Multiple Bonds between Main-Group Elements and Transition Metals. 136.[1] "Polymerization" of an Organometal Oxide: The Unusual Behavior of Methyltrioxorhenium(VII) in Water

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Abstract: The title compound CH_3ReO_3 (**1**), the simplest organometallic oxide known to date, undergoes an aggregation process in aqueous solution which is unprecedented in organometallic chemistry. From the acidic colorless solutions of **1** in water, a golden-colored, highly refractory precipitate separates slowly at room temperature or within hours at 70 °C. The product **2** forms in 70% yield, with the composition of vacuum-dried material being $\{H_{0.5}[(CH_3)_{0.92}ReO_3]\}_\infty$. Thus, only 8% of the original methyl groups eliminate during formation of **2** in water. The nonstoichiometric compound ("poly-MTO") represents the first known "polymeric" organometallic oxide. The most striking physical properties—golden color, graphite-like consistence, reflectance, electric conductivity, weak paramagnetism—result from a two-dimensional structure containing a sufficient concentration of d^1 Re^{VI} centers to establish the electric conductivity of the material. The Re^{VI} centers mostly originate from homolytic loss of methyl groups ($Re^{VII} \rightarrow Re^{VI}$) during formation of "poly-MTO" (**2**). Thermal degradation in moist atmosphere yields highly pure, crystalline rhenium trioxide, which itself is an electrically conducting material.

Introduction

Methyltrioxorhenium(VII) (**1**, MTO) was first observed by Beattie and Jones in 1979.[2] It is now available in high yields and purity through several general synthetic strategies that have opened the chemistry of this compound and of its more recent higher congeners.[3,4] In addition, an unexpected broad field of catalytic applications has been uncovered in a series of publications.[5] We now report on the behavior of the title compound **1** in aqueous solutions. The results seem to define a new dimension of organometallic chemistry.

Results and Discussion

The complexity of the topic to be discussed in this paper warrants a systematic organization of the results we obtained. Therefore, we refer briefly to the status of the field and give some basic information with regard to the precursor compound **1**.[6a] Two subsequent papers (structure and theory, respectively) are associated with the present account.[6b,c]

(1) Methyltrioxorhenium(VII) and Water. There is ample evidence that **1** has a pronounced Lewis acidity that originates from the electron-deficient, low-coordinated rhenium center (coordination number 4). Typical base ligands such as pyridine, 2,2′-bipyridine, quinuclidine, and chloride ions form 1/1 and 1/2 adducts, depending on the basicity and steric bulk of these ligands.[4,7] Reactive bases, e.g. hydroxide, can lead to decomposition of the compound, e.g. $CH_3ReO_3 + [OH]^- \rightarrow [ReO_4]^- + CH_4$, with perrhenate and methane being the thermodynamic sinks of such degradations.[7b] Aqueous solutions of **1**, however, exhibit a remarkably high (thermal) stability. The solubility of **1** in water amounts to approximately 50 $g{\cdot}L^{-1}$. These solutions are of moderate acidity (pH ≈ 4) but become strongly acidic upon standing (pH < 1.3). At the same time, a *golden-colored precipitate* begins to form. The initial Brønsted acidity of the system CH_3ReO_3/H_2O is explained by the equilibria of eq 1 that account for both the Lewis acidity and the known coordination chemistry of **1**. Potentiometric titrations of the system CH_3ReO_3/H_2O and pH measurements of freshly aqueous solutions yielded a pK_A of ca. 7.5 at 25 °C.[8]

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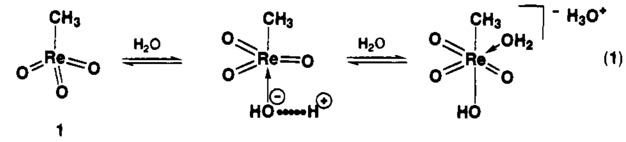


(1)

(2) Structural Aggregation of Methyltrioxorhenium(VII) in Water. If aqueous solutions of **1** (10−50 g·L^{-1}) are stirred at ambient or at elevated temperatures (*e.g.*, hot or boiling water), a completely insoluble precipitate **2** forms. It appears golden-colored in reflected light and, depending on the speed of its formation, blue to violet when viewed in transmitted light. Strikingly, the total yield is rather constant at 70% irrespective of the reaction temperature (40−85 °C). The standard conditions of preparation of **2** are $t = 70-85$ °C and $c(CH_3ReO_3) \geq 0.13$ mol·L^{-1}. However, the physical appearance of **2** depends on the method of making and workup: gold-colored grains are obtained on washing with water, ether, and pentane. A golden reflective coating is left on the walls of the vessel when the suspension is decanted and the residue vacuum-dried. Finally, a highly dispersed powder of **2** forms upon treatment of the precursor compound **1** in water with ultrasound at 70 °C. Other reagents (reducing agents, H^+, $[ReO_4]^-$) and light are not required for the formation of **2** or for an improvement of yield.

A "polymeric" structure for **2** was suggested purely by the physical properties: (i) insoluble in organic solvents and in water, (ii) lack of volatility (in striking contrast to **1**, which begins to sublime at room temperature), (iii) graphite-like appearance and properties such as (iv) electric conductivity and lubricity.

The formation of "poly-MTO" (**2**) seems to be complex, comprising several steps. The subsequent appearance of various colors (greenish, dark blue, black, golden) indicates the presence of redox reactions to accompany the "*polymerization*" process in the sense of a *polycondensation* of $[CH_3ReO_3{\cdot}(H_2O)_n]$ units, finally yielding **2**. An intense blue intermediate is tentatively assigned to solvated electrons (a very broad absorption band in the UV vis spectrum).

NMR kinetics revealed a first-order rate law for the consumption of **1** in acidic solution: $k = (8.0 \pm 1.4) \times 10^{-4}$ s^{-1} (50 °C, 0.16−1.19 M HCl, $c(\text{MTO}) = 2.5 \times 10^{-2}$ to 7.0×10^{-2} M).[9] The enthalpy of activation resulting from these data is $\Delta H^* = 1.12 \times 10^2$ kJ·mol^{-1} ($\tau_{1/2} = 240$ d at 0 °C). The MTO concentration should thus exceed approximately 10^{-2} mol·L^{-1} in order to achieve significant formation of **2**.

Formation of "poly-MTO" does not occur under strongly oxidizing conditions, *cf.* $c(HClO_4) = 0.1$ mol·L^{-1}, while oxygen dissolved in the water does have no effect on the formation of **2**. Reducing, noncoordinating agents such as $SnCl_2$, however, cause *spontaneous* coloration of MTO solutions in water at ambient temperature, with immediate formation of a precipitate. The pale-golden product obtained in the presence of $SnCl_2$ exhibits a relative composition of Re:Sn:Cl = 3.5:1.5:1.0. This particular product possibly belongs to the class of intercalation compounds (*e.g.*, $SnCl_2$ in "poly-MTO") but has not yet been eludicated structurally.

During formation of **2** at 70 °C, the pH decreases exponentially (Figure 1) but remains constant after approximately 60 min even though the polymerization process is far from being complete. Reduction of the $[H]^+$ concentration also accelerates the aggregation process of MTO **1**. For example, "poly-MTO" precipitates after >30 min at pH = 4 (40 °C) but already after several minutes at pH = 5 at 40 °C (golden mirror of **2**). However, the total yield of **2** decreases with increasing pH since hydrolysis becomes more important as the $[OH]^-$ concentration is raised (see above, section 1). Notably, no "poly-MTO" is formed in protic, *absolutely dry* solvents such as CH_3OH and C_2H_5OH. Addition of little water to these solutions induces aggregation of small amounts of **2** (<5% yield).

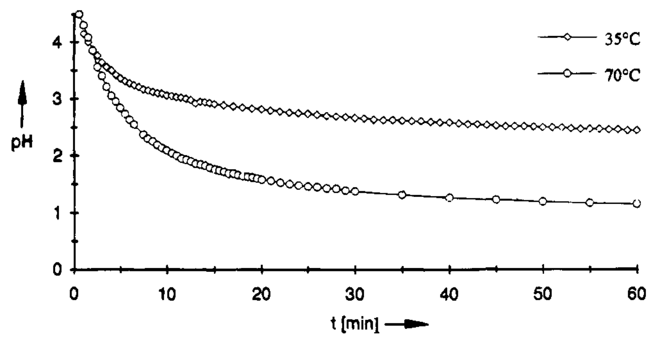
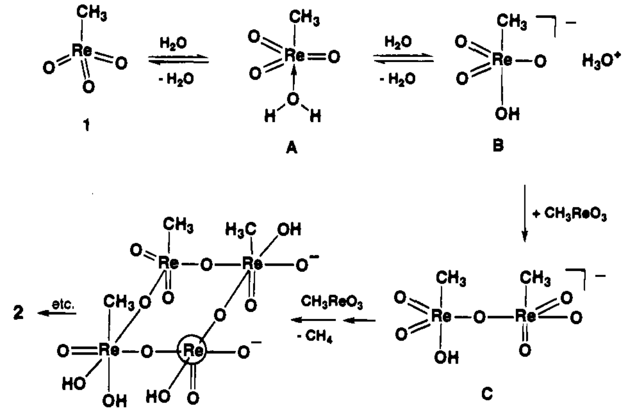


Figure 1. Acidity *vs* time plot for the behavior of CH_3ReO_3 (MTO) in aqueous solution. Increasing acidity is due to formation of $H[ReO_4]$ as a result of partial "demethylation" of MTO during formation of "poly-MTO", *e.g.* $CH_3ReO_3 + H_2O \rightarrow H[ReO_4] + CH_4$.

Scheme 1. Acid-Induced Aggregation of CH_3ReO_3 in Aqueous Solution[a]



[a] Steps A−C are evident from the physical data of MTO in water. The CH_3-free rhenium (8% statistically of the entire metal content) is encircled in this representation.

This and the pH dependence prove that *water* plays the decisive role in the nucleation of MTO. Protolysis of the intermediate **A** to form species such as **B** is reasonable to assume with respect to the pronounced Brønsted acidity of $CH_3ReO_3{\cdot}H_2O$. Nucleophilic attack of **B** at CH_3ReO_3 would first promote "dimerization" to **C**, which would then further add CH_3ReO_3, resulting in one-dimensional chains and two-dimensional sheets of oligomers and polymers finally yielding **2** (Scheme 1).

Nucleophilic attack of σ- and π-donor species, *e.g.* amines, 1,2-dihydroxybenzene, thiolates, and chloride, has repeatedly been observed for MTO **1**[4,7a−c,10] and is actually a typical reaction of this compound. *Condensation* products of MTO with protic reagents have thus been synthesized, with the catecholate complex $CH_3Re(O_2C_6H_4)O_2{\cdot}py$ being a typical example.[10] There is also precedent for nucleation induced by the dinuclear radical anion $[\{(CH_3)_2ReO_2\}_2]^{\bullet-}$, which yields the *tri*nuclear anion $[\{(CH_3)_2ReO_2\}_3]^-$ *via* (air) oxidation.[11] The reason for partial elimination of methyl groups with concomitant reduction of rhenium (Re^{VI}) is not yet clear, but the surprisingly

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reproducible results (8% average loss of CH_3), *irrespective* of conditions, suggest a specific thermodynamic stabilization of the resulting lattice structure at this stage of methyl loss. One must assume that the loss of CH_3 groups is statistical.

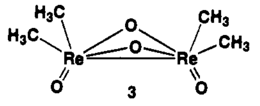
(3) Composition of "Poly-MTO". Total elemental analyses of more than 30 samples synthesized under various conditions, in addition to other analytical and spectroscopic data (see section 7), provided clear proof that, most notably, this "polymer" still contains 92% of the original carbon of CH_3ReO_3 in the form of CH_3 units. The Re/O ratio amounts to 1/3. In addition, the presence of approximately one-half an hydrogen equivalent is concluded from these analyses, while the yield of **2** is invariable to 70 ± 2%, with the rest of the rhenium showing up in approximately 28–31% of perrhenic acid and in <1% of $(CH_3)_4Re_2O_4$. The overall empirical equation for the formation of **2** can be written as in eq 2. The small deviation from 100% is

$$CH_3ReO_3 + H_2O \longrightarrow {}^{0.7}/_n\,\underset{\mathbf{2}}{\{H_{0.5}[(CH_3)_{0.92}ReO_3]\}_n} + 0.31\,H[ReO_4] + 0.34\,CH_4 \quad (+\,O_2 + CH_3OH) \qquad (2)$$

due to analytical inaccuracy, some minor byproducts (see above and section 4), and residual water from the preparation. It has been shown that **2** can be formulated as $\{H_{0.5-2x}[(CH_3)_{0.92}ReO_{3-x}]\cdot(H_2O)_x\}_\infty$, depending on the amount of water present as interlayers.[6b] Both $H[ReO_4]$ and CH_4 have been determined and quantified among the products. The formation of O_2 (concluded from the redox chemistry of eq 2) could not be analyzed by GC. However, CH_3OH as another oxidation product was determined by NMR. The preparation of **2** is not influenced by the absence or presence of oxygen.

If **2** is synthesized from CH_3ReO_3 in D_2O (>99.8% D), the net formula is $\{D_{0.5}[(CH_3)_{0.92}ReO_3]\}_n$, while CD_3ReO_3/H_2O produces $\{H_{0.5}[(CD_3)_{0.92}ReO_3]\}_n$. Neither the monomer **1** nor the "polymer" **2** thus undergoes an acid-catalyzed H/D exchange of the metal-attached methyl groups.

(4) The Byproducts. A careful search for byproducts (see above) revealed a tiny but mechanistically relevant amount of the known dinuclear Re^{VI} complex $(CH_3)_4Re_2O_4$ (**3**)[3a] exhibiting



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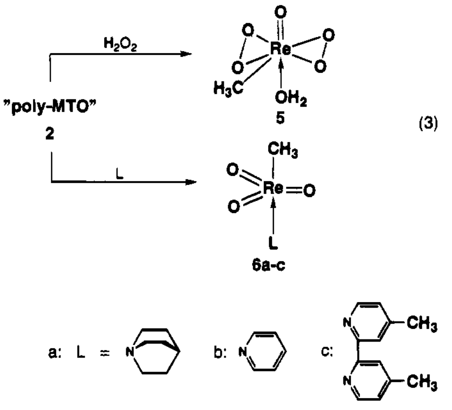
two methyl groups per rhenium. We have identified this species by means of an X-ray diffraction analysis to be absolutely sure about the structure. These results provide evidence for a *methyl group transfer* from and to **1** in the aqueous medium. In light of the known radical decomposition of compounds $RReO_3$ (R = alkyl, aryl)[4a,b,e] and the observed methyl deficiency of **2**, we suggest that *methyl radicals* are transferred to $(CH_3)ReO_n$ fragments under the conditions of the formation of **2**. CH_3 radicals were indeed directly observed by ESR in hot aqueous solution of CH_3ReO_3.[17] We remind the reader that water is an ideal "solvent" for CH_3 radicals due to the high O–H bond strength as compared with other protic solvents (*e.g.*, CH_3OH).

(5) Solubility and Volatility. "Poly-MTO" is insoluble in practically all inorganic and organic solvents (*e.g.*, HCl(aq), H_2SO_4, H_2O) unless a reaction occurs, *e.g.* pyridine (*N*-donor ligand) or acetate (chelating ligand) or H_2O_2 (see below). The compound is also completely involatile, even under the high-vacuum conditions of mass-spectrometric techniques (EI, CI, FD).

(a) Hydrogen Peroxide. Dilute (1–5 wt %) and concentrated peroxide (80 wt %) dissolves **2** instantaneously. The known bis(peroxo) complex **5** (Re^{VII})[5f] is formed *quantitatively*, based on the CH_3 equivalents present in **2** (UV–vis and NMR spectra, see the Experimental Section), with the *isolated* yield amounting to 85% (eq 3). The rest of the rhenium of **2** (ca. 8%, section 3) is ultimately converted to perrhenic acid ($2ReO_3 + H_2O_2 \rightarrow 2H[ReO_4]$). Solutions of "poly-MTO"/H_2O_2 are catalytically active in olefin epoxidation,[5,6a] which clearly proves the presence of CH_3ReO_n units in **2**.

(b) Nitrogen Bases. Quinuclidine, pyridine, and 4,4′-dimethyl-2,2′-bipyridine similarly yield the *mononuclear* Re^{VII} complexes **6a**, **6b**, and **6c**, respectively. However, absolutely dry pyridine dissolves **2** only very slowly and incompletely; wet pyridine dissolves **2** at 40–80 °C. It is reasonable to assume that a small concentration of water (or hydroxide, respectively) is necessary to break up the polymeric structure *via* intercalation as the first step of reaction (see eq 3 and ref 6b). In an aqueous acetate buffer, reaction occurs with formation of CH_3ReO_3 (ca. 30% yield, GC/MS analysis), with the major part of **2** being hydrolyzed.



(3)

(6) Other Organorhenium Oxides $RReO_3$. Products analogous to **2** have not yet been obtained from the higher alkyl and aryl congeners of CH_3ReO_3. For example, *ethyl*trioxorhenium (ETO)[4a,b] forms acidic solutions in water (pH ≈ 1.5) but no defined products result. Instead, a black powder with a low carbon and hydrogen content is isolated. Ethane and ethylene (55 and 40%, respectively) are the predominant hydrocarbon products, with the rest of nearly 5% representing C_4 and C_5 hydrocarbons. This product pattern indicates a radical decomposition pathway involving homolytic cleavage of the Re–C bond. The black residue constitutes a mixture of various rhenium oxides, predominantly ReO_2. Several other compounds of formula $RReO_3$ (with R = η^5-$C_5(CH_3)_5$, C_2H_5, *n*-C_3H_7, $CH_2Si(CH_3)_3$, C_6H_5, $C_6(CH_3)_3H_2$ [= mesityl]) were tested for their reactivity with water. Extensive hydrolytic degradation at the rhenium–carbon bonds prevails in all these cases; no aggregations to polymeric organometal oxides were observed.

(7) Physical Properties. "Poly-MTO" exhibits several physical properties that originate from the extended "polymeric" (polycondensed) structure and from partial reduction of the heptavalent rhenium.

(a) Electric Conductivity. While the colorless title compound CH_3ReO_3 (**1**) is a diamagnetic insulator (d^0 Re^{VII}), the novel "poly-MTO" (**2**) exhibits excellent conductivity for the electric current, including high currents >10 A. A pressed sample, prepared and stored under air- and moisture-free conditions, had a total charge of 32 000 C (0.33 mol of elemental charge carriers) passed through it in 6 h. No saturated current could be seen in the current/voltage (*I*/*V*) characteristics, which strongly indicates *electronic conductivity*. Both composition and properties of the samples were not changed by the electric current. A specific resistivity of $\varrho = 5.6 \times 10^{-3}\ \Omega$ cm was recorded for a freshly pressed pellet of **2** (*d* = 1.2 mm) by means

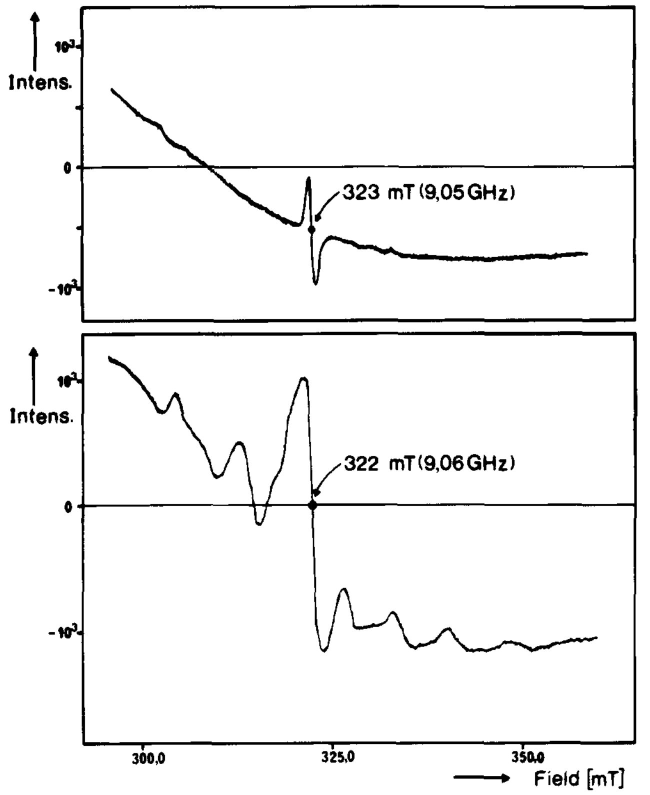


Figure 2. ESR spectrum of "poly-MTO", recorded at 120 K in a 1% KBr matrix (below), as compared with that of authentic ReO_3 (above) under the same conditions.

of the four-point probe technique. This value remained almost constant over a wide range of temperature (5.6×10^{-3} Ω cm at 300 K to 4.9×10^{-3} Ω cm at 20 K). For rhenium trioxide (ReO_3, d^1 Re^{VI}), $\varrho = 10^{-5}$ Ω cm was recorded at 25 °C, which decreases with decreasing temperatures (metal-type conductivity).[12]

(b) ESR and ESCA Spectra, Magnetism. The failure to obtain a solid-state ^{13}C NMR spectrum of **2** under various conditions indicated the presence of paramagnetic centers. The solid-state ESR spectrum at 120 K (KBr matrix, 1% of **2**) is complex: the main signal at 322 mT (9.06 GHz) corresponds to the data of ReO_3 (323 mT, 9.05 GHz). In both cases, no hyperfine splitting is seen (fast relaxation of the various electronic states). Additional signals in the ESR spectra of **2** prove the existence of further chemically different paramagnetic centers in the structure of this material (Figure 2). Some Re^{IV} and Re^{VI} species (and some Re^0 besides Re^{VII}) are evident from the ESCA spectra which, in terms of line shape and signal intensities, are reminiscent of ReO_3 (Figure 3).

Monomeric MTO **1** is diamagnetic, as expected ($\chi_{mol} = -55 \times 10^{-6}$ $cm^3 \cdot mol^{-1}$, 25 °C). Magnetic properties of "poly-MTO" are shown in Figure 4. At first sight, it is surprising that the material is magnetically indifferent at 100–298 K ($\chi_{mol} = 7 \times 10^{-5}$ $cm^3 \cdot mol^{-1}$). Only at very low temperature antiferromagnetic coupling of the paramagnetic centers cannot be observed. The magnetic susceptibility of **2** increases upon cooling to temperatures below 100 K (Figure 4), $\chi_{mol} = 2.1 \times 10^{-4}$ $cm^3 \cdot mol^{-1}$ at 10 K. A qualitatively similar magnetic behavior is known for ReO_3.[13]

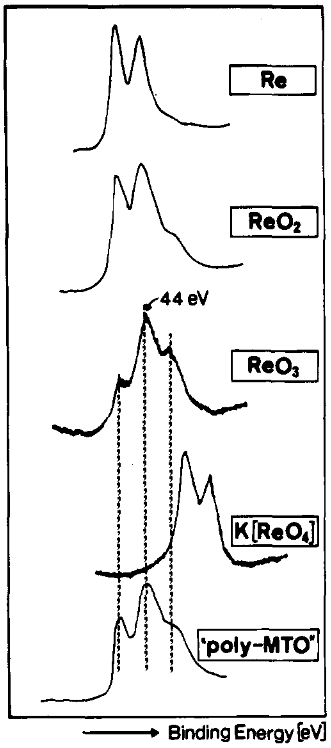


Figure 3. ESCA spectrum of "poly-MTO" (bottom) compared with those of authentic Re, ReO_2, ReO_3, and $K[ReO_4]$. The similarity between "poly-MTO" and ReO_3 is striking.

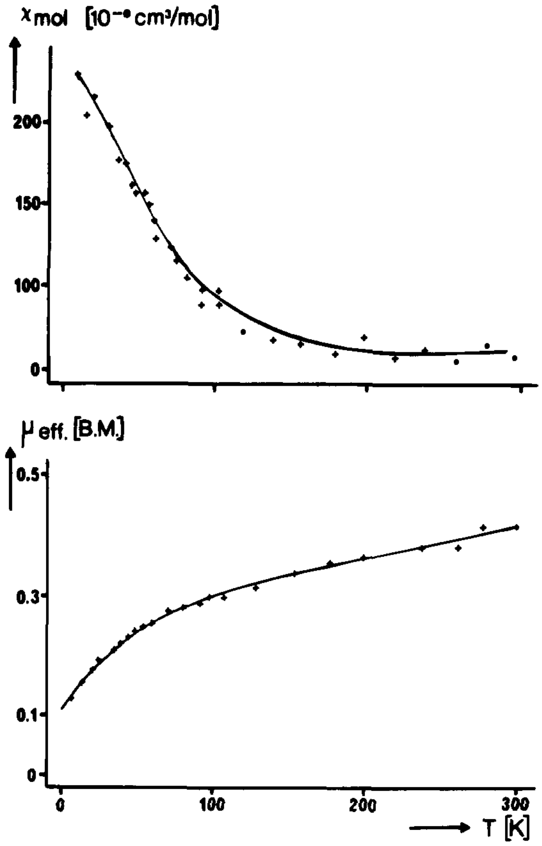


Figure 4. Magnetic susceptibility (above) and magnetic moment (below) of "poly-MTO" between 10 and 300 K.

(8) Spectroscopy. (a) Infrared, Raman, and Solid-State NMR Spectra. High reflection and low transmissions pose a major problem in recording IR spectra of **2**. Diffuse-reflectance, emission, and transmission spectra can be obtained, however, under special conditions. These spectra are quite similar to those

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Table 1. IR and Raman Data of CH_3ReO_3 and "Poly-MTO"

CH_3ReO_3 (**1**)		"poly-MTO" (**2**)		
IR	Raman	IR	Raman	
2989 (m)	2985 (m)	2950 (m)	*a*	
2986 (vw)		2923 (s)	*a*	CH (str)
2900 (m)	2898 (s)	2854 (m)	*a*	
1347 (m)	1375 (w)	1280 (m)	*a*	(A_1, B_2) CH_3 (asym)
1364 (m)	1361 (w)	1210 (sh)	1220 (vvw)	def.
998 (vs)	995 (vvs)		990 (vs)	(B_1) Re=O (str)
959 (vvs)	960 (m)	912 (vs)	912 (sh)	(A_1)
		881 (sh)	894 (s, b)	(B_1) ReO_4 (str)
		851 (sh)	860 (sh)	(A_1, E)
740 (m)	740 (w)	758 (m)	760 (m, b)	(E) CH_3 (rock)
572 (ms)	576 (s)	550 (w)	560 (vvw)	(A_1) Re−C (str)
		494 (w)	480 (sh)	(A_1)
			448 (m)	(B_1)
			408 (vs, vb)	(B_2) Re=O (deform)
325 (s)	326 (w)	343 (s, b)	340 (sh)	(E)
		232 (s)	*a*	(E)

[a] Not observed.

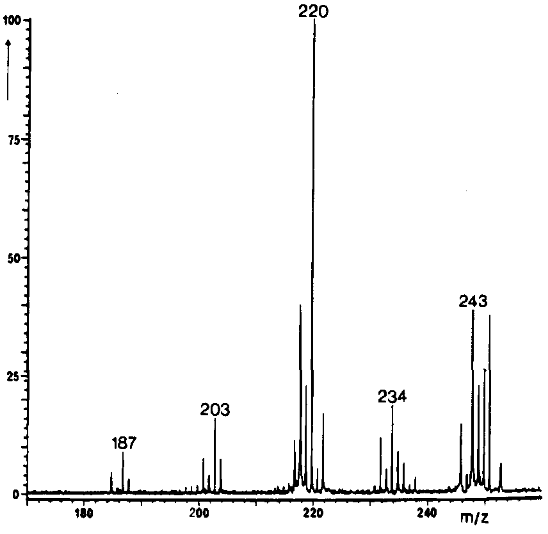

Figure 5. FT-ICR-MS experiment of "poly-MTO" (see text), showing the spectrum of monomeric CH_3ReO_3. This species is obviously generated by laser-induced degradation of the lattice. The highest (small) peak corresponds to $m/z = 253$.

of ReO_3. ν_a(ReO) bands at 912 (vs), 881 (sh), and 851 cm^{-1} (sh) are observed (CD_3 derivative: 910, 870), a ν_s(ReO) band at 962 cm^{-1} (vw)), and ReO deformation bands at ca. 343 (st, br) and 232 cm^{-1} (s). A comparison of IR and Raman data of monomeric **1** and **2** (especially C−H and Re−C vibrations) is given in Table 1. The splitting of various modes in the spectra of **2** is due to lattice effects and strongly supports the assignment of a polymeric structure to **2**.

The solid-state ^1H NMR of **2** shows a strong, sharp resonance at $\delta = 0$ ppm (line width = 2.2 kHz, external standard H_2O $\delta = 4.60$ ppm). This signal originates from the highly mobile (rotation) CH_3 units of **2** (for comparison, $\delta((CHReO_3) = 2.0$ ppm). A second broad signal at $\delta = 80$ ppm ($\lambda_{1/2} = 25$ kHz) is assigned to *acidic hydrogen* atoms in the lattice of **2**, see also ref 6b.

(b) **Mass Spectra.** Standard MS techniques proved unsuccessful in characterizing "poly-MTO" (lack of volatility!). It was at least possible, however, to generate the monomeric fragment CH_3ReO_3 from solid **2** by laser-induced vaporization of oligomeric/polymeric domains of **2** in FT-ICR-MS equipment (pulsed Nd:YAG laser, 20 mJ), see Figure 5. This result once again supports the presence of these units in the polymeric structure. Additional intense signals attributable to $[CH_3ReO_2(OH)]^{\bullet+}$ ($m/z = 251$, ^{187}Re) and $[H_2ReO_4]^{\bullet+}$ (m/z 253) are also in accord with the proposed structure.[14] Monomeric CH_3ReO_3 was also detected in FAB mass spectra of **2** using xenon atoms to "activate" the surface of *freshly* prepared samples ($m/z = 250$, ^{187}Re, $[CH_3ReO_3]$), see Figure 6.

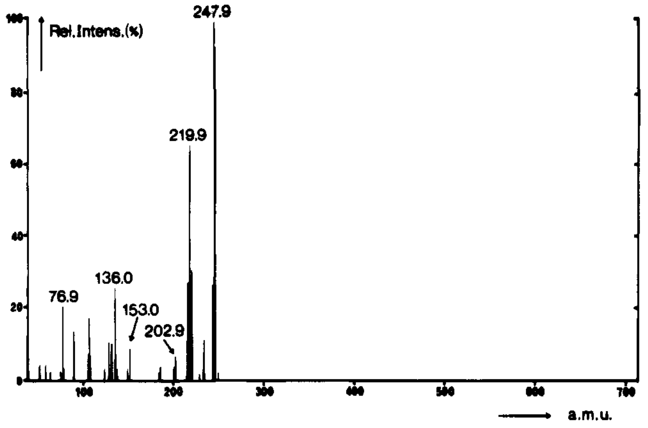

Figure 6. Fast atom bombardment (FAB) mass spectrum of "poly-MTO", showing the formation of *monomeric* CH_3ReO_3 with its typical fragmentation pattern.[3a]

By way of contrast, only demethylated $[Re_mO_n]^{\bullet+}$ species ($m = 1, 2$; $n = 0-2$) were detected when "aged" samples of **2** were used. The relative intensities of $Re^{\bullet+}$, $[ReO]^{\bullet+}$, $[ReO_2]^{\bullet+}$, $[Re_2]^{\bullet+}$, and $[Re_2O]^{\bullet+}$ change only little from sample to sample. The pattern corresponds surprisingly well to spectra of authentic samples of ReO_2 and ReO_3. Since FAB-MS is a surface spectroscopy, our data show that fresh samples of **2** contain CH_3 groups (*e.g.*, CH_3ReO_3) in the surface layers. The surface gets oxidized and/or hydrolyzed when the samples age in the atmosphere or at storage under water, resulting in some loss of methyl groups. It is noteworthy that decomposition of **2** to CH_4 and $H[ReO_4]$ proceeds only very slowly upon action of alkali hydroxides (in marked contrast to monomeric **1**!), presumably because the presence of an oxidic coating prevents further attack by $[OH]^-$ at the sublayers.

(9) **Thermal Degradation.** A TGA/MS study[15] supported the chemical and crystallographic results: ca. 6 wt % of the sample is lost when heated to 230−290 °C.[6b,14,15] This quantity corresponds quite accurately to a *complete loss of methyl groups* (theoretically 5.81 wt %) that form 92−99% CH_4 and small amounts of C_2H_4, C_2H_6, C_3H_8, and C_4H_{10} (GC/MS detection). For the degradation step **2** → ReO_3 of eq 4, a molar heat of

$$\mathbf{2} \xrightarrow[(H_2O)]{240\text{-}275\ °C} ReO_3 + CH_4 \qquad (4)$$

formation $\Delta H = -8.21$ kJ·mol^{-1} was determined by a DSC experiment.[15] The *exothermic* character of the degradation **2** → ReO_3 is in line with the easy conversion of **2** to ReO_3 upon treatment with *any* kind of energy, *e.g* heat, UV light, pressure, MAS-NMR energy, or even thermal neutrons.[14,18] If moisture is present, the degradation is much faster due to the availability of "free" (protic) hydrogen equivalents necessary for the methane to be formed.

The TG results are identical for both fresh and "aged" samples, provided air and moisture were excluded upon prolonged storage. The monomeric title complex **1** resists temperatures as high as 200 °C, with no decomposition occuring up to ca. 350 °C. Upon thermal treatment at 450 °C in a hot-

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(14) Fischer, R. W. Ph.D. Thesis, Technische Universität München, 1993.

(15) (a) Kleine, M. Ph.D. Thesis, Technische Universität München, 1994. (b) Herrmann, W. A.; Kleine, M.; Kühn, F. E.; Fischer, R. W. *Inorg. Chem.*, in press.

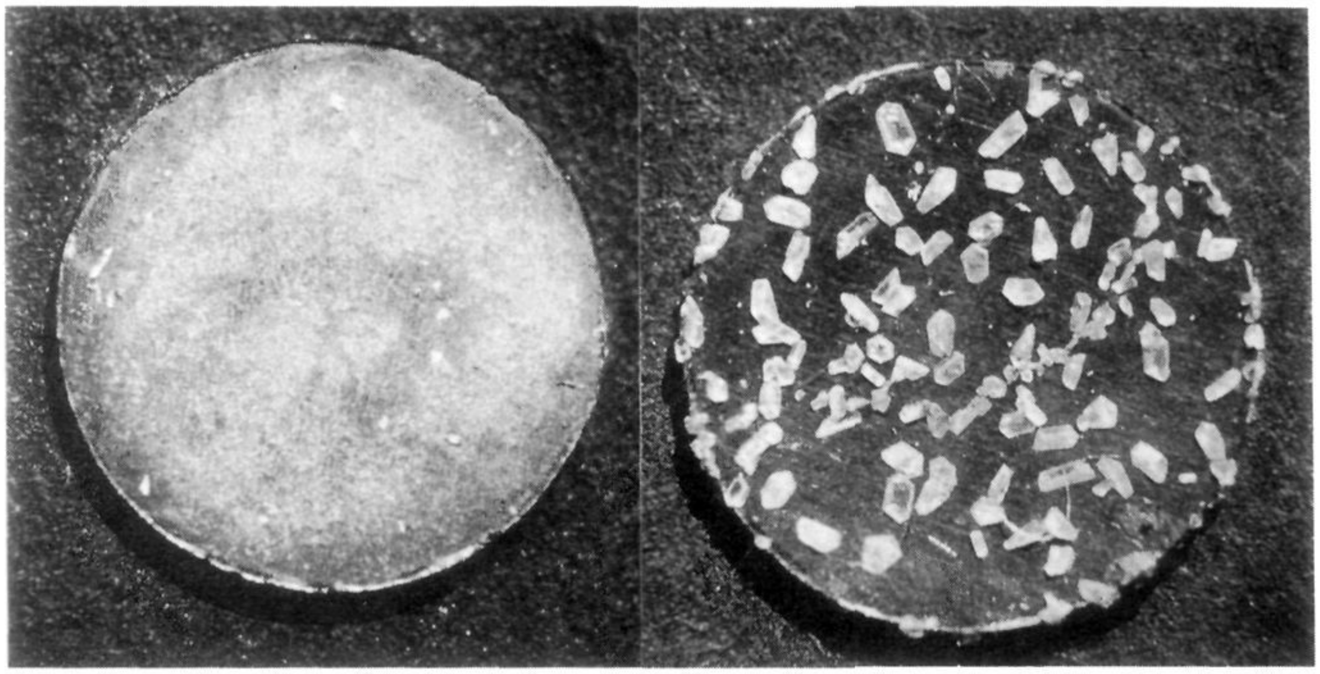
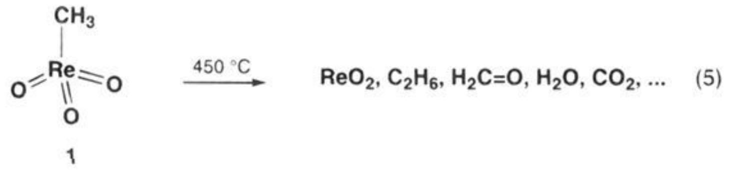
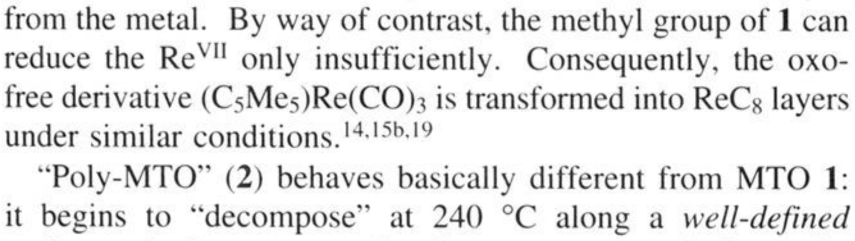


Figure 7. (left) Pellets of freshly prepared "poly-MTO" and (right) pellets after high-pressure treatment and subsequent standing in ordinary atmosphere. The picture at the right shows violet ReO_3 with colorless crystals of CH_3ReO_3, see text.

tube (1 mbar), gaseous monomeric CH_3ReO_3 decomposes mainly to reduced rhenium oxides, predominantly (black) ReO_2, see eq 5.[14,15b]



Interestingly, the π-aromatic complex (η^5-C_5Me_5)ReO_3 (**4**) inspite of the high carbon content, gives clean *metallic rhenium* (>99.8% purity) under the same conditions (eq 6).[19] This striking difference with regard to thermal degradation originates quite obviously from the fact that **4** exhibits enough reduction equivalents in the π-ligand, capable to fully remove the oxygen from the metal. By way of contrast, the methyl group of **1** can reduce the Re^{VII} only insufficiently. Consequently, the oxo-free derivative (C_5Me_5)$Re(CO)_3$ is transformed into ReC_8 layers under similar conditions.[14,15b,19]



"Poly-MTO" (**2**) behaves basically different from MTO **1**: it begins to "decompose" at 240 °C along a *well-defined pathway*. In the presence of moisture, very clean ReO_3 can be made quantitatively on a preparative scale (see also ref 6b).

(10) Stability. Isolated and carefully dried samples of "poly-MTO" (**2**) can be stored under exclusion of moisture *for years* without changes in composition and morphology. In the presence of moisture, however, methane gradually forms, while the samples change color through brownish to dark violet (ReO_3). Notably no decomposition occurs upon storage of **2** under water (almost identical composition after 9 mo). It is conceivable that an oxidic cover protects the compound from hydrolytic degradation under these conditions.

"Poly-MTO" has no defined melting point. However, composition and appearance begin to change at 200−220 °C. Above 240 °C, exhaustive demethylation occurs to finally yield highly pure, crystalline ReO_3 (see section 9 and the Experimental Section).

The slight hygroscopicity of **2** suffices to guarantee the amount of water necessary to form methane from the methyl groups. When water was scrupulously excluded in a series of X-ray powder diffraction experiments, degradation of **2** to (black) ReO_2 rather than to (violet) ReO_3 occurs.[6b,18] This clearly shows the requirement of protic hydrogens for methane formation.

(11) Photolytic Degradation. Clean but relatively slow degradation of the title compound to ReO_3 occurs photolytically, too. The array of hydrocarbons formed upon photolysis (mercury middle-pressure lamp, ca. 20 °C, 6 h) is typical of radical pathways: CH_4 (71%), C_2H_4 (6%), C_2H_6 (18%), C_3H_6 (1.5%), C_3H_8 (0.7%), C_4H_8 (1.7%), and trace amounts of C_5 hydrocarbons.

It must be emphasized that, in contrast to the thermal degradation, water is necessary: no reaction occurs in an absolutely dry environment. Nevertheless, the material is sensitized by light. Thus, intensively irradiated dry samples of **2** stay unchanged during irradiation and afterward (*no* ReO_3 formation) when moisture is *totally* excluded. If water is then admitted to such samples in the dark, a color change to violet (ReO_3) occurs reproducibly ("memory effect"). It can be concluded that photoactivation of the material occurs without visible change of structure. The same effect has been observed when **2** was subjected to other energy sources, *e.g.* attack with thermal neutrons or fast rotation in the magnetic field under solid-state NMR conditions (MAS). Admission of water then leads to fast reaction with the activated sites that seem to have formed and have a sufficient lifetime.

Monomeric MTO **1** does *not* yield ReO_3 upon irradiation under analogous conditions (intensity, time), neither in the gas phase nor in the solid state. Only minor degradation occurs. In solution, however, photolytical formation of ReO_3 has been observed[16] and *free* CH_3 radicals were detected by ESR spectroscopy.[17]

(12) Pressure-Induced "Depolymerization". Pellets of "poly-MTO" are made by pressure on the order of 150 bar. On the surface of these golden-colored pellets, little colorless crystals of **1** begin to appear after ca. 10−15 h (Figure 7). After

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(16) Kunkely, H.; Türk, T.; Teixeira, C.; de Mèric de Bellefon, C.; Herrmann, W. A.; Vogler, A. *Organometallics* **1991**, *10*, 2090.

(17) Herrmann, W. A.; Kühn, F. E.; Fiedler, D. Unpublished results. *Cf.* Kühn, F. E. Ph.D. Thesis, Technische Universität München, 1994.

(18) Scherer, W. Ph.D. Thesis, Technische Universität München, 1994.

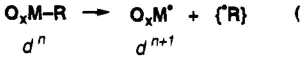
(19) Herrmann, W. A.; Fischer, R. W. Ger. Pat. 4318310 A.1 (SKW Trostberg AG), June 2, 1993.

several weeks, most of the surface is covered by colorless **1**. Removal of the crystals, repeated application of pressure to the remaining pellet, and further standing in the atmosphere yields more **1** and finally a violet material which is predominantly ReO_3 (Figure 7b). Fully deuterated **2** shows the same phenomena. This unprecented "depolymerization" indicates again that **2** is a *metastable* compound which can use various sources of energy to enter degradation pathways that finally yield the thermodynamic stable products CH_3ReO_3, ReO_3, and CH_4. The formation of the stable ReO_3 structure is certainly a major thermodynamic driving force because no extensive structural rearrangement is necessary.[6b]

Conclusion and Perspectives

The "polymerization" (polycondensation) of organometallic oxides is an as yet unprecedented technique of making oxidic materials that still contain organic ligands. The latter are prone to subsequent thermal or photochemical elimination. The graphite-type structure and properties of the "polymeric", methyl-deficient methyltrioxorhenium not only demonstrate how easily this type of molecular nucleation can occur but also indicate that organic ligands may disturb a metal oxide lattice in the third dimension, thus stabilizing quasi-two-dimensional structures.[6b] Beyond that, homolytic cleavage of the $Re^{VII}-CH_3$ units occurs cleanly and enters a first organometallic way of making pure, electrically conducting ReO_3 *films* (Re^{VI}) without any C,H contamination. The new "polymer method" appears as an interesting alternative to chemical vapor deposition techniques (CVD) using organometallic precursor compounds of well-defined composition and structure. Morphology control seems possible, too.

The process presented here for the synthesis of "poly-MTO" (and thus the simple production of phase-pure rhenium trioxide as powders or films) offers a general new approach to oxide ceramics: homolysis of metal−alkyl bonds leads inevitably to metal reduction (*e.g.*, $CH_3ReO_3 \rightarrow {}^{\bullet}ReO_3 + \{{}^{\bullet}CH_3\}$), so that in some cases oxides of ReO_3-type structure with metallic conductivity will be obtained (eq 7). In any case, metal oxides



$$\underset{d^{n}}{O_xM{-}R} \longrightarrow \underset{d^{n+1}}{O_xM^{\bullet}} + \{{}^{\bullet}R\} \qquad (7)$$

exhibiting a d^{n+1} configuration ($n \geq 0$) will be formed from d^n systems by homolytic alkyl (aryl) elimination. Many additional applications are obvious and warrant investigation, *e.g.* intercalation compounds of "poly-MTO". Such intercalation is already documented for the title compound by way of third-dimension ordering effects through interlayered water (see following paper).[6b]

Experimental Section

IR spectra were recorded on a Perkin-Elmer 1650 FT-IR spectrometer, with Digilab FTS-20C and Bomem MB-102 equipped with DTGS detectors. Raman spectra were recorded on a Cary-82 spectrometer using the 514.5 nm line of a Spectra Physics Model 165 argon-ion laser for excitation. UV/vis spectra were obtained from a Perkin-Elmer Lambda 2 spectrometer. ^1H NMR solution spectra were recorded with a JEOL-JNM-GX 400 NMR spectrometer, the ^1H NMR solid-state spectra on a Bruker MSL 300 spectrometer (external standard H_2O $\delta = 4.60$ ppm), and the ESR spectra on JEOL JES RE-2X equipment. FAB-MS spectra were done on a Varian MAT 311-A, and the FT-ICR-LASER-MS was equipped with a Quanta-Ray GCR3 (25 Hz pulse frequency). TG-MS analyses were obtained from a Perkin-Elmer TGA 7 equipped with a QMG-MS 420 (Balzers). For further details see, ref 14.

(1) Alkylrhenium Trioxides. Methyltrioxorhenium(VII) (1) of >99% purity was synthesized as described in ref 3a−c and especially in ref 3d. Ethyltrioxorhenium(VII) and (η^5-pentamethylcyclopentadienyl)trioxorhenium(VII) were synthesized as described in ref 4a,b and especially in ref 5g.

(2) Polymeric Methyltrioxorhenium (2, "Poly-MTO"). A solution of 5.00 g (2.0 mmol) of **1** in 100 mL of high-purity water was sealed in a round-bottom flask which was almost completely filled (in order to avoid sublimation of **1**). The system was heated to 70−85 °C while being stirred for 3−4 days. The golden-colored, fine-crystalline precipitate was then filtered off and washed several times with water to remove the perrhenic acid formed in this preparation. The residue was then carefully washed with absolutely dry solvents (THF, diethyl ether, *n*-pentane) and finally dried in a high vacuum ($<10^{-3}$ mbar, 25 °C) for 24−48 h. The yield of **2** was 3.80 g (70%). Typical elemental analysis: C, 4.43%; H, 1.33%; O, 19.51%; Re, 74.72%. These data correspond to the empirical formula $C_{0.92}H_{3.30}ReO_{3.04}$, see text. The rest of the rhenium ended up in ca. 30% of perrhenic acid and small amounts of higher alkylated rhenium oxides (*e.g.*, yellow $(CH_3)_4Re_2O_4$). The major part of the eliminated methyl groups (34%) was transferred into methane (99%).

No polymerization of **1** occurred under oxidizing conditions (*e.g.*, $c[HClO_4] = 0.10$ mol·L^{-1}), as contrasted by reducing conditions that induce rapid polymerization (0.250 g [1.0 mmol] of **1** in 15 mL of H_2O containing 0.040 g (0.177 mol) of $SnCl_2$). In the latter case, a pale golden precipitate with an empirical formula of $C_{1.14}H_{5.72}ReO_{4.96}Sn_{0.43}Cl_{0.29}$ was obtained after workup as described above. This product obviously contained a rather high amount of water. The yield of $H[ReO_4]$ was determined by three methods that gave identical results within experimental error: (i) as $K[ReO_4]$, (ii) *via* the pH of the solution(s), (iii) by atomic absorption spectroscopy (AAS) directly from solution.

(3) Degradation Chemistry of 2. (a) Solubility in H_2O_2. A 56 mg sample of **2** (0.2067 mmol CH_3 units) was dissolved in 5 mL of D_2O containing 250 μL of H_2O_2 (30 wt %). To this mixture was added 0.0280 g (0.682 mmol) of freshly distilled acetonitrile as an internal standard. The ratio of intensities of the observed signals in the ^1H NMR spectra of $CH_3ReO(O_2)_2{\cdot}H_2O$ (formed by dissolving **2**, $\delta = 2.67$ ppm) and of the standard CH_3CN ($\delta = 1.84$ ppm) was 1/3.35, which is close to the theoretical value 1/3.30.

1 (24.4 mg) and **2** (27.2 mg) were dissolved in 0.1 L of THF/H_2O_2 (10 wt %). The observed absorbance at $\lambda_{max} = 362$ nm ($\epsilon_\lambda = 700$ L·mol^{-1}·cm^{-1}) were 0.98 and 1.05, respectively, which again proves that—within analytical error—every carbon atom of **2** is a methyl group, *cf.* section 3.

(b) Solubility in Nitrogen Bases. A 0.20 g sample (0.80 mmol) of **2** was suspended in a solution of 0.270 g (2.43 mmol) of quinuclidine in 10 mL of THF. To dissolve **2**, the suspension was treated with ultrasound for 18 h at 50 °C. The filtered yellow solution was vacuum-dried. The excess of quinuclidine was then sublimed off. The yellow product thus obtained was recrystallized from diethyl ether/pentane (3/1) at −30 °C, yielding 130 mg (45%) of **1**·[quinuclidine], see ref 4a,b.

A 100 mg (0.40 mmol) sample of **2** was suspended in a stirred solution of 75 mg (0.55 mmol) of 4,4′-dimethyl-2,2′-bipyridine in 15 mL of toluene. The yellow solution was filtered after 18 h at 80 °C. After removal of the solvent, 110 mg (64%) of the yellow powder of **1**·[4,4′-dimethyl-2,2′-bipyridine] was isolated, see ref 7.

(c) Thermolysis. A 300 mg (1.20 mmol) sample of solid **2** was sealed in a small glass tube. The sample was then heated slowly (within 6 h, rate 5 °C/min) to 230 °C and held at this temperature for 24 h. Under these conditions, **2** is degradated to phase-pure (>99.8%) ReO_3 (260 mg, 93%). The entire C,H content is converted into methane (99%) and ethane (0.9%).

(d) Photolysis. A 50 mg sample of solid **2** was exposed for 10 h to the intense light of a mercury middle-pressure lamp: yield of ReO_3, 40 mg (85%); purity, 99%. Upon exposure of **2** to UV light under *absolute* dry conditions, no degradation to ReO_3 could be observed.

(e) Pressure-Induced Structural "Disproportionation". A 250 mg (1.00 mmol) sample of **2** was exposed to 150 bar for 1 h. After storage for 12 h at 1 bar and 25 °C, the formation of small, colorless crystals of **1** on the surface of the compressed sample of **2** could be observed. The entire surface of the tablet of **2** was covered with big single crystals of **1** within approximately 2−3 weeks (IR, MS, X-ray). After several cycles of this treatment, complete formation of **1** (ca. 40%), ReO_3 (ca.

60%), and CH_4 could be observed. No depolymerization took place under absolutely water-free conditions.

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