhenium(VII).[12] Also, the bond distances of the rhenium to pinacolato oxygen compare closely to those of the other complexes. The distance Re1−O3 = 1.836(5) Å is not unexpected, whereas the literature value for the corresponding distance in trimethylsilylperrhenate[8d] of 1.67(8) Å does not seem to be particularly reliable in view of the large standard deviation.

An Anionic Trioxorhenate(VII). Deprotonation of **3** with lithium 2,2,6,6-tetramethylpiperidinate in THF affords the moisture sensitive anionic trioxorhenate(VII) **5** in 79% yield (eq 4). A sterically hindered nitrogen base was employed in order to remove the proton without causing reduction at the Re(VII) center.



(4)

The IR spectrum of **5** is similar to that of **3**, with the only major difference being the absence of the O−H stretching vibration.

The ^1H NMR spectrum has one peak at $\delta = 1.15$ ppm for the glycolate ligand; two signals are observed in the ^{13}C NMR spectrum: $\delta = 25.5$ (CH_3), and 85.4 ppm (quarternary C). In **5**, the chelating oxygen atoms near the Re center should be good donors and carry a significant negative charge. This could be the reason for the stronger high-field shift (ca. 130 ppm) of the terminal oxygen atoms in the ^{17}O NMR spectrum of **5** as compared to those of **2** and **3**. A comparatively strong high-field shift also occurs if the phenyl group of $PhReO_3$ is substituted by a mesityl group ($\Delta\delta(^{17}O)$ ca. 110 ppm).[2g,9b] However, the shift difference between $CpReO_3$ and Cp^*ReO_3 is not as large ($\Delta\delta(^{17}O)$ ca. 45 ppm).[2k,9b] The same is true for the ^{17}O shift difference between cationic $[(9N3)ReO_3]^+$ and neutral $(9N3\text{-}H)ReO_3$ ($\Delta\delta(^{17}O)$ ca. 30 ppm; 9N3 = 1,4,7-triazacyclononane).[9b,13]

Mechanisms of Formation. The formation of compounds **1**−**4** is thought to follow Scheme 2. According to this proposal, in the first step the silyl ether forms a donor complex with the Lewis-acidic rhenium center of $Me_3SiOReO_3$. This reagent appears to behave as a “perrhenyl” complex in the reactions to form **1**−**4** (containing the $[ReO_3]^+$ synthon) rather than as a “perrhenate” complex.[14f,15]

Several complexes of formula $XO{-}ReO_3{\cdot}L_n$ are known (X = ReO_3, $C(O)CF_3$,[2h,4] $C(O)CCl_3$,[4b] etc.; L = THF, acetonitrile, pyridine, dimethoxyethane, etc.).[14] In all of these complexes, XO− acts as a leaving group. This property is also evident in the reactions of $Me_3SiOReO_3$ to form **1**−**4**. For example, when ^{17}O-labeled $Me_3SiO^*Re(O^*)_3$ is mixed with Me_3SiOR, labeled hexamethyldisiloxane, $Me_3SiO^*SiMe_3$ ($\delta(^{17}O) = 42$ ppm), and O_3^*ReOR with an unlabeled alkoxide oxygen atom are observed. The Re−$OSiMe_3$ bond breaks during the reaction, showing that $Me_3SiOReO_3$ behaves as a $[ReO_3]^+$ synthon. An alternative mechanism yielding **1**−**4** could involve the transfer of a $SiMe_3$ group to a Re=O* of $Me_3SiO^*Re(O^*)_3$ to give an intermediate with a composition of $(Me_3SiO^*)_2Re(^*O)_2(OR)$ from which $Me_3SiO^*SiMe_3$ is then extruded. However, no such reaction has ever been documented and must be qualified as unlikely.

Conclusions

(Methoxy)trioxorhenium(VII), CH_3OReO_3, exists in the solid state as a dimer with *μ*-alkoxy bridges. This is in contrast to the monomeric nature of the alkyl congeners with the formula $RReO_3$ (e.g., CH_3ReO_3). Intramolecularly stabilized monomeric

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(13) Mink, J.; Keresztury, G.; Stirling, A.; Herrmann, W. A. *Spectrochim. Acta* **1994**, *50A*, 2039.

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(15) (a) Herrmann, W. A.; Roesky, P. W.; Kühn, F. E.; Scherer, W.; Kleine, M. *Angew. Chem.* **1993**, *105*, 1768; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1714. (b) Bradley, D. C.; Mehrotra, R. C.; Gaur, P. D. *Metal Alkoxides*; Academic Press: London, New York, San Francisco, 1978. (c) Mehrotra, R. C. Transition Metal Alkoxides. In *Advances in Inorganic and Radiochemistry*; Emeleus, H. G., Sharpe, A. G., Eds.; Academic Press: London, New York, San Francisco, 1983; Vol. XXVI, pp 269−335. (d) Chisholm, M. H. *Inorganic Chemistry towards the 21st Century*; American Chemical Society; Washington, DC, 1983; Chapter 16, pp 243−273.

trioxorhenium alkoxides of the *O*,*O*′-chelate type are more stable and easier to handle than intermolecular adducts such as $[CH_3OReO_3{\cdot}CH_3OH]_2$ (**1**). ^{17}O NMR spectroscopy indicates that the rhenium centers of the neutral Re(VII) alkoxides have a greater Lewis acidity than that of (ionic) perrhenates ($\delta(^{17}O) \approx 560$ ppm). The nonrigid behavior of complexes like $O_3Re{-}OCMe_2CMe_2OMe$ (**2**) in solution might allow for open coordination sites during catalytic cycles, which can be used to add substrates without destabilizing the molecules. These last two observations are promising indicators for catalytic activity. It must be considered, however, that the rhenium(VII)−alkoxy bonds may be quite susceptible to hydrolytic cleavage.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere by using standard vacuum line and Schlenk techniques. Toluene, *n*-pentane, and tetrahydrofuran were distilled from Na/K alloy under N_2. Dichloromethane was distilled from calcium hydride, and methanol was stirred with sodium methoxide and then distilled under N_2. Deuterated chloroform (Merck) was stirred with P_2O_5 and then distilled under N_2. Deuterated tetrahydrofuran (Merck) was dried and stored over 4-Å molecular sieves. $Me_3SiOReO_3$ and ^{17}O-1abelled $Me_3SiO^*Re(O^*)_3$ were prepared by literature methods.[8a,9b,c] Me_3SiOMe ($d_{20} = 0.756$ g cm^{-3}), $HOCMe_2CMe_2OH$, $C_7H_7SO_2OCH_3$ (methyl *p*-toluene sulfonate), 1.6 M *n*-BuLi in hexane, and Me_3SiCl ($d_{20} = 0.856$ g cm^{-3}) were purchased from Aldrich and used as received. IR samples were prepared in an inert atmosphere box as Nujol mulls or as solutions between KBr plates as noted. Chemical shifts for the ^1H NMR spectra are relative to the residual protons in the deuterated solvent. ^{17}O NMR experiments were conducted with labeled $Me_3SiO^*Re(O^*)_3$ starting material in sealed NMR tubes. The chemical shifts in the ^{17}O NMR spectra are reported relative to the oxygen atom in D_2O. Elemental analysis were conducted at the Microanalytical Laboratory of our institute (M. Barth).

Lithium 2,2,6,6-tetramethylpiperidinate was synthesized *via* deprotonation of 2,2,6,6-tetramethylpiperidine with 1.6 M *n*-BuLi in *n*-pentane with subsequent washing with 2 20 mL portions of cold *n*-pentane before being dried in vacuo. $Me_3SiOCMe_2CMe_2OH$ (bp: 178 °C, 1 atm) and $Me_3SiOCMe_2CMe_2OSiMe_3$ (bp: 205 °C, 1 atm) were prepared by lithiating $HOCMe_2CMe_2OH$ (5.91 g, 50 mmol and 3.54 g, 29.8 mmol, respectively) in THF at −50 °C with 1.6 M *n*-BuLi (34.4 mL, 55.0 mmol and 20.6 mL, 33.0 mmol, respectively) and the addition of Me_3SiCl (6.93 mL, 54.6 mmol and 13.9 mL, 109 mmol, respectively). Yields: 5.2 (55%) and 4.8 mL (61%), respectively. $Me_3SiOCMe_2CMe_2OMe$ (bp: 171 °C, 1 atm) was prepared by lithiation of $Me_3SiOCMe_2CMe_2OH$ (4.0 mL, 21 mmol) with 1.6 M *n*-BuLi (13.1 mL, 21.0 mmol) in tetrahydrofuran at −50 °C and the addition of $C_7H_7SO_2OCH_3$ (3.3 mL, 22.0 mmol). Yield: 1.0 mL (24%). Distillation of these moisture sensitive products was conducted under N_2. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): $Me_3SiOCMe_2CMe_2OH$, $\delta = 1.20$ (s, $-C(CH_3)_2-$), 1.09 (s, $-C(CH_3)_2-$), 0.09 (s, $-Si(CH_3)_3$); $Me_3SiOCMe_2CMe_2OSiMe_3$, $\delta = 1.09$ (s, $-C(CH_3)_2-$), 0.07 (s, $-Si(CH_3)_3$); $Me_3SiOCMe_2CMe_2OMe$, $\delta = 3.20$ (s, $-OCH_3$), 1.18 (s, $-C(CH_3)_2-$), 1.08 (s, $-C(CH_3)_2-$), 0.07 (s, $-Si(CH_3)_3$) ppm.

Preparation of Bis[trioxo(methanol-*O*)(μ-methoxy)rhenium(VII)] (1). Method A. $Me_3SiOReO_3$ (0.324 g, 1.0 mmol) was dissolved in 7 mL of *n*-pentane, and Me_3SiOMe (0.28 mL, 2.0 mmol) was added dropwise. A white precipitate began to form after 15 min of vigorous stirring. The reaction was allowed to proceed for a total of 2 h. The volatile materials were then removed in vacuo, and the white precipitate was suspended in 25 mL of cold CH_2Cl_2. CH_3OH (0.05 mL, 1.2 mmol) was added slowly to the suspension, and the white precipitate slowly dissolved upon warming to room temperature to give a colorless solution. The solution was concentrated to 20 mL and upon cooling (−20 °C) afforded colorless crystals of **1** (0.211 g, 71%).

Method B. Five milliliters of CH_2Cl_2 was added to 0.324 g of $Me_3SiOReO_3$ (1.0 mmol) in a 20 mL Schlenk tube. The resulting colorless solution was layered with 12 mL of *n*-pentane. A mixture of Me_3SiOMe (0.28 mL, 2.0 mmol) and CH_3OH (0.05 mL, 1.2 mmol) was then carefully placed on top of the *n*-pentane layer. After the Schlenk tube was stored in a freezer at −20 °C for 2 weeks, X-ray quality rectangular crystals of **1** were isolated by decantation of the mother liquor (0.231 g, 78%). Compound **1** is only sparingly soluble in chlorinated hydrocarbons and insoluble in aromatic and aliphatic hydrocarbons. Chloroform solutions of **1** at room temperature and under nitrogen slowly decompose to unidentified green and black precipitates within 24 h. Compound **1** is extremely moisture sensitive, turning to a black oily material upon exposure to the atmosphere. However, crystals may be kept in a freezer at −20 °C for many weeks without significant decomposition.

^1H NMR (400 MHz, $CDCl_3$, 20 °C), δ: 3.94 (br s, $\nu_{1/2} = 36$ Hz, OCH_3), 1.87 ppm (br s, $\nu_{1/2} = 21$ Hz, OH). ^1H NMR (400 MHz, $CDCl_3$, 20 °C, **1** dried under vacuum for 10 min), δ: 3.78 ppm (s, $[ReO_3(OCH_3)]_n$). ^{17}O NMR (54.21 MHz, $CDCl_3$), δ: 750 ($Re{=}O^*$, $\nu_{1/2} = 800$ Hz, 20 °C), 756 ppm ($Re{=}O^*$, $\nu_{1/2} = 530$ Hz, −20 °C). IR (Nujol, dried in vacuo): 1011 (m), 978 (s), 964 (s), 950 (s), 924 (m), 899 (m), 832 (m), 721 (m). IR (**1** in $CDCl_3$): 3160 (m br), 2944 (m), 2833 (w), 1442 (m), 1412 (m), 1264 (w), 1013 (s), 967 (s), 867 (m), 831 (m), 574 (s). Compound **1** loses its methanol ligands very easily when under vacuum for short periods of time (ca. 5−10 min) to give $[ReO_3(OMe)]_n$ (characterized by IR and ^1H NMR).[4a] For this reason, we were unable to obtain an accurate analysis on a dried sample of **1**. A sample dried in vacuo for a few minutes was analyzed as $[ReO_3(OMe){\cdot}{}^1/_8MeOH]_2$. Anal. Calcd for $[(MeO)ReO_3{\cdot}{}^1/_8MeOH]_2$ (538.5): C, 5.02; H, 1.31; Re, 69.16. Found: C, 5.01; H, 1.29; Re, 68.38.

Preparation of [(2,3-Dimethyl-3-methoxy)propane-2-olato]trioxorhenium(VII) (2). To a vigorously stirred solution of $Me_3SiOReO_3$ (0.324 g, 1.0 mmol) in 10 mL of *n*-pentane was added $Me_3SiOCMe_2CMe_2OMe$ (0.21 mL, 1.02 mmol). After 3 min of stirring, an off-white precipitate formed. The reaction was stirred for an additional 2 h, the volatile materials were removed in vacuo at −20 °C, and the white residue was dissolved in 2 mL of toluene. This solution affords colorless crystalline plates of **2** after 3 days in a freezer at −20 °C. Compound **2** is moderately moisture sensitive, has good solubility in toluene, dichloromethane and chloroform, but is only sparingly soluble in *n*-pentane. Yield: 0.293 g (80%).

^1H NMR (270 MHz, $CDCl_3$, 20 °C), δ: 1.19 (s, 6 H, $-C(CH_3)_2-$), 1.40 (s, 6 H, $-C(CH_3)_2-$), 3.61 ppm (s, 3 H, $-OCH_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 20 °C), δ: 18.6, 24.1 ($-C(CH_3)_2-$), 52.0 ($-OCH_3$), 82.9, 93.4 ppm ($-C(CH_3)_2-$). ^{17}O NMR (54.21 MHz, CH_2Cl_2/tol-d_8, −90 and 20 °C), δ: 764 ($Re{=}O^*$, $\nu_{1/2} = 230$ Hz, −90 °C), 730 ($Re{=}O^*$, $\nu_{1/2} = 220$ Hz, −90 °C), 744 ($\nu_{1/2} = 30$ Hz, 20 °C), 225 ($Re{-}OCMe_2{-}$, $\nu_{1/2} = 339$ Hz, 20 °C), 58 ppm ($Re{-}OMe$, $\nu_{1/2} = 305$ Hz, 20 °C). IR (Nujol): 1408 (m), 1214 (m), 1183 (m), 1146 (s), 1126 (s), 1045 (s), 1007 (m), 934 (s), 894 (s), 792 (m), 716 (m), 621 (m). Anal. Calcd for $C_7H_{15}O_5Re$ (365.4): C, 23.01; H, 4.14; Re, 50.96. Found: C, 22.80; H, 4.01; Re, 50.18.

Preparation of [(2,3-Dimethyl-3-hydroxy)propane-2-olato]trioxorhenium(VII) (3). $Me_3SiOReO_3$ (0.324 g, 1.0 mmol) was dissolved in 10 mL of *n*-pentane, and $Me_3SiOCMe_2CMe_2OH$ (0.20 mL, 1.0 mmol) was added dropwise. A white precipitate starts to form approximately 1 min after addition of $Me_3SiOCMe_2CMe_2OH$. After the reaction mixture was stirred for 30 min, the solvent was removed under reduced pressure and the white precipitate was dissolved in 5 mL of CH_2Cl_2. The resulting pale yellow solution was cooled to −20 °C. Colorless parallelepiped-shaped crystals appeared after 3 days (0.289 g, 82%). Compound **3** is moisture sensitive, has moderate solubility in chlorinated hydrocarbons and tetrahydrofuran, is badly soluble in toluene, and is insoluble in *n*-pentane.

^1H NMR (400 MHz, $CDCl_3$, 20 °C), δ: 1.26 (s, 6 H, $-C(CH_3)_2-$), 1.44 (s, 6 H, $-C(CH_3)_2-$), 5.38 ppm (s, 1 H, $-OH$). ^1H NMR (400 MHz, THF-d_8, 20 °C), δ: 1.31 ppm (s, 2 $-C(CH_3)_2-$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 20 °C), δ: 23.3, 24.0 ($-C(CH_3)_2-$), 78.5, 95.0 ppm ($-C(CH_3)_2-$). $^{13}C\{^1H\}$ NMR (100.5 MHz, THF-d_8, 20 °C), δ: 23.6, 24.2 ($-C(CH_3)_2-$), 78.0, 92.8 ppm ($-C(CH_3)_2$).^{17}O NMR (54.21 MHz, $CDCl_3$, 20 °C), δ: 747 ($Re{=}O^*$, $\nu_{1/2} = 40$ Hz), 74 ppm ($Re{-}OH$, $\nu_{1/2} = 118$ Hz). ^{17}O NMR (54.21 MHz, THF/$CDCl_3$, 20 °C), δ: 751 ($Re{=}O^*$, $\nu_{1/2} = 40$ Hz), 73 ($Re{-}OH$, $\nu_{1/2} = 200$ Hz), 216 ppm ($Re{-}OCMe_2{-}$, $\nu_{1/2} = 600$ Hz). IR (Nujol): 3182 (s br), 1233 (w), 1192 (w), 1160 (m), 1133 (m), 1127 (m), 984 (m), 953 (s), 925 (s), 892 (s), 863 (s), 842 (s), 715 (m), 668 (w), 615 (m). Anal. Calcd for $C_6H_{13}O_5Re$ (351.4): C, 20.48; H, 3.73; Re, 52.99. Found: C, 20.41; H, 3.72; Re, 53.23.

Preparation of Dioxo(η^2-*O,O′*-pinacolato)(trimethylsilanolato)rhenium(VII) (4). $Me_3SiOReO_3$ (0.324 g, 1.0 mmol) was dissolved in 5 mL of *n*-pentane, and $Me_3SiOCMe_2CMe_2OSiMe_3$ (0.26 mL, 1.0 mmol) was added dropwise. The resulting yellow solution was stirred for 24 h, concentrated to 2 mL, and placed in a freezer at −20 °C. Large rectangular-shaped yellow crystals appeared after 2 days (two crops, 0.323 g, 76%). The crystals of **4** are very volatile. They melt at room temperature to initially give a yellow liquid which then rapidly turns dark brown. *n*-Pentane solutions of **4** under nitrogen turn orange-brown over a 3 day period, while toluene and chloroform solutions change color over 1−2 h at room temperature. The identity of the orange-brown reduction products has not been determined.

^1H NMR (400 MHz, $CDCl_3$, 20 °C), δ: 0.22 (s, 9 H, $-Si(CH_3)_3$), 1.37 (s, 12 H, 2 $-C(CH_3)_2-$) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 20 °C), δ: 0.31 ($-Si(CH_3)_2$), 24.7 (br, $\nu_{1/2} = 53$ Hz, $-C(CH_3)_2-$) ppm. ^{17}O NMR (54.21 MHz, $CDCl_3$, −20 °C), δ: 755 (Re═O*, $\nu_{1/2} = 40$ Hz), 731 (Re═O*, $\nu_{1/2} = 55$ Hz), 199 (Re−OC, $\nu_{1/2} = 150$ Hz), 186 (Re−O*Si, $\nu_{1/2} = 120$ Hz), 59 ppm (Re−OSi (ether)). IR (Nujol): 1251 (s), 1198 (w), 1170 (m), 1146 (s), 1004 (w), 989 (m), 962 (s), 948 (s), 912 (s), 884 (s), 846 (s), 756 (m), 721 (s), 673 (w), 638 (m), 623 (m). Elemental analysis was not successful as a consequence of the moisture and temperature sensitivity of the crystals.

Preparation of Lithium Trioxo(tetramethylethylene glycolato-*O,O′*)rhenate(VII) (5). Compound **3** (0.351 g, 1.0 mmol) was dissolved in 8 mL of THF. The solution was cooled to −60 °C. In a separate flask, lithium 2,2,6,6-tetramethylpiperidinate (0.147 g, 1.0 mmol) was dissolved in 5 mL of THF. This solution was slowly added by cannula to the flask containing the solution of **3**, and the combined solutions were allowed to slowly warm to room temperature. The resulting light yellow solution was concentrated to ca. 5 mL, and 15 mL of a 3:1 CH_2Cl_2/*n*-pentane mixture was added. A flocculent white precipitate immediately formed, and the precipitate was filtered off and washed with 20 mL of *n*-pentane and 10 mL of CH_2Cl_2. The precipitate was dried under reduced pressure, and the crude product was collected (0.281 g, 79%). Crystallization from THF by layering with *n*-pentane gave white feathery crystals (0.241 g, 68%).

^1H NMR (400 MHz, THF-d_8, 20 °C), δ: 1.15 ppm (s, 2 $-C(CH_3)_2-$). $^{13}C\{^1H\}$ NMR (100.5 MHz, THF-d_8, 20 °C), δ: 25.5 (2 $-C(CH_3)_2-$), 85.4 ppm (2 $-C(CH_3)_2-$). ^{17}O NMR (54.21 MHz, THF-d_8, 20 °C), δ: 621 ppm (Re═O, $\nu_{1/2} = 50$ Hz). IR (Nujol): 1205 (w), 1154 (m), 1141 (w), 1012 (w), 972 (m), 963 (s), 909 (w), 878 (s), 846 (s), 722 (s), 626 (s). Anal. Calcd for $LiC_6H_{12}O_5Re$ (357.3): Li, 1.94; C, 20.17; H, 3.38; Re, 52.11. Found: Li, 1.80; C, 19.49; H, 3.33; Re, 51.41.

X-ray Crystal Structure Determinations. All crystals were prepared in dried paraffin oil under air. After the crystal was fixed on top of a glass rod, they were moved very quickly into the cooling nitrogen stream of the diffractometer. All crystals were colorless fragments. Determination of the crystal size was uncertain due to the preparation method. All data collections were carried out with graphite-monochromatized Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer. Final cell constants were obtained by least-squares refinement of 25 automatically centered reflections (**1**, $40.7 < 2\Theta < 49.8$; **2**, $30.6 < 2\Theta < 36.8$; **3**, $30.3 < 2\Theta < 39.1$; **4**, $2.8 < 2\Theta < 18.1$). Data were collected in the ω-scan mode. Orientation control reflections were monitored every 100 reflections, and intensity control reflections were monitored every 60 min. All data sets were corrected for Lorentz and polarization terms. A decay in intensity was corrected for in **2**, **3**, and **4**. Empirical absorption correction (ψ-scans) was applied to the data sets of **1**, **2**, and **3** (T_{max}/T_{min}: **1**, 1.0/0.37; **2**, 1.0/0.60; **3**, 1.0/0.67). No extinction correction was necessary. Crystal data and refinement parameters are summarized in Table 6.

The structures were solved by Patterson methods and subsequent difference Fourier techniques. Full-matrix least-squares refinements were carried out by minimizing $\sum w(|F_o| - |F_c|)^2$. Hydrogen atoms were calculated in their ideal positions (d_{C-H}/d_{O-H}: 0.96/0.92 Å, $U_H = 1.3U_{C/O}$) and included in the data set but not refined. In **1**, one hydrogen atom was found at C1 and was used to determine the orientation of the methyl group. The position of the methanol proton at O2 was determined by the short intermolecular oxygen−oxygen distance of 2.77 Å, suggesting the presence of a hydrogen bridge. A Chebyshev polynomial weighting scheme was used in all refinements.[16a] The refinements were stopped at shift/err <0.001. Final difference Fourier maps showed residual electron density in **1** (5.6 eÅ^{-3} 0.97 Å near Re) and **4** (4.5 eÅ^{-3} 0.84 Å near Re) indicating unsatisfactory absorption corrections. All calculations were performed on MicroVAX 3100 and DECStation 5000/25 computers using the programs or program systems STRUX-IV,[16b] CRYSTALS,[16c] PLATON-93,[16d] SDP,[16e] and SHELXS86.[16f]

Table 6. Crystallographic Data of Complexes **1**−**4**[a]

	1	**2**	**3**	**4**
fw	594.56	365.40	351.37	423.55
space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)	*C*2/*c* (No. 15)	*P*2$_1$/*c* (No. 14)
a (Å)	6.276(3)	8.263(2)	12.327(5)	12.042(8)
b (Å)	6.720(3)	10.884(3)	10.973(3)	10.782(2)
c (Å)	8.005(4)	22.963(5)	14.491(6)	12.485(9)
α (deg)	109.39(3)			
β (deg)	99.48(3)		90.22(2)	117.44(3)
γ (deg)	110.31(2)			
V (Å^3)	238.3	2065.2	1960	1439
D_{calc} (g cm^{-3})	3.49	2.35	2.38	1.96
Z	1	8	8	4
μ (cm^{-1})	214	117.6	123.8	85.3
temp (°C)	−80 ± 4	−80 ± 4	22 ± 3	−80 ± 4
measured	2129	4221	3073	4797
unique data	982	1719	1611	2436
data used	982	1550	1611	2069
$I/\sigma(I)>$	0	1	0	2
parameters	73	178	109	145
R^b	0.050	0.044	0.047	0.044
$R_w{}^c$	0.056	0.028	0.030	0.044

[a] **1**, $[ReO_3(OMe)(MeOH)]_2$; **2**, $ReO_3(OCMe_2CMe_2OMe)$; **3**, $ReO_3(OCMe_2CMe_2OH)$; **4**, $(Me_3SiO)ReO_2(OCMe_2CMe_2O)$. [b] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers. CSD-406127 (**1**), CSD-406128 (**2**), CSD-406129 (**3**), and CSD-406130 (**4**).

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Supporting Information Available: Tables of ^{17}O NMR data of perrhenyl and perrhenate complexes, IR data of selected perrhenate complexes, and ^{17}O NMR data of complexes **1** to **5** (2 pages). X-ray crystallographic files in CIF format for compounds **1** to **4** are available on the Internet only. Access and ordering information is given on any masthead page.

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