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Multiple Bonds between Main-Group Elements and Transition Metals. 86.[1] Methyltrioxorhenium(VII) and Trioxo(η^5-pentamethylcyclopentadienyl)rhenium(VII): Structures, Spectroscopy, and Electrochemistry

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Abstract: Two key compounds of organometal oxides, methyltrioxorhenium(VII) (**1**) and trioxo(η^5-pentamethylcyclopentadienyl)rhenium(VII) (**2**), have been structurally characterized by means of electron diffraction techniques, showing that the ReO_3 fragments of these compounds have trigonal-pyramidal structures in the gas phase. The rhenium–carbon distance of the 14e complex **1** amounts to 206.0 (9) pm, which is the shortest Re–C(sp^3) bond so far recorded. The pentamethylcyclopentadienyl derivative **2** has the longest known rhenium–carbon bond (240.5 (6) pm) due to the size of this particular π-bonded ligand and the σ/π-donor properties of the oxo ligands ("trans influence"). Infrared and Raman spectra show a much higher triple-bond contribution in the rhenium–oxygen bonds of **1** (force constant $\kappa = 8.16$ mdyn/Å) compared with **2** ($\kappa = 6.99$ mdyn/Å). The π-donor qualities of the ring ligand of **2** are considered the major effect to reduce the rhenium–oxygen bond order of this 18e compound since the σ-aryl complex (σ-$C_6H_2Me_3$)ReO_3 (**3**) has a force constant of $\kappa = 8.08$ mdyn/Å. According to cyclovoltammetric data, the methyl derivative **1** is more easily reduced ($E_{pc} = -0.84$ V vs Ag/AgCl, THF, 20 °C) than the half-sandwich congener **2** ($E_{pc} = -1.72$ V), again reflecting the electronic situation of the two compounds (14e vs 18e, respectively). The first vertical PE ionization energies of **1** and **2**, 11.8 and 8.6 eV, differ by 3.2 eV due to their different radical-cation ground states, $\tilde{X}(a_2n_0)$ and $\tilde{X}(e,\pi_{Cp\bullet})$. The equivalent oxygen lone pair type ionization of **2**, $IE^V{}_2(a_2,n_0) = 9.9$ eV, is lower by 1.9 eV and gives proof of the electron donation from the η^5-bonded π-ligand C_5Me_5. In addition, the PE spectrum of trioxo(η^1-mesityl)rhenium(VII) (**3**) has been recorded: Its first ionization energy of 9.00 eV exceeds the corresponding one of mesitylene by 0.6 eV, thus demonstrating the considerable acceptor effect of the ReO_3 substituent group toward an η^1-bonded π ligand. The high electric dipole moment of **2** ($\mu = 6.2$ D; benzene, 25 °C) appears reasonable in light of the high polarizability of the C_5Me_5–Re bond (approximately 4 D); the ReO_3 unit has a dipole increment of ca. 2.2 D in **1** and **2**. NMR and PE spectra clearly show that the ReO_3 functionality is a strong electron-withdrawing substituent, stereoelectronically comparable with the SO_3H substituent in organic compounds.

Introduction

High oxidation state organometallic oxides[3] have been attracting attention in many terms, particularly since the organorhenium(VII) key complexes CH_3ReO_3 (**1**)[3-5] and (η^5-C_5Me_5)ReO_3 (**2**; Me = CH_3)[3,6] are now accessible via directed syntheses. The chemistry of the half-sandwich complex **2** has set the scene for practical applications of this and related species, with the catalytic versatility of methyltrioxorhenium(VII) for oxidation and metathesis of olefins as well as for the olefination of aldehydes adding further justification to continued work in this area.[7,8] Related chemistry promises interesting synthetic applications of these and similar compounds.[9,10]

Slightly oversimplistic but still meeting the facts, one can conclude that the less reactive complex **2** *models* reactions that are *catalytic* with the methyl derivative **1**.[7] Any possible method of characterization is thus required to gain better understanding of the differences in chemical behavior: structural investigations, vibrational and NMR spectroscopy, dipole moment measurements,

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[2] (a) Technische Universität München. (b) University of Oslo. (c) Universität Frankfurt. (d) Institute of Isotopes. (e) University of Arizona. (f) Postdoctoral Research Fellow of the Alexander von Humboldt Foundation, 1988/1990. (g) Doctoral Fellow of the Fonds der Chemischen Industrie. (h) Doctoral Fellow of the Hanns Seidel-Stiftung e.V.

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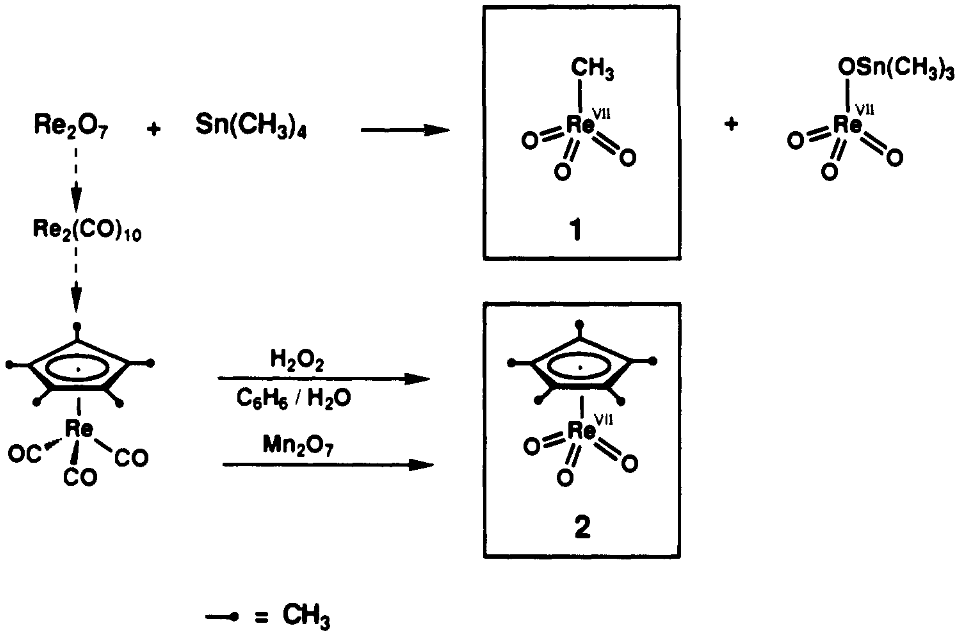
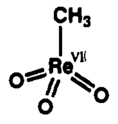
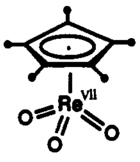
Scheme I



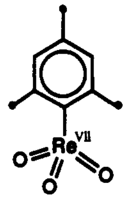
photoelectron ionization patterns, electrochemistry. As the first comprehensive report in this area, this paper summarizes and explains our results, including a comparison of the title compounds **1** and **2** with the σ-mesityl complex **3**[11a] and related derivatives **4** (silaneopentyl)[11b] and **5** (hydridotris(pyrazolyl)borato).[11c]



1



2



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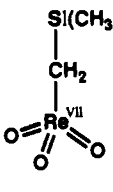

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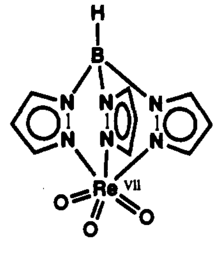

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Results and Discussion

The compounds under discussion were prepared according to Scheme I by direct alkylation of dirhenium heptoxide (for **1**) and by oxidation of the carbonylrhenium(I) precursor ($(\eta^5\text{-}C_5Me_5)Re(CO)_3$) with dimanganese heptoxide (for **2**). The latter procedure is most effective unless quantities of ca. 5 g are exceeded. The oxidant Mn_2O_7 can be handled in carbon tetrachloride solutions according to Trömel[12] without danger of explosion (cf. the Experimental Section). Small amounts of pure **2** can be generated by using dimethyldioxirane as a new, clean oxidant.[5a] A detailed procedure for methyltrioxorhenium(VII) was given in a previous publication of this series.[5b]

Both compounds can easily be purified by sublimation in vacuo (white and yellow needles, respectively). They are thermally very stable and robust against oxygen. While **2** is not attacked by tertiary amines and dilute aqueous hydroxides, the electronically unsaturated, sterically more easily accessible methyltrioxorhenium(VII) (**1**) forms adducts with various amines.[5b] Furthermore, the compound instantaneously "decomposes" in alkaline solutions according to eq 1, with the same chemistry applying to

$$CH_3ReO_3 + [OH]^- \rightarrow [ReO_4]^- + CH_4 \qquad (1)$$

the less stable technetium complex CH_3TcO_3.[13] The π complex **2** survives both LiOH and concentrated HCl in THF solution for several days at room temperature. Only concentrated aqueous alkaline hydroxide effects (slow) decomposition (THF solution, 25 °C) with formation of pentamethylcyclopentadiene and sodium perrhenate (cf. eq 1).

The two rhenium compounds display a striking difference in their behavior toward water: CH_3ReO_3 (**1**) dissolves in water with quick exchange of the oxygen atoms (labeling experiments with $H_2{}^{17}O$).[14] By way of contrast, $(\eta^5\text{-}C_5Me_5)ReO_3$ (**2**) is insoluble in water and it does not exchange the oxygen atoms in a THF/$H_2{}^{17}O$ solution. Indirect syntheses are therefore to be used for oxygen-labeled samples of **2**.[15]

The byproduct (trimethylstannyl)perrhenate, $(CH_3)_3SnOReO_3$ (Scheme I), has been assigned a polymeric chain-type structure (five-coordinate tin; X-ray diffraction) that accounts for the low volatility of this particular compound.[16]

Structural Studies: Gas-Phase Electron Diffraction

The crystallographic problem that we had encountered with the half-sandwich complex **2** could be solved by using the less symmetrical *ethyl* derivative $(\eta^5\text{-}C_5Me_4Et)ReO_3$ (**2'**), the crystal structure determination of which was of good precision.[17] It was thus shown that this class of compounds is monomeric in the crystal, having a π-bonded organic ring ligand.[17]

(1) Methyltrioxorhenium(VII). Since methyltrioxorhenium(VII) decomposes under X-ray irradiation even at low tempera-

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Table I. Geometrical Parameters and Root-Mean-Square Amplitudes of Vibration (*l* Values) for Methyltrioxorhenium(VII) (**1**) in the Gas Phase[a]

Distances, pm		
bond dist	r_a	l
Re=O	170.9 (3)	3.1 (2)
Re—C	206.0 (9)	6.2 (7)
C—H	110.5 (1.2)	6.1 (1.6)
nonbonding dist	r_a	l
Re···H	268 (3)	13 (3)
O···O	284.6 (3)	6.0 (5)
O···C	301.8 (7)	8.7^c
O···H(long)	397 (3)	11.7^c
O···H(short)	328 (3)	15.4^c
H···H	177 (5)	13.3^c
Angles, deg		
Re-C-H	112 (3)	
C-Re-O	106.0 (2)	
O-Re-O[d]	113.0 (3)	

[a] The estimated errors are the least-squares standard deviations multiplied by 2 in order to compensate for the systematic errors introduced by the assumptions and added 0.1% for the uncertainty in the *s* scale. [b] $R(50) = 3.1$; $R(25) = 7.2$; $R(\text{tot}) = 4.0$; see Table II for definition of *R*. [c] Fixed values, taken from preliminary harmonic force field calculations. [d] Dependent angle.

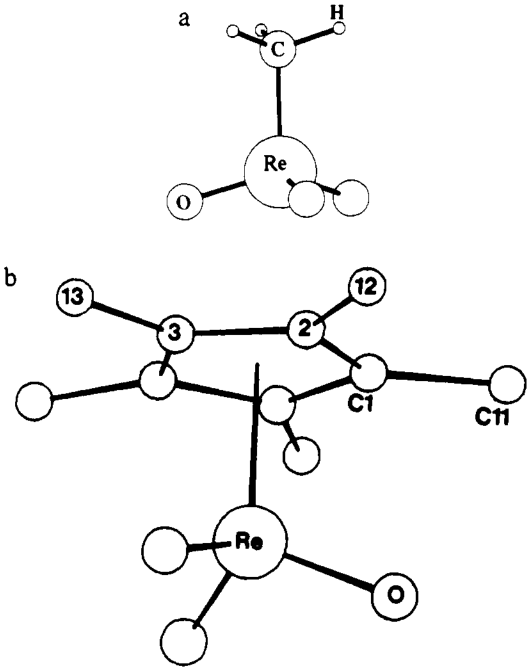

Figure 1. Molecular models of the rhenium(VII) title compounds **1** (a) and **2** (b) in the gas phase.

tures,[18] we determined the structure in the gas phase by virtue of electron diffraction techniques. The final geometrical parameters and root-mean-square amplitudes of vibration (*l* values) are summarized in Table I. The molecular model is presented in Figure 1, while Figures 2 and 3 show radial distribution and molecular intensity curves, respectively.

(a) Rhenium–Carbon Bond. The electron diffraction data of methyltrioxorhenium(VII) are consistent with a molecular model of C_{3v} symmetry. The *rhenium–carbon bond distance* of 206.0 (9) pm is remarkably short. The structurally analogous σ-mesityl compound **3** (203 pm, average)[11] and complexes $(C_6H_5)_3Re[PEt_2(C_6H_5)]_2$, $Re(o\text{-tolyl})_4$, and $O_2Re(mesityl)_4$ (202–206 pm)[19] have slightly shorter metal–carbon distances but exhibit sp^2-hybridized carbon atoms attached to the metals so a π-bond contribution is likely. In the neopentylrhenium(VII) oxide $[(CH_3)_3CCH_2]_3ReO_2$, rhenium–carbon bonds between 212 and 217 pm have been found.[20] All known rhenium–carbon single bonds, no matter which type of carbon ligand is attached to the metal, range from 202 to 230 pm by distance.[21]

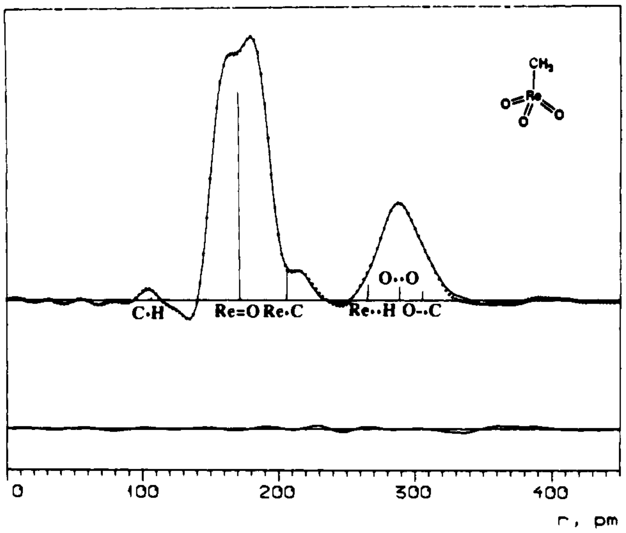

Figure 2. Theoretical radial distribution (RD) curve with experimental points for methyltrioxorhenium(VII) (**1**). The main distances are indicated by bars, with heights approximately proportional to the scattering contribution of the distance. In the lower part of the figure the difference between experimental and theoretical curves is drawn.

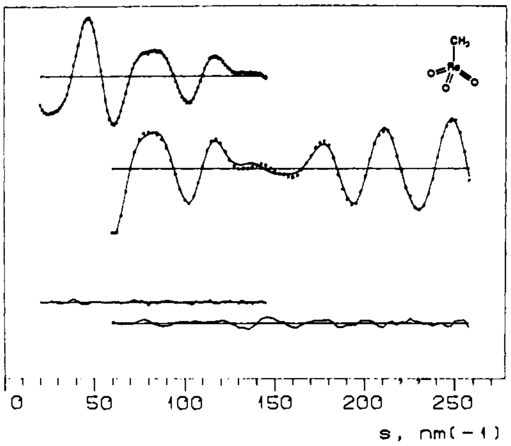

Figure 3. Theoretical molecular intensity curves with experimental points for methyltrioxorhenium(VII) (**1**). In the lower part of the figure the difference between experimental and theoretical curves is drawn.

A schematic representation of single-, double-, and triple-bond ranges is given in Figure 6. It can be seen that the title compound **1**, in spite of the short distance, is to be classified as an alkyl complex; a carbenoid bonding contribution cannot be concluded from the structural data. High oxidation state metals in general favor short bonds, but steric effects may reverse this trend. Methyltrioxorhenium(VII) is the least strained organometal oxide known, so we believe the recorded quantity of ca. 206 pm corresponds to a standard Re(VII)–C(sp^3) distance for CN 4 rather

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(18) Tentative X-ray crystal structure data were gratefully submitted to us by Dr. Nugent of DuPont, Wilmington: *d*(Re–C) ≈ 204 pm; *d*(Re–O) ≈ 168 pm. Identical results were obtained in our structure laboratory (X-ray diffraction): Herrmann, W. A.; Kiprof, P. Unpublished results, 1988/89. Kiprof, P. Ph.D. Thesis, Technische Universität München, 1991.

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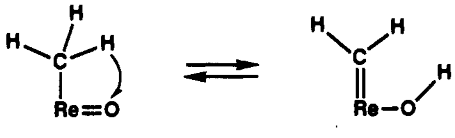
(21) Data obtained from a *CAS* on-line evaluation (95 compounds containing Re–C bonds), Jan 1990. Cf.: Kuchler, J. G. Ph.D. Thesis, Technische Universität München, 1990.

Table II. Geometrical Parameters, Root-Mean-Square Amplitudes of Vibration (*l* Values), and *R* Factors for Trioxo(η^5-pentamethylcyclopentadienyl)rhenium(VII) (**2**) in the Gas Phase (Results Obtained by Using the Phase Shifts for Atomic Numbers 75 and 78 for the Rhenium Atom Are Shown)[a]

	η (Z = 75)		η (Z = 77)	
	r_a	l	r_a	l
	Bond Distances, pm			
Re=O	171.5 (4)	3.1 (8)	171.6 (3)	3.9 (5)
h^b	206.2 (10)		207.0 (10)	
Re—C(C_5Me_5)	239.8 (7)	8.0 (10)	240.5 (6)	8.0 (7)
C(1)—C(2)	144.0 (7)	4.8^c	143.9 (7)	$5.8\ (9)^d$
C(1)—C(11)	150.3 (9)	5.3^c	150.9 (9)	$6.3\ (9)^d$
C—H	113.0 (13)	10.9 (14)	112.2 (10)	10.6 (9)
	Nonbonding Distances, pm			
Re···C(CH_3)	342	17.2 (14)	343	17.0 (11)
Re···H(long)	439	22^c	441	22^b
Re···H(short)	355	30^b	359	30^b
C(1)···C(3)	233	6.6^c	233	6.6^c
C(1)···C(12)	262	7.7^c	263	7.7^c
C(1)···C(13)	379	8.0^c	379	8.0^c
C(11)···C(12)	321	12.6^c	321	12.6^c
C(11)···C(13)	513 (3)	6.6 (30)	514 (2)	6.8 (24)
O···O	275	7.0 (20)	277	7.6 (16)
	Angles, deg			
C_5–C(1)–C(11)	0.0 (9)		0.0 (8)	
C–C–H	107.3 (19)		109.7 (15)	
S–Re–O	112.0 (10)		111.3 (8)	
	R Factors[e]			
R(50)	3.8		3.1	
R(25)	13.9		10.4	
R(tot)	6.2		4.8	

[a] Estimated errors are $3\sigma_{ls}$. [b] Length of line through rhenium and orthogonal to the C_5Me_5 ring. [c] Fixed values. [d] Refined with equal shift in the least-squares analyses. [e] $R = [w(I_o - I_c)^2/wI_o^2]^{1/2}$.

than representing an exceptionally short bond. We have not found evidence for a carbene-type contribution B on the basis of vibrational and NMR spectroscopy. For example, the ^{13}C NMR spectrum of **1** exhibits a quartet at $\delta(CH_3)$ = 19.03 ppm with ^2J(C,H) = 138 Hz—quite normal for an sp^3-hybridized alkyl carbon atom (solvent $CDCl_3$, 20 °C). No hydroxy band is seen in the IR spectra. "Agostic" interactions between hydrogen and oxygen atoms of **1** are not evident.



A **B**

(b) Rhenium-Oxygen Bonds. A statistical study of *rhenium-oxygen bond distances* in trioxo complexes of the type $LReO_3$ gives a mean value of 170.8 pm and a median of 171.0 pm[22] so the distance of 170.9 (3) pm found for **1** is unexceptional. The C-Re-O bond angle of 106.0 (2)° reflects the steric demand of the three oxygen atoms, showing that similar steric requirements are present in the σ-aryl compound **3** (C-Re-O = 108°, average).[11]

(2) Trioxo(η^5-pentamethylcyclopentadienyl)rhenium(VII). The gas-phase structure of the half-sandwich complex **2** (Table II; Figures 1, 4, and 5) is consistent with a molecular model where the ReO_3 fragment has local C_{3v} symmetry and the C_5Me_5Re fragment has C_{5v} symmetry. The main structural parameters are identical within the standard deviations with those of a previous X-ray crystal structure of the derivative (η^5-C_5Me_4Et)ReO_3.[17] A comparison of data is given in Table III.

The very long Re-C bond distances are independently confirmed by the present electron diffraction study. These bonds are ap-

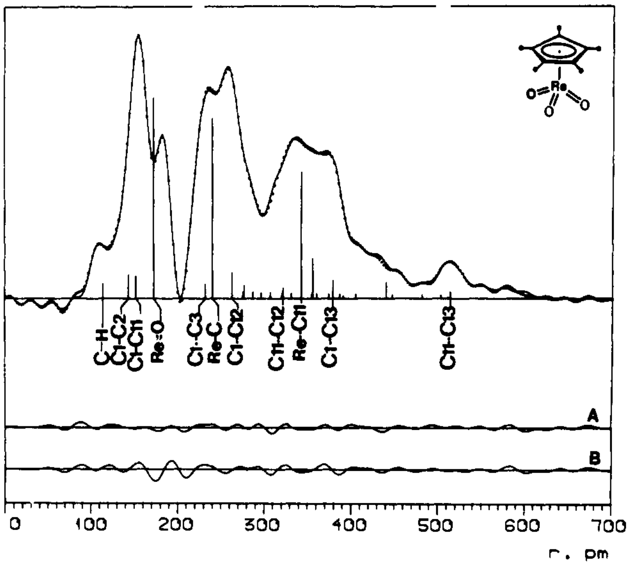


Figure 4. Theoretical radial distribution (RD) curve for trioxo(η^5-pentamethylcyclopentadienyl)rhenium(VII) (**2**). The main distances are indicated by bars with heights approximately proportional to the scattering contribution of the distance. In the lower part of the figure the differences between experimental and theoretical curves by using phase factors corresponding to atomic numbers 78 (A) and 75 (b) for Re are drawn.

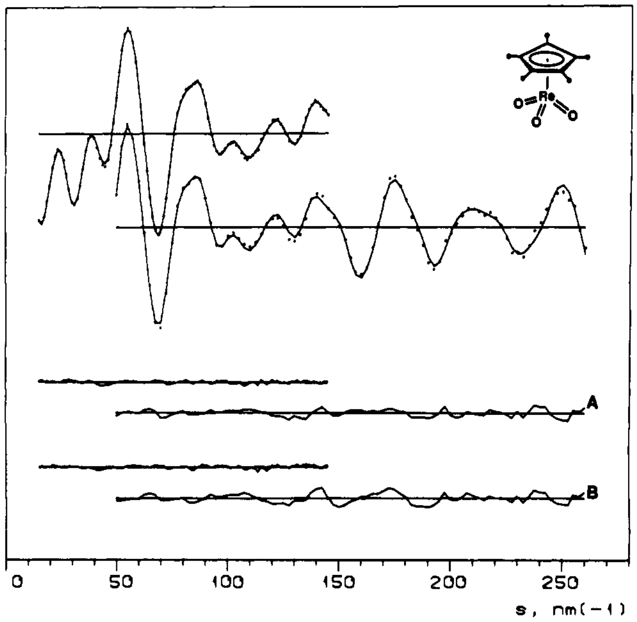


Figure 5. Theoretical molecular intensity curves with experimental points for trioxo(η^5-pentamethylcyclopentadienyl)rhenium(VII) (**2**). In the lower part of the figure the differences between experimental and theoretical curves by using phase factors corresponding to atomic number 78 (A) and 75 (B) for Re are drawn.

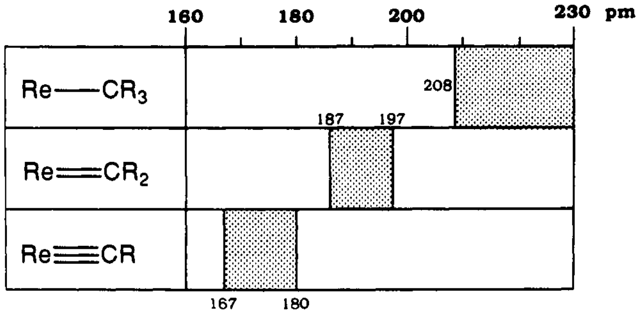


Figure 6. Rhenium-carbon bond lengths: single, double, and triple bonds. This schematic classification is based upon 95 compounds that appeared in a Cambridge Data File search in Jan 1990.

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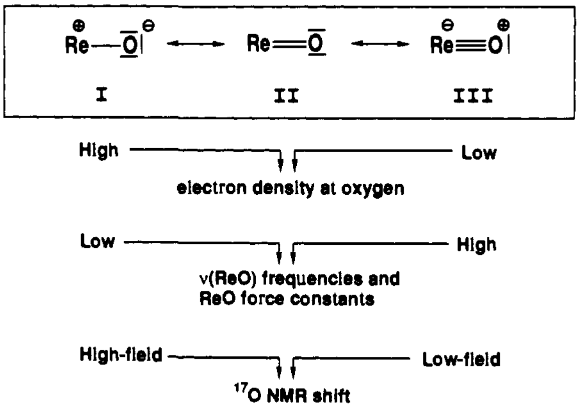
(22) Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899.

Table III. Comparison of Relevant Bond Distances (pm) and Angles (deg) of the Organorhenium(VII) Oxides **1**, **2**, **2′**, and **3**[a]

	1[b] (gas phase)	**2**[b] (gas phase)	**2′** (crystal)	**3** (crystal)
Re–C	206.0 (9)	240.5 (6)	240 (av)	203 (av)
Re–O	170.9 (3)	171.6 (3)	170 (av)	168.5 (av)
O–Re–O′	113.0 (3)	107.0 (3)	105 (av)	110 (av)

[a] Data for **2′** from ref 17; data for **3** from ref 11. [b] This paper.

Scheme II



proximately 10 pm *longer* than in the closely related hydrido compound (η^5-C_5Me_5)ReH_6, the value of which (230.9 (4) pm)[23] is comparable with those of π-cyclopentadienyl complexes lacking oxo ligands, e.g., (η^5-C_5H_5)$Re(CO)_3$.[17] In light of this comparison, our early proposal that strong π donation of the three oxo ligands elongates the Re–C bonds in trans positions receives support.[24] This has been called an anti effect since the elongation is observed anti to the oxo ligand(s).[25] An explanation for the lengthening in terms of molecular orbitals has been given on the basis of ab initio Hartree–Fock calculations of the (hypothetical) compound (η^5-C_5H_5)ReO_3[62] and of (known) (η^5-C_5H_5)$Re(CO)_3$.[26] Within a "molecules in molecule" MO perturbation approach, the weakening is a consequence of increased metal d character of the LUMO of the ReO_3 fragment compared to that of the $Re(CO)_3$ fragment, which is predominantly of p character. In qualitative MO arguments, the increased d character should result in a poorer overlap with the π system of the C_5H_5 ring ligand and thus in a weaker and longer C_5H_5–Re bond.[26] Hydrido ligands do not display electron donation properties or trans influence, so the shorter Re–C distances of (η^5-C_5Me_5)ReH_6 are reasonable.[23]

Vibrational and NMR Spectra

A bonding description of oxorhenium compounds (ReO_x fragments) relies on vibrational and NMR data (Tables IV and V) since metric parameters from electron or X-ray diffraction studies prove rather insensitive with respect to structural changes. Rhenium–oxygen bond distances of 165–176 pm cover the entire range of oxidic rhenium compounds.[10,21,22] It is thus not surprising that compounds **1**–**3** exhibit very similar rhenium–oxygen bond distances of approximately 170 pm. Even potassium perrhenate is close to this value (172 pm, average)[27] in spite of the negative charge that is expected to drive the ground-state resonance contribution toward I (Scheme II).

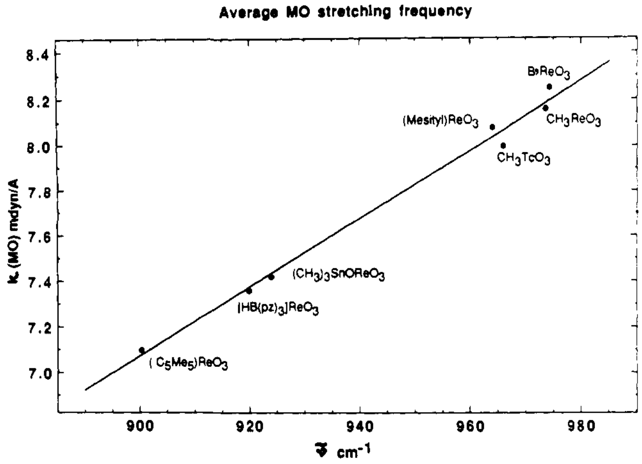


Figure 7. Correlation between metal–oxygen stretching force constants κ(MO) and average Mo stretching frequencies (ν), with $\nu = {}^1/_3[2\nu(e) + \nu(a_1)]$, for compounds of type $XReO_3$ and $XTcO_3$. Frequencies are taken from Table IV and force constants from Table VI. It can be seen that the two title complexes **1** and **2** cover the entire range between high and low ReO bond orders, respectively (see text).

The valence resonance formulas II and III represent the bond formalism in organometal oxides. High-frequency ReO stretching vibrations in the IR spectra and low-field signals in the ^{17}O NMR spectra indicate the double-bond contribution III. As can be judged from the positions of the ν(ReO) bands in the infrared spectra and particularly from the calculated force constants (Table VI), the rhenium-oxygen bond order *increases* in the series

$$\underset{\mathbf{2}}{(\eta^5\text{-}C_5Me_5)ReO_3} < \underset{\mathbf{5}}{[HB(pz)_3]ReO_3} < CH_3TcO_3 < \underset{\mathbf{3}}{(\sigma\text{-Mes})ReO_3} < \underset{\mathbf{1}}{CH_3ReO_3}$$

The *decreasing* electron density at oxygen in the same order is reflected in a low-field chemical shift as observed in the ^{17}O NMR spectra (Table IV). The high-field signal in the ^{17}O NMR spectra of the perrhenate ion (δ 562, Table IV) is explained in terms of the negative charge distributed about the four oxygen atoms (resonance contribution I). Since the geometrical details of compounds **1**–**3** and of $[ReO_4]^-$[27] are similar, we invoke electronic factors to be responsible for the observed differences in rhenium–oxygen bond orders. Thus, the π-bonded *pentamethylcyclopentadienyl* ligand acts as a rather strong electron-donating ligand to the ReO_3 fragment so the resonance contribution III is less important. In the *methyl* derivative **1**, no such electron-releasing ligand is present; electron donation from three oxo ligands (π donation) is the only way to alleviate electron deficiency at the metal atom, compatible with a stronger contribution of form III. The σ-mesityl derivative **3** stands between the aforementioned two compounds: In electronic terms, the σ-bonded aryl ligand is closer to a methyl group than to the five-membered π ligand. This assessment is also supported by the *ReO* force constant of $BrReO_3$, κ = 8.25 mdyn/Å (Table IV), in which case the electronegativity of the bromo ligand prevents extensive π back-bonding, so Br and CH_3 are similar in their effect upon the ReO bonding.[30] A correlation between ReO force constants and average ReO stretching frequencies is shown in Figure 7.

In keeping with this argument, compounds **1**, **3**, and **4** form adducts with N bases such a quinuclidine, react with organolithiums RLi to form anions $[XReO_3R]^-$ (X = CH_3, mesityl),[28] exchange oxo groups with (labeled) water, and react with hydroxides to form perrhenate and the corresponding hydrocarbon (eq 1). By way of contrast, complex **2** is rather inert.

Table IV also shows that the stannylperrhenate $(CH_3)_3SnOReO_3$[4,16] spectroscopically relates to simple perrhenate.

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(23) (a) Herrmann, W. A.; Okuda, J. *Angew. Chem.* **1986**, *98*, 1109; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1092. (b) Herrmann, W. A.; Theiler, H. G.; Kiprof, P.; Tremmel, J.; Blom, R. *J. Organomet. Chem.* **1990**, *395*, 69.

(24) Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165.

(25) Parkin, G.; Marsh, R. E.; Schaefer, W. P.; Bercaw, J. E. *Inorg. Chem.* **1988**, *27*, 3262.

(26) Szyperski, T.; Schwerdtfeger, P. *Angew. Chem.* **1989**, *101*, 1271; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1228.

(27) (a) Lock, C. J. L.; Turner, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1764. (b) Krebs, B.; Hasse, K.-D. *Ibid.* **1976**, *B32*, 1334.

(28) Herrmann, W. A.; de Méric de Bellefon, C.; Kiprof, P. Unpublished results, 1990.

(29) Review: Schröder, M. *Chem. Rev.* **1980**, *80*, 187.

(30) Preliminary account: Mink, J.; Keresztury, G.; Herrmann, W. A.; Kuchler, J. G. XIV International Conference on Organometallic Chemistry, Aug 19–24, 1990, Detroit; Abstract 115.

Table IV. IR and ^{17}O NMR Data of Selected Organorhenium and Organotechnetium Complexes Including the Title Compounds **1–3**

compd	symmetry	ν(ReO), cm^{-1}			$\delta(O)$,[b] ppm (solvent)
CH_3ReO_3 (**1**)	C_{3v}	999 w	966 vs	(C_6H_6)	829 ($CDCl_3$)
		993	947	(Raman)	870 (THF-d_8)
		1001 w	965 vs	(CS_2)	
		1005 w	958 vs, br	(KBr)	
		1003	941	(diffuse reflectance)	
CD_3ReO_3 (**1**-d_3)	C_{3v}	995 vs	949 m	(Raman)	
CH_3TcO_3	C_{3v}	1002	948	(CS_2)	
(η^5-C_5Me_5)ReO_3 (**2**)	C_{5v}	920 m	890 s	(C_6H_6)	646 ($CDCl_3$)
		924 m	894 s	(CS_2)	
		921 m	890 s	(KBr)	
(σ-$C_6H_2Me_3$)ReO_3 (**3**)		986 vs	953 vs	(CS_2)	811 ($CDCl_3$)
$ClReO_3$	C_{3v}	1001 w	961 s	(CS_2)	
$[HB(pz)_3]ReO_3$	C_3	944 s	908 vs	(CsI)	785 (THF-d_8)
$K[ReO_4]$	T_d	971 m	918 vs	(KBr)	562 (THF-d_8)
$(CH_3)_3SnOReO_3$	C_{3v}[d]	950 m, sh	911 vs	(KBr)	574 (THF-d_8)

[a] If structure known (electron or X-ray diffraction); see text. [b] 54.21 MHz, 20–28 °C, δ vs external H_2O ($\delta = 0.00$ ppm). For recording data, see: Kneuper, H. J.; Härter, P.; Herrmann, W. A. *J. Organomet. Chem.* **1988**, *340*, 353. [c] $[Na(benzo\text{-}15\text{-}crown\text{-}5)][ReO_4]$.[5] [d] Polymeric crystal structure with five-coordinate tin; *monomeric* in solution. For details consult ref 16.

Table V. Experimental Frequencies of the Infrared- and Raman-Active Vibrations of Methyltrioxorhenium(VII)[a]

mode	no. of frequency[b]	frequency, cm^{-1}	assignment
A_1	ν_1	2899 (IR)	ν (sym, CH)
	ν_2	998 (IR), 993 (R)	ν (sym, ReO)
	ν_3	575 (IR, R)	ν (ReC)
	ν_4	1205 (IR)	δ (sym, CH_3)
	ν_5	324 (R)	δ (sym, ReO_3)
E	ν_6	2989 (IR)	ν (asym, CH)
	ν_7	947 (IR), 941 (R)	ν (asym, ReO)
	ν_6	1363 (IR)	δ (asym, CH_3)
	ν_9	739 (IR)	ρ (CH_3)
	ν_{10}	252 (R)	δ (CReO)
	ν_{11}	238 (R)	ρ (asym, ReO_3)

[a] Key: IR = infrared (diffuse reflection), R = Raman; ν = stretching mode, δ = bending mode, ρ = rocking mode. [b] CH_3 torsional mode (A_2 species) is omitted.

Table VI. Metal–Oxygen Stretching Force Constants of Organorhenium and Related Oxides XMO_3 (M = Re, Tc, Os)

compd	κ,[a] mdyn/Å	formal Re–L bond order	remarks
$BrReO_3$	8.25	1.00	*a*
CH_3ReO_3 (**1**)	8.16	1.15	*b*
(σ-Mes)ReO_3 (**3**)	8.08	1.17	*d*
CH_3TcO_3	8.00		*c*
$(CH_3)_3SnOReO_3$	7.42	1.83	*d*
$[HB(pz)_3]ReO_3$ (**5**)	7.36	1.81	*d*
(η^5-C_5Me_5)ReO_3 (**2**)	6.99	2.29	*d*
	7.10		*b*
$[ReO_4]^-$	7.56		*e*
	9.32		*f*
$[TcO_4]^-$	8.27		*f*
OsO_4	8.29		*e*
	7.95		*a*

[a] Müller, A.; Krebs, B.; Höltje, W. *Spectrochim. Acta* **1967**, *23A*, 2753. ReO stretching frequencies for $BrReO_3$ are 997 and 963 cm^{-1}. Formal bond orders are calculated on the basis of Figure 1 of the quoted reference. 1 mdyn/Å = 10^2 $N{\cdot}m^{-1}$. [b] Result of force constant refinement using frequencies of Tables IV and V (see ref 60). [c] Data calculated from simplified model of ref 59. [d] Results from a simplified model using L as point mass in $LReO_3$ (see ref 59). [e] Data taken from ref 10, pages 121–126, Tables 4.6 and 4.9. [f] Values calculated by using the fundamental frequencies (ν_1–ν_4) 971, 331, 920, and 331 cm^{-1} and 912, 325, 912, and 336 cm^{-1} for $[ReO_4]^-$ and $[TcO_4]^-$, respectively.[60]

It has in fact a crystal structure that is built from trigonal-planar $(CH_3)_3Sn$ units attached to two ReO_4 groups so that five-coordinate tin (tbp) results.[16] It is not possible to explain on the basis of the force constants why CH_3TcO_3 and OsO_4 are similar in their reactions with olefins ([3+2] cycloaddition).[7,13,29]

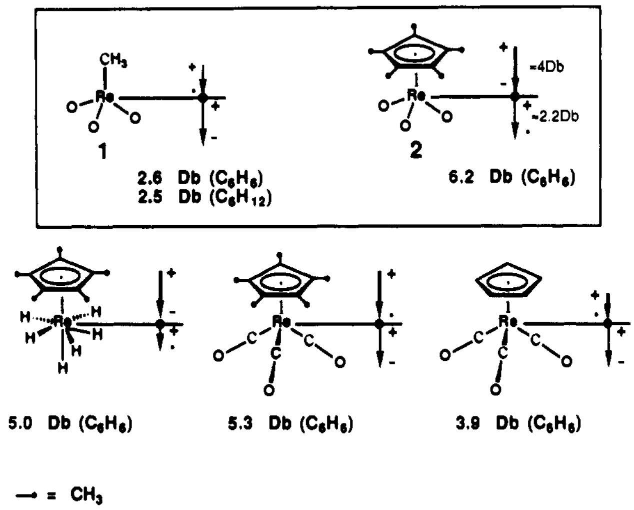

Figure 8. Compounds **1** and **2** in comparison with related organorhenium complexes: electric dipole moments.

For fragments of symmetry C_{3v}, *two* ReO vibrations are predicted for both the infrared (A_1 and E) and the Raman spectra (A_1 and E). Table IV is a compilation of the Raman data recorded for **1** and **2** in comparison with related compounds of type XMO_3 (X = halogen, alkyl, aryl; M = rhenium, technetium). In Table V is the fully assigned fundamental frequency set for **1**. The ReO force constants suggest a lengthening of this bond and some O–Re–O′ bond angle changes in the case of **2** as compared with CH_3ReO_3 (**1**) and $BrReO_3$. If a standardized ReO bond order of 2.00 is assigned to $BrReO_3$, then values of 1.95 result for CH_3ReO_3 and 1.57 for (η^5-C_5Me_5)ReO_3 from the data of Tables IV–VI.

Electric Dipole Moments

The dipole moments[31] also reflect the above conclusions. Since the contribution of resonance form III is *relatively* unimportant for compounds of type $XReO_3$, the negative charge will always concentrate at the oxygen side of the ReO_3 fragment. Early work of Fischer and others has shown that in cyclopentadienylmetal complexes of type $(Cp)MX_3$ (X = CO, Hal, O), the positive terminus of the dipole moment is localized at the π ligand.[31] Comparison of the *tricarbonyl* derivatives (η^5-C_5R_5)$Re(CO)_3$ (R = H, CH_3; Figure 8) and (η^6-C_6R_6)$Cr(CO)_3$ (R = H, $\mu = 4.92$ D; R = CH_3, $\mu = 6.22$ D)[32b] shows that higher dipole moments result from the electron-releasing effect of methyl groups in (η^n-C_nMe_n)M fragments.

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(31) For the method, see: Hedestrand, G. *Z. Phys. Chem. B* **1929**, *2*, 428.

(32) (a) Lindner, H.-H. Ph.D. Thesis, Technische Hochschule München, 1964. (b) Fischer, E. O.; Schreiner, S. *Chem. Ber.* **1959**, *92*, 938. (c) Weiss, E.; Hieber, W. *Z. Anorg. Allg. Chem.* **1956**, *287*, 223. (d) Fichtel, K. Ph.D. Thesis, Ludwig-Maximilians-Universität München, 1961.

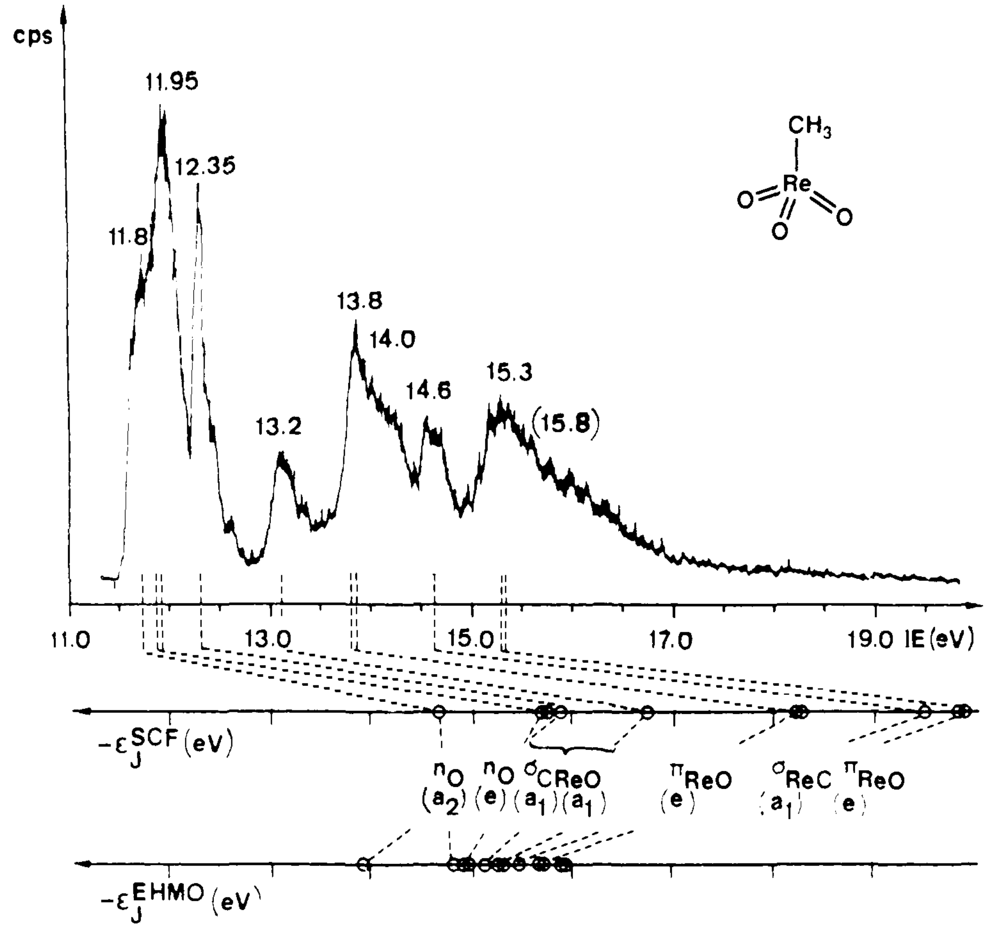

Figure 9. He I photoelectron spectrum of methyltrioxorhenium(VII) (**1**) with Koopmans' assignment by both Xα and double-ζ EHMO eigenvalues.

The half-sandwich complex **2** has a dipole moment of 6.2 D (Figure 8), which appears rather high at first sight. If one considers that dipole increments as high as 2.0–2.5[32c] and ca. 3 D[32d] have been found for cyclopentadienylmetal fragments, however, then a moment ca. 4 D is expected for pentamethylcyclopentadienylmetal units in light of earlier work by Fichtel et al.[32d] A *dipole increment of ca. 2.2 D thus results for the pyramidal ReO_3 unit* present in **1**–**3**.

The data are fully consistent with this interpretation: (i) CH_3ReO_3 (**1**) has a dipole moment of 2.6 D (2.2 D for ReO_3, see above, and of 0.4 D for Re-CH_3).[32d] (ii) (η^5-C_5Me_5)Re$(CO)_3$ gives a value of 5.3 D, with a contribution of ca. 1 D from the Re$(CO)_3$ fragment.[32,33] The slight deviation of that calculated from the recorded value reminds us that dipole moments do not behave additively but rather effect each other within a given molecule. (iii) (η^5-C_5Me_5)ReH_6 exhibits 5.0 D (Figure 8) as a result of ca. 4.3 D (C_5Me_5Re) and ca. 0.7 D (ReH_6). Fichtel assumes ca. 0.4 D for a Re–H bond.[32d] Electronegativities of 1.46 and 1.9, respectively, are given for rhenium[34] and of 2.1 for hydrogen.[33] Five of the six Re–H bonds hardly contribute to the dipole moment because they are only slightly off the equatorial plane in the pentagonal-bipyramidal structure of this molecule.[23b]

Table VII. Dipole Moments of Organorhenium Complexes

compd	wt fraction	ϵ_{12}	n_{12}	solvent	μ, D
$(C_5Me_5)ReO_3$	0.00	2.2802	1.501 10	benzene	6.2 ± 0.1
	0.98×10^{-3}	2.2925	1.501 10		
	2.59×10^{-3}	2.3125	1.501 34		
	4.86×10^{-3}	2.3409	1.501 64		
	8.92×10^{-3}	2.3862	1.501 71		
$(C_5Me_5)ReH_6$	0.00	2.2780	1.501 10	benzene	5.0 ± 0.1
	0.89×10^{-3}	2.2860	1.501 15		
	1.17×10^{-3}	2.2880	1.501 22		
	2.06×10^{-3}	2.2960	1.501 22		
	5.30×10^{-3}	2.3150	1.501 35		
CH_3ReO_3	0.00	2.2837	1.501 10	benzene	2.6 ± 0.1
	1.37×10^{-3}	2.2875	1.501 18		
	2.07×10^{-3}	2.2894	1.501 22		
	5.32×10^{-3}	2.2991	1.501 24		
	9.68×10^{-3}	2.3132	1.501 28		
CH_3ReO_3	0.00	2.0187	1.426 83	n-hexane	2.5 ± 0.1
	1.37×10^{-3}	2.0234	1.426 83		
	2.20×10^{-3}	2.0250	1.426 93		
	4.40×10^{-3}	2.0305	1.427 25		
	11.2×10^{-3}	2.0464	1.427 84		
(C_5Me_5)-Re$(CO)_3$	0.00	2.2837	1.501 10	benzene	5.3 ± 0.1
	1.12×10^{-3}	2.2919	1.501 10		
	4.23×10^{-3}	2.3157	1.501 19		
	9.14×10^{-3}	2.3549	1.501 41		
	17.2×10^{-3}	2.4206	1.501 68		

Photoelectron Spectroscopy[37]

The PE spectrum of (η^5-C_5Me_5)ReO_3 (**2**) has already been published in ref 38, with the conclusion of a d^0 metal configuration. The radical-cation state sequence proposed, $\pi_{Cp} < n_O(a_2) < n_O(e) < n_O(a_1)$, has recently been supported by ARPP (energy *a*djusted

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(33) Cf.: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 2nd ed.; Interscience Publishers: New York, 1966; p 728.

(34) (a) Allred, A. L. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264. (b) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(35) Herrmann, W. A.; Romao, C. C.; Fischer, R.; Kiprof, P.; de Meric de Bellefon, C. *Angew. Chem.* **1991**, *103*, 183; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 185.

(36) Chemistry of [HB(pz)$_3$]ReO_3: Degnan, I. A.; Behm, J.; Cook, M. R.; Herrmann, W. A. *Inorg. Chem.*, in press. See, also: Degnan, I. A.; Herrmann, W. A.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 1347.

(37) Photoelectron Spectra and Molecular Properties. 124. Part 123: Rypdal, K.; Herrmann, W. A.; Eder, S. J.; Albach, R. W.; Watzlowik, P.; Bock, H.; Solouki, B. *Organometallics*, in press.

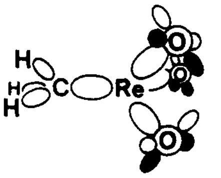
(38) Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem.* **1984**, *96*, 364; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 383.

Table VIII. Koopmans' Assignment of the CH_3ReO_3 Ionization Pattern IE^v_n by Xα and Double-ζ EHMO Eigenvalues ϵ_J with Orbital Characterization by Irreducible Representation χ, Notation n, σ, and π, and Contributions (%) of the Individual Centers

MO		Xα					EHMO	exptl
χ	type	ϵ_J, eV	% Re	% O	% C	% H	ϵ_J, eV	IE^v_n, eV
$1a_2$	n_O	−14.66		100			−14.74	11.80
5e	n_O	−15.70	8	92			−14.92	11.95
$5a_1$	σ_{CReO}	−15.87	11	71	18		−13.94	12.35
$4a_1$	σ_{CReO}	−16.74	11	73	16		−15.11	13.2
4e	π_{HCReO}	−18.30	19	76	2	3	−15.22	13.8
$3a_1$	σ_{CReO}	−19.57	36	30	29	5	−15.42	14.6
3e	π_{HCReO}	−19.86	36	59	2	3	−15.67	15.3
2e	σ_{H3C}	−22.31	8	4	49	39	−15.89	(15.8?)

*r*elativistic *p*seudo*p*otential) and SCF calculations with relatively large basis sets.[26] The much simpler PE spectrum of CH_3ReO_3 (**1**) shown in Figure 9 not only further confirms our previous assignments but also yields additional information as to its electronic structure and, via comparison with equivalent radical cation states of chemically related molecules, to the substituent effects of the $Re^{VII}O_3$ moiety.

The eight-atom molecule CH_3ReO_3 contains 32 valence electrons, that, according to a useful rule of thumb, $[\sum(1s_H + np_E + md_M)/2 = IE^v_n(\text{He I})]$,[39] should give rise to 11 ionizations within the He I measurement region. From a localized bond model of C_{3v} structure, for all radical cation states generated by a single valence-electron expulsion, the following irreducible representations result:



$$\Gamma = 5a_1 + 1a_2 + 5e$$

The photoelectron spectrum (Figure 8) is well resolved and exhibits between 11.5 and 17 eV six bands of a spectrometer-adjusted intensity ratio 3:1:1:2:1:(3?), i.e., presumably the estimated total of 11 ionizations. Due to the unpredictable and widely differing electronic relaxations of individual radical cation states of medium-sized organometallic compounds,[40] as well as the potentially pronounced spin–orbit coupling expected for formally degenerate radical cation states with larger Re contribution, in addition to double-ζ EHMO calculations[37,41] Fenske–Hall calculations[42,43] were also carried out. Their results (Table VIII; Figure 9) are largely comparable except for two distinct differences: Compared with the experimental He I ionization region of CH_3ReO_3 stretching over about 5 eV and approximately reproduced by the Xα eigenvalues despite their 3–4 eV Koopmans' defect, the EHMO eigenvalues are compressend into into a 2.5-eV range. Concerning the M^+ state sequences, however, the only deviation is the $1a_2 \leftrightarrow 5a_1$ exchange within the EHMO approximation (Figure 9).

The assignment of the CH_3ReO_3 ionization pattern (Figure 9) follows Koopmans' correlation with the Xα eigenvalues (Table VIII). Accordingly, the radical cation ground state, $\tilde{X}(^2A_2)$, is the only one with irreproducible representation a_2 and, therefore, in accord with the nodal plane through the central σ_{CRe} bond the positive charge is almost exclusively localized at the three oxygens of the ReO_3 group. A predominant oxygen contribution is also predicted (Table VIII) for the first excited $CH_3ReO_3^+$ state, $\tilde{A}(^2E)$, and, expectedly, no spin–orbit splitting of the needlelike band at 12.0 eV can be detected. For the other ionization needle at 12.35 eV as well as for the somewhat broader band at 13.2 eV, the calculations suggest both a_1 symmetry as well as considerable oxygen participation. Oversimplyfing, therefore, the four lowest energy ionizations of CH_3ReO_3 may be considered to represent four out of its six p-type oxygen lone pairs. Only with the fifth M^+ state, $\tilde{D}(^2E)$, does the Re percentage calculated for the respective orbital (Table VIII, 4e) start to grow. Correspondingly, the two visible photoionizations twin peaks at 13.8 and 14 eV are assigned to spin–orbit-coupled ionization events. At least three more bands at 14.6, 15.3, and 15.8 eV are striking (Figure 9). They should belong (Table VIII) to the $\tilde{E}(^2A_1)$ state and either to more strongly spin–orbit-coupled $\tilde{F}(^2E)$ or to separate $\tilde{F}(^2E)$ and $\tilde{G}(^2E_1)$ states, for which a considerable Re participation is calculated (Table VIII).

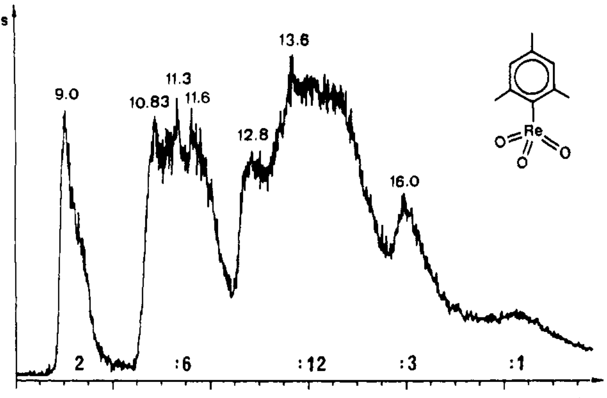


Figure 10. He I photoelectron spectrum of trioxo(η^1-mesityl)rhenium(VII) (**3**) with band intensity ratios.

To further elucidate the electronic structure of CH_3ReO_3, which according to the EHMO calculation should possess a rather charge-polarized central backbone $C^{-0.2}$–$Re^{+3.2}$–$(O^{-1.0})_3$, advantageous comparison with equivalent radical cation states[42] of the following increasingly chemically related compounds is attempted: (η^5-C_5Me_5)Re(CO)$_3$,[38,45] $(CH_3)_4OsO$,[35] (η^5-C_5Me_5)ReO_3,[38] and (η^1-mesityl)ReO_3 (Figure 10). Starting with the tricarbonyl, one notes that almost everything differs from CH_3ReO_3 including the number of valence electrons, and in addition, due to badly overlapping PE bands, the higher M^+ states cannot be assigned.[38,45] From the chemically closer related tetramethyl monooxo derivative of the neighboring metal osmium exhibiting its π_{OsO} ionization at the spin–orbit-averaged ionization energy of 9.76 eV, one gathers a 2-eV difference to the $n_O(a_2)$ ionization of CH_3ReO_3 at 11.8 eV, e.g., a considerable increase on replacing three CH_3 groups by two oxygens. The reverse effect is displayed in the PE spectrum of (η^5-C_5Me_5)ReO_3, the comparable first n_O ionization of which is lowered by 1.9 eV to 9.9 eV[36] and thus clearly demonstrates the π-electron donation by the η^5-bonded C_5Me_5 ligand. This observation is in agreement with both the rather high dipole

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(45) Cf., e.g.: Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*; Halstead Press: New York, 1981.

Table IX. Cyclovoltammetry of Organorhenium Oxides and Dirheniumheptoxide[a,b]

compd	E_{pc} or $E_{1/2}$, V (vs Ag/AgCl/3 M KCl)
Re_2O_7	−0.50 (ir, THF, 296 K)
$(CH_3)_6Re_2O_3$	−0.58 (r, ΔE = 66 mV, i_{pa}/i_{pc} = 1, CH_3CN, 296 K)
$[\sigma\text{-}C_6H_2(CH_3)_3]ReO_3$ (**3**)	−0.61 (qr, ΔE = 114 mV, i_{pa}/i_{pc} = $^1/_2$, DMF, 296 K) −0.69 (qr, ΔE = 133 mV, i_{pa}/i_{pc} = $^1/_2$, THF, 301 K) −0.75 (ir, DMF, 243 K)
$(CH_3)_4Re_2O_4$	−0.65 (qr, ΔE = 160 mV, i_{pa}/i_{pc} = 1, CH_3CN, 296 K) −0.71 (qr, ΔE = 110 mV, i_{pa}/i_{pc} = 1, THF, 301 K)
$CH_3ReO_2(\eta^2\text{-}O_2C_6H_4)$[c]	−0.69 (ir, THF, 293 K)
CH_3ReO_3 (**1**)	−0.69 (ir, CH_3CN, 296 K) −0.84 (ir, THF, 293 K)
$(CH_3)_3SiCH_2ReO_3$ (**4**)	−0.84 (ir, THF, 296 K)
CH_3ReO_3(2,2′-bipy)	−0.98 (ir, THF, 296 K)
$[HB(pz)_3]ReO_3$ (**5**)	−1.50 (ir, THF, 243 K) −1.55 (ir, THF, 296 K)
$[\eta^5\text{-}C_5(CH_3)_5]ReO_3$ (**2**)	−1.72 (ir, THF, 296 K)

[a] Potentials are recorded at 200 mV·s^{-1}. All solvents contain 0.1 M $(n\text{-}C_4H_9)_4PF_6$. Ferrocene is used as an internal standard ($E_{1/2}$ = 0.441 V). [b] Abbreviations: ir, irreversible; qr, quasi-reversible; DMF, *N,N*-dimethylformamide; THF, tetrahydrofuran. [c] $O_2C_6H_4$ = catecholato-*O,O′*.

moment of 6.2 D determined for **2**, which drastically exceeds the quantity of only 2.2 D measured for CH_3ReO_3, and the assumption that the positive pole points toward the C_5Me_5 ring.

The *pronounced acceptor property of the ReO_3 group* is further, and most convincingly, demonstrated by the PE spectrum of (η^1-mesityl)Re^{VII}O$_3$ (Figure 10). There is no doubt that the low-energy ionization band at 9.0 eV (Figure 10) has to be assigned to the first ionization energy of the six-membered ring π system (benzene: $IE_1^V(e_{1g})$ = 9.25 eV[45]). Compared to the one of the free D_{3h} ligand mesitylene, $IE^V(e)$ = 8.41 eV,[46] the increase due to combined first- and second-order perturbation[47] of the mesitylene π system by the ReO_3 substituent amounts to 0.6 eV. The electron gain by the ReO_3 group is also obvious from the observed band maxima at 10.83, 11.3, and 11.6 eV of the PE band hill at higher energy, which are analogously assigned (Table VIII; Figure 9) to radical cation states with predominant oxygen lone-pair contribution: Their average value IE_{2-4} = 11.2 eV is lowered by 0.8 eV relative to IE_{1-3} = 12.04 eV in CH_3ReO_3. Additional comparison with the average value for (η^5-C_5Me_5)Re^{VII}O$_3$, IE_{3-5} = 10.47 eV, expectedly further confirms the rather strong π donation $C_5Me_5 \rightarrow ReO_3$ and, above all, demonstrates the suitability of largely n_O-type ionizations to provide information on the electronic structure of differently substituted organometal oxides.

Electrochemistry

Chemical reduction of the metal occurs in most reactions of the title compound **1** with derivatives of penta- and hexavalent rhenium being formed predominantly.[3,4] As a matter of consequence, the resonance contribution II becomes favored in these cases. Compounds **1**–**3**, the recently obtained derivatives **4**[35] and **5**[36], and several related complexes were examined electrochemically.

They can be classified in two groups: (1) complexes with a π-aromatic or analogous (tripod) ligand (**2**, **5**); (2) complexes with a σ-bonded ligand (aromatic, **3**, **8**; nonaromatic, **1**, **4**, **7**). The compounds of the first group are very resistant to electrochemical reduction: The potentials are −1.72 V for the irreversible 1e wave of **2** and −1.55 V for **5**. Chemically, both complexes can be reduced by organophosphanes in the presence of alkynes[3a,3c,48] and sodium–amalgam, but for the latter reaction no definite products are isolable. Compounds of group 2 are much easier to reduce electrochemically, with their reduction potentials ranging between −0.61 V (**3**) and −0.84 V (**4**); cf. Table IX.

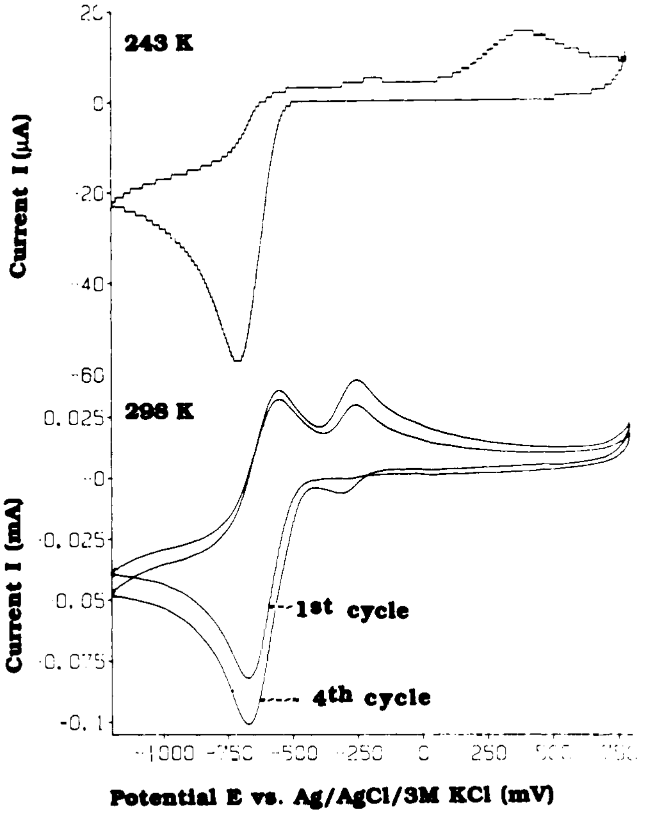

Figure 11. Cyclovoltammogram of the σ-mesityl complex **3** in DMF at ambient temperature. The habitus of this voltammogram is typical of reductive dimerization; cf. ref 49b.

The following order of *decreasing* stability against reduction is thus observed: $(C_5Me_5)ReO_3 \gg (\sigma\text{-alkyl})ReO_3 > (\sigma\text{-aryl})ReO_3$. Electron-donating ligands (bipy) and substituents ($SiMe_3$; **4**) enhance this stability. Dinuclear complexes are normally quite easily reduced (Table IX).

Since for irreversible CV waves the peak potential is a superposition of the standard potential E_0 and the rate by which the radical anion decomposes, a direct comparison of the electronic influence of the ligands is not strictly possible. However, the potentials of Table IX parallel the conclusions drawn from PE, IR, and NMR data (vide infra): electron-releasing ligands (C_5Me_5, $HB(pz)_3$) result in higher charges so reduction becomes more difficult, while alkyl and related σ-coordinated groups (CH_3, $CH_2Si(CH_3)_3$, mesityl) do not transfer electron density to the metal; electrochemical reduction is thus facilitated. Unlike tin alkyls,[49a] none of the present organorhenium oxide undergoes electrochemical oxidation within the potential range of CH_3CN and THF.

Chronoamperometry for the reductions of **1** and **3** yielded diffusion coefficients of 1.10 × 10^{-5} cm^2·s^{-1}, respectively. Just as with the dinuclear complex $(CH_3)_4Re_2O_4$ (D = 3.45 × 10^{-5} cm^2·s^{-1}) for which a SET has been established,[9b] these reductions are 1e processes followed by dimerization. The cyclovoltammograms are typical of reductive dimerization processes (Figure 11).[49b]

For the chemical reduction of **3** by cobaltocene, the primary product $[3]^{\bullet-}[(C_5H_5)_2Co]^+$ quickly yields a green compound upon

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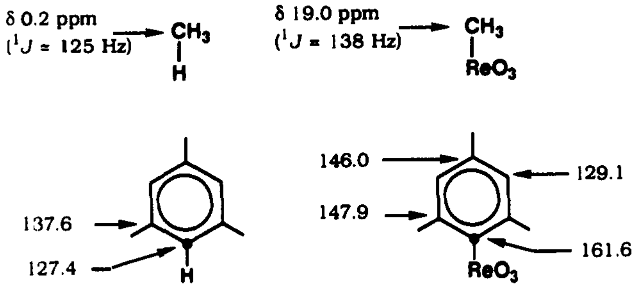

Figure 12. ReO_3 as a strongly electron-withdrawing ligand: evidence from ^{13}C NMR data (see also PE spectra and text). The data (*δ*, ppm, 28 °C) correspond to solutions in $CDCl_3$ (except for CH_4, neat) and are referenced to internal tetramethylsilane. The strong chemical shift difference $\Delta\delta(C)$ of the directly attached carbon atom to lower field by ca. 19 and 54 ppm, respectively, is especially noted. This large a shift difference is in the series of benzene derivatives C_6H_5X only seen for the strongest electron-withdrawing groups X, such as NO_2, SO_3H, and SO_3CH_3.

attempted workup. The precise composition of this material is not yet fully established, but the formula $[(mesityl)_2Re_2O_5H]^-$ is assigned by the FD mass spectra. Due to extreme air sensitivity, no further characterization was possible yet. It is evident, however, that 1e reduction opens up a whole new chemistry of high oxidation state organometallics.[9b]

Conclusion

All methods that we have employed to characterize the title compounds are consistent with several straightforward conclusions that seem to apply to organometallic oxides in general:

(i) High oxidation state rhenium depends on a ligand environment of electron donation quality, e.g. the σ/π-donator ligand oxygen and/or π-aromatic ligands. The three oxygen atoms make the fragment ReO_3 very flexible in its coordination chemistry; thus, simple σ-bonded or π-bonded ligands such as methyl or pentamethylcyclopentadienyl,[50] respectively, can be coordinated to give stable compounds. In the latter case, less electron density for the metal center has to be provided by the oxygen ligands, resulting in a lower *ReO* bond order. By way of contrast, the metal-attached oxygen groups must donate more electron density to the metal (resulting in higher *ReO* bond order) in case only σ ligands are present (e.g., methyl). ^{17}O NMR and infrared data give clear proof of this statement.

(ii) As the first metal oxide fragment, the group ReO_3 has been qualified in terms of its stereoelectronic properties: According to PE and ^{13}C NMR spectra, this fragment behaves as a *very strong* electron-withdrawing group, probably even stronger than sulfonic acids, SO_3H (Figure 12). Dipole moment measurements are in accord with this general conclusion.

Further work in support of these assessments on organic oxides of other metals, e.g., osmium, is in progress and will be reported shortly. It is evident that the oxo ligand is electronically flexible enough to stabilize high and intermediate oxidation states of metals in quite different ligand environments.

Experimental Section

The title complexes **1** and **3** were prepared according to published procedures,[5b,11] while **2** was made from $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ and Mn_2O_7 as described below. The carbonyl complex was prepared from $Re_2(CO)_{10}$ (Strem Chemicals Inc.) and an excess of freshly distilled 1,2,3,4,5-pentamethylcyclopenta-1,3-diene *without solvent* at 150–210 °C.[51] An alternative synthesis of **2** is oxidation of the same precursor compound $(\eta^5\text{-}C_5Me_5)ReO_3$ with hydrogen peroxide.[6,17a]

(1) Preparation of Trioxo(η^5-pentamethylcyclopentadienyl)rhenium(VII) (2). For the preparation of a solution of Mn_2O_7 in CCl_4, we followed the procedure of Trömel et al.[12] However, we generally used lower concentrations. A typical preparation for our purposes is as follows:

(a) Mn_2O_7 in Solution. To 20 mL of CCl_4 and 4.8 mL of concentrated H_2SO_4 (50 mL round-bottom flask), chilled in an ice bath to 0 °C, were added in small portions over a 2-h period a total amount of 2 g (12.6 mmol) of $KMnO_4$. After complete addition, chilling was stopped, and the solution was stirred for another 3 h at room temperature. Parts of the organic layer were then transferred through a Teflon canulae under a slight pressure of nitrogen gas into a 25-mL round-bottom flask, and this solution was stored at −30 °C. The rest of the solution can be disposed by pouring on ice. Iodometric determination of the Mn_2O_7 concentration gave 49 mg/g solution (theory 69.9 mg/g).

(b) $(\eta^5\text{-}C_5Me_5)ReO_3$. To a solution of 150 mg (0.37 mmol) of $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ (0.37 mmol) in 3 mL of CCl_4 and 6 mL of acetone was added dropwise under vigorous stirring 3.70 g of the Mn_2O_7-containing solution (see above) through a Teflon canulae at −78 °C. For a high yield, *slow but continuous* addition is most important. After the addition was complete, stirring was continued for another 10 min. The reaction mixture was then allowed to cool to room temperature, and the MnO_2 was filtered off by means of a glass frit, thus yielding a bright yellow solution. The solvent was stripped off in vacuo and the remaining yellow powder recrystallized as described elsewhere;[6,17b] yield 110 mg (81%) of analytically pure **2**. No decrease of yields is observed upon scale-up of this procedure to 1–5 g of $(\eta^5\text{-}C_5Me_5)Re(CO)_3$.

(2) Dipole Moments. Electric dipole moments were calculated by the method of Hedestrand.[31] Measurements of dielectric constants and light refraction were carried out on very dilute solutions (solvents: benzene or cyclohexane) at a temperature of 20 ± 0.02 °C. Dielectric constants were determined with a dipolmeter DM01 of the Wissenschaftlich-technische Werkstätten Weilheim (Germany) in a thermostated 50-mL cell. This apparatus works according to the known method of superposition at a frequency of 2 MHz. The accuracy of the dipole meter is $\Delta\epsilon/\epsilon = 10^{-5}$. Calibration was done by linear interpolation of three fixed points with very pure benzene, *n*-hexane, and cyclohexane (Merck Uvasols). More information about the technique of measurement is given in ref 32c. Refraction of the solutions was measured with an Abbe refractometer (Carl Zeiss Co., D-7082 Oberkochen/Germany) at sodium D light (λ = 589 nm).

(3) Electron Diffraction. Gas-phase electron diffraction (GED) patterns of CH_3ReO_3 (**1**) and $(\eta^5\text{-}C_5Me_5)ReO_3$ (**2**) were recorded on a Balzers Eldiograph KD-G2[52] with an accelerating potential of 42 kV. The electron wavelength was calibrated against diffraction patterns of benzene (r_a(C–C) = 139.75 pm), with an estimated uncertainty of 0.1%. A standard stainless steel high-temperature nozzle was used.[53] For **1** the nozzle and reservoir temperatures were 66 (5) °C. Six photographic plates were used from the experiment with a nozzle to plate distance of 498.24 mm, with *s* ranging from 20.00 to 145.00 nm^{-1} and Δs = 1.25 nm^{-1}. Five plates were used from the experiment with a nozzle to plate distance of 248.45 mm, with *s* ranging from 60.00 to 250.75 nm^{-1} and Δs = 2.50 nm^{-1}. For **2** the nozzle and reservoir temperatures were 185 (5) °C. Four plates were used from each experiment (502.41 and 252.92 mm), with *s* ranging from 15.00 to 145.00 nm^{-1} and Δs = 1.25 nm^{-1} (long camera distance) and from 50.00 to 260.00 nm^{-1} with Δs = 2.50 nm^{-1} (short camera distance). The plates were subjected to photometry and the optical densities processed by standard procedures.[54] The background was computer drawn by a least-squares fit of the sum of a polynomial and a theoretical molecular intensity curve to each of the experimental leveled intensity curves. Least-squares refinements of the structure parameters were performed on the average curves for each data set. Complex atomic scattering factors $f'(s)$, and phase factors, $\eta(s)$, were calculated from an analytical representation of the atomic Hartree–Fock–Slater potentials for C and O[55] and from a bonded potential for H.[56] Tabulated scattering factors were used for Re.[57] The molecular intensities were modified by multiplication by $s/|f'_{Re}||f'_C|$. As previously observed for oxo compounds of elements of the third transition series,[58]

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the position of the Re=O beat-out in **1** and the **2** seems to be underestimated, which results in a poor fit of the theoretical molecular intensity curves to the experimental data around the beat-out point between 150 and 160 nm^{-1} on the *s* scale. We therefore tried to scale the Re phase factors in order to displace the beat-out point. A scaling of 76/75 for **1** and 78/75 for **2** gave the best fit. This is illustrated in Figure 6 and by the *R* factors in Table II for **2** where the effect was most marked. When using a higher scale of **2**, the discrepancy in the Re=O peak in the RD curve was displaced to the Re–C peak, which indicates that it is the strong Re=O bonds that cause the perturbation. This is also supported by the nonproblematic analysis of $(\eta^5\text{-}C_5Me_5)ReH_6$.[23b]

(4) Infrared and Raman Spectroscopy. Infrared spectra were recorded with a Nicolet 740 FTIR spectrometer coupled with a Nicolet 620 work station permitting spectral accumulation and processing. Liquids were recorded in a sodium chloride cell (0.2-mm path length). The spectra of solid samples were determined by means of a diffuse reflectance accessory produced by Spectra-Tech Inc. (Great Britain). In all measurements the spectral resolution was 2 cm^{-1}.

Raman spectra were recorded with a Jobin Yvon THR 1000 spectrometer equipped with a micro Raman accessory using back-scattering technique. The 647.1-nm line from a Spectra-Physis Model 165 krypton laser was used as the excitation source, with a power of 100 mW at the source.

All Raman and infrared spectra were obtained at room temperature. Solids were studied as finely ground powders in KBr or CsI disks (infrared) or as individual crystals (Raman). For measurements of solutions, the solids were dissolved to give a saturated solution.

Force constant calculations were performed with use of the program NCRDWC[59] or the program described in ref 60. For **1** all stretching vibrations were used and calculated with the program[60] while the geometry was determined by electron diffraction. It was assumed that CH_3TcO_3 has the same geometry as **1**. For the sake of comparison, the other $XReO_3$-type molecules **2** and **3** were also calculated with the presumption of a local C_{3v} symmetry at Re. Average Re–O bond lengths and O–Re–O′ angles were taken from the X-ray structures of **3**[11] and gas-phase electron diffraction of **2** (Table III). For further details of measurement and interpretation, cf. ref 61.

(5) Photoelectron Spectra and Assignment. The ionization patterns of **1** and **3** have been recorded at 10^{-3} mbar with use of a high-performance Leybold Heraeus UPG 200 spectrometer with up to 50 000 cps and an average resolution of 20 meV. Their calibration is based on both the $^2P_{3/2}$ peaks of Xe at 12.13 eV and of Ar at 15.76 eV.

For assignment, nonrelativistic Fenske–Hall calculations as well as EHMO calculations have been performed. Starting from the C_{3v} gas-phase structure, both calculations converged well and showed no unusual behavior.

The basis functions for the Fenske–Hall calculations were generated by the Xα atomic orbital program[40] in conjunction with the Xα Slater basis program.[41] For the carbon and oxygen centers, ground state electron configurations were employed, while the rhenium was given a $d^{n+1}s^0$ cationic configuration. The EHMO calculations were performed with the following Re parameters within a double-ζ basis set (Slater coefficients): $\alpha(6s) = -9.36$ eV (2.398), $\alpha(6p) = -5.96$ (2.372), and $\alpha(5d) = -12.66$(5.343 and 2.277) with $C_1 = 0.6662$ and $C_2 = 0.5910$.[42]

(6) Electrochemistry. All potentials are given for scan rates $v = 200$ $mV{\cdot}s^{-1}$ in 0.1 M $[(n\text{-}C_4H_9)_4N][PF_6]$ vs Ag/AgCl. All irreversible waves hold sufficiently to the relation $E_{pa} = f(\ln \sqrt{v})$ so for all experiments the interpolation to this standard scan rate was possible, in case direct values were not available. **3** was investigated vs SCE; the values were corrected according to $E(Ag/AgCl) = E(SCE) + 0.01$ V.

All cyclic voltammograms were recorded in nitrogen- or argon-saturated solvents containing less than 2 ppm H_2O. A glassy carbon working electrode of 7 mm^2 and a platinum counter electrode of 100 mm^2 were used with a computer-controlled EG&G 173 potentiostate. The software was adapted from W. Amslinger (Arbeitsgruppe Angewandte Elektrochemie, Technische Universität München). When a platinum working electrode of the same surface area was used for the investigation of **3**, differences did not show up. Chronoamperometric measurements were performed in the laboratory of Prof. Astruc (University of Bordeaux/France).

Acknowledgment. Our work on organometallic oxides is being supported by the Deutsche Forschungsgemeinschaft (Leibniz Award to W.A.H.), the Fonds der Chemischen Industrie (fellowship to R.W.A.), the Alexander von Humboldt Foundation (fellowship to R.A.), and the Hanns Seidel-Stiftung (fellowship to J.B.). We greatly appreciate the continuous and generous support by these institutions. The Oslo group is indebted to the Norwegian Research Council for Science and the Humanities and to the Norwegian VISTA program.

Registry No. 1, 70197-13-6; **2**, 90695-83-3; **3**, 125923-26-4; **4**, 131457-03-9; **5**, 127540-97-0; Re_2O_7, 1314-68-7; $(CH_3)_6Re_2O_3$, 100894-27-7; $(CH_2)_4Re_2O_4$, 112440-05-8; $CH_3ReO_2(\eta^2\text{-}O_2C_6H_4)$, 131011-51-3; CH_3ReO_3(2,2′-bpy), 126001-31-8.

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[62] **Note Added in Proof**: This compound, (η^5-cyclopentadienyl)trioxorhenium(VII), has recently been synthesized and shown to be a rather stable compound: Herrmann, W. A.; Taillefer, M.; de Méric de Bellefon, C. *Inorg. Chem.*, in press. The Re–C distances of $(\eta^5\text{-}C_5H_4CH_3)ReO_3$ amount to 236.0–245.9 pm (X-ray diffraction, single-crystal study), thus supporting the above conclusions.