

Invited review

Essays on organometallic chemistry, VII. Laboratory curiosities of yesterday, catalysts of tomorrow: organometallic oxides [☆]

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Abstract

A systematic investigation of organorhenium- and organoosmium oxides, following the initial discovery of trioxo(η^5 -pentamethylcyclopentadienyl)rhenium(VII) in 1984 by Herrmann, Serrano and Bock, has yielded a plethora of high-oxidation-state organometallics. The key compound methyltrioxorhenium(VII) is now easily accessible and has displayed a surprisingly broad range of catalytic activities, most notably in olefin metathesis, olefin epoxidation, and aromatic oxidation (vitamin K₃). In this context, general problems related to synthesis and reactivity, to structure and bonding, as well as to thermal and photochemical stability were tackled and solved. Organometallic oxides can also serve as structurally well-defined molecular or polymeric precursor compounds for the synthesis of inorganic oxides, the formation of rhenium trioxide being the first example to result from the polymer route.

Keywords: Metal oxides; Rhenium; Synthesis; Structure; Bonding; Catalysis

1. Introduction

At the time when Volume 1 of the *Journal of Organometallic Chemistry* appeared in the fall of 1963, the author of the present essay was still a high-school student. At the time that he received his Ph.D. he admired the contributions of Volume 100 (1975) and later had the privilege to be among the contributors to the special Volumes 250 and 300 (1983, 1986) [2,3]. After having taken over the Regional Editorship from E.O. Fischer (from Volume 464), he feels honoured to contribute to the present Volume 500, thus adding to 193 900 JOM-pages printed up to the present.

In the past 32 years, this journal has presented a good part of the history of modern organometallic chemistry (ca. 20 000 papers). As a matter of fact, in 1963 homogeneous catalysis had just begun to be developed but was far from being fully recognized or even established as a discipline. It was the time when the Wacker–

Hoechst process for making acetic aldehyde had just appeared [4], when rhodium was found to be superior to cobalt in a number of C–C bond forming reactions [5,6], and when bis(allyl)nickel (by Wilke), metal–metal multiple bonds (by Cotton), and metal carbenes (by Fischer) were discovered [7–9]. Catalysis soon became an intellectually attractive and industrially most useful application of organometallic compounds, and the interdependence of synthesis, structure, and chemistry of organometallics has greatly assisted the mechanistic understanding of catalytic processes [10]. The present account summarizes our work on organometallic oxides, showing how an interest in structure and bonding can pave the way for catalysis, and lead to a gradual approach to the goal of catalyst design.

2. Organometallic chemistry and catalysis — active fields of research

As the account below must concentrate on organorhenium oxides for reasons of matter and space, other current research activities in our laboratory can only briefly be mentioned here (Fig. 1, Tables 1 and 2).

[☆] In memory of Ricardo Serrano, who died 30 January 1992. For Part VI of this series see Ref. [1].

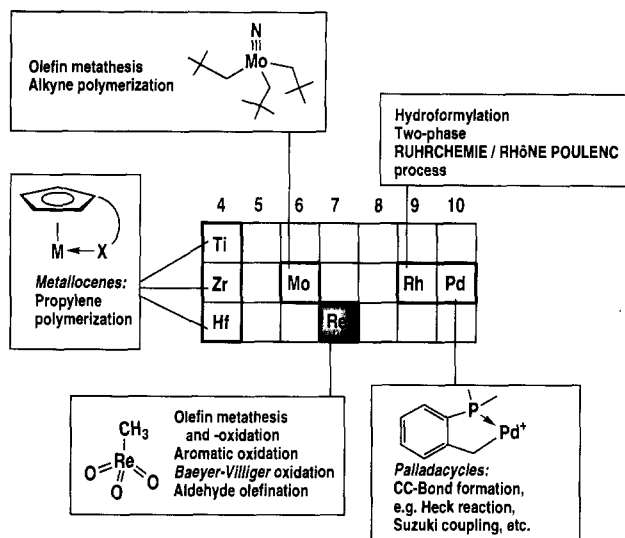
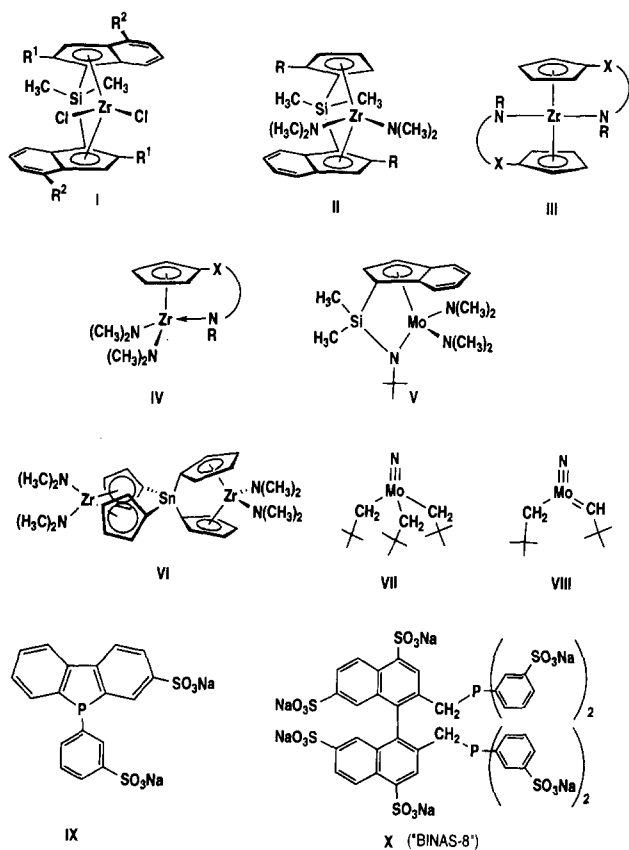


Fig. 1. Ongoing research activities in catalysis in the author's laboratory (summer 1995).

Table 1

Typical ligands and metal complexes in the context of the organometallic catalysis research of the Munich laboratory (1985–1995)



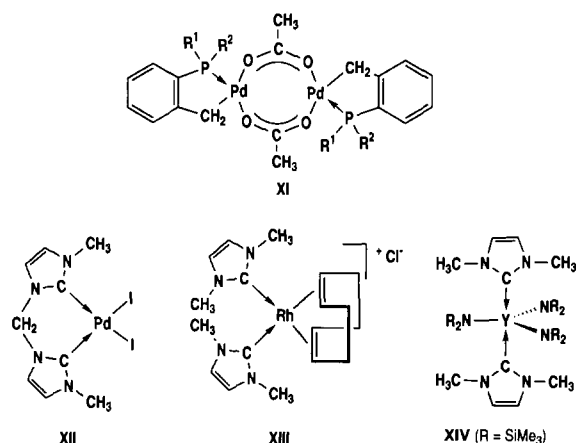
(1) The work on *metallocene-type chemistry* begun in 1986 (J. Rohrmann and coworkers [11a–c], jointly with the central research laboratory of Hoechst AG, Frankfurt am Main), has yielded a number of improved catalysts **I** for isospecific propylene polymerization [11]. Reviews by Küber include the results of the collaboration [12]. More recently, N. Morawietz of our research group has exploited the metal amide route for the straight-forward synthesis of some remarkable half-sandwich- and metallocene-type complexes **II–VI** of titanium, zirconium, hafnium and molybdenum [13]. The chemistry of these amides seems more flexible in respect of both synthesis and catalysis than that of the usual halide complexes.

(2) In the field of *organometal nitrides*, still rare in molecular chemistry, our work was focussed on tris(neopentyl)nitridomolybdenum(VI) **VII** in studies by S. Bogdanović, R. Poli and coworkers in 1993/94 [14]. This compound polymerizes 2-butyne quite efficiently and is an olefin metathesis catalyst, the unstable carbene **VIII** probably being an intermediate. Surface-immobilized species of this kind are being developed together with J.-M. Basset (Lyon).

(3) Catalysis with *water-soluble organometallics*, mostly containing sulfonated phosphines as ligands, has been developed for two-phase processes in a joint effort with Hoechst AG, Oberhausen, where a large-capacity hydroformylation plant for butyric aldehyde is in operation (ca. 300 000 tons per year, Ruhrchemie–Rhône Poulenc process, Cornils and coworkers [15]). J. Kulpe, J. Kellner, Ch. W. Kohlpaintner, R. Manetsberger and G. Albanese have made significant contributions in this field since the collaboration started in 1986 [16,17]. The catalyst Rh^I/BINAS (Table 1), developed jointly with

Table 2

New types of catalysts: palladacycles and metallocenes of *N*-heterocycles [19,22,23]



H. Bahrmann and P. Lappe of Hoechst AG, is unprecedented in terms of activity, productivity and selectivity for propene hydroformylation. An improved synthesis of sulfonated phosphines such as **IX** and **X**, avoiding *P*-oxidation (boric acid route; 1994) promises to have broad application and sets the scene for the use of a variety of otherwise inaccessible catalysts in two-phase processes [18].

(4) Studies on *palladium-catalyzed C–C-coupling* reactions, particularly in the field of olefin vinylation and -arylation (Heck reactions, Suzuki coupling, alkyne coupling), revealed a new catalyst structural principle in 1993/94. Work with Ch. Broßmer, M. Beller, H. Fischer, C.-P. Reisinger and K. Öfele showed that palladacycles of type **XI** (Table 2) are highly efficient in C–C-coupling of aryl bromides (and aryl boronic acids) with olefins. Activation of the much less reactive aryl chlorides seems possible, too [19]. This structural principle also holds for other metals, e.g. rhodium.

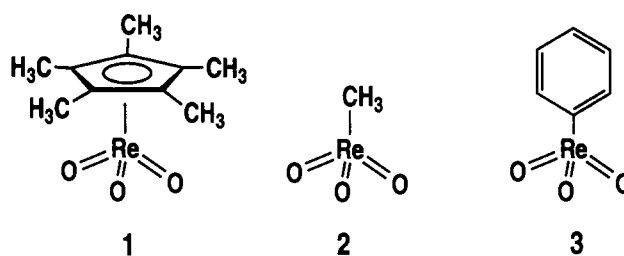
(5) A most recent discovery, still under active investigation, arises from the early work by K. Öfele of this laboratory [20]. We found that metal complexes exhibiting *N-heterocyclic carbenes* [21] act as both active and extraordinarily thermally and chemically stable catalysts in a number of *CC*-coupling reactions [22], for example Heck reactions and hydroformylations (M. Elison, J. Fischer, Ch. Köcher and K. Öfele, 1994/95). Typical catalysts are the palladium(II)- and rhodium(I) complexes **XII** and **XIII** (Table 2) which survive temperatures of approx. 300°C. The Pd-complex can be employed in Heck reactions at temperatures above 150°C. Since imidazole-derived carbenes have an extremely versatile coordination chemistry (low and high oxidation states of the metal), they may become a new class of ligands for use in homogeneous catalysis. Several synthetic routes have been developed to their complexes with metals throughout the Periodic Table, including the lanthanoid and actinoid elements [21,23] (cf. compound **XIV** synthesized by F. Munck (Table 1)).

While these areas still merit a great deal of mechanistic investigation, our research on organometallic oxides has given so much information that a present review of the findings is justified and timely. Comparison with previous accounts of this topic fortunately shows that earlier predictions and perspectives were not too bold [3,24]. Studies in the field have also flourished in the hands of other researchers [25,71].

3. Organometallic oxides

Unexpectedly at the time of its discovery by Herrmann et al. in 1984 [26], studies of the organorhenium(VII) oxide ($\eta^5\text{-C}_5\text{Me}_5$)ReO₃ (**1**) have entailed rapid development of new organometallic catalysts and investigation of their chemistry. It is in particular the

parent compound methyltrioxorhenium(VII) (**2**), nowadays known as MTO, that has proved so effective in olefin metathesis, olefin epoxidation, Baeyer–Villiger oxidation, aromatic oxidation, and Diels–Alder cycloaddition. Steric accessibility (low coordination number, small ligands), a strong metal–carbon bond (with $\Delta H \geq 237 \text{ kJ mol}^{-1}$), and a pronounced Lewis acidity at the metal (Re(VII)) are the favorable features of MTO that result in its catalytic applications. The cyclopentadienyl- and phenyl congeners **1** and **3**, respectively, suffer from either steric crowding (**1**) or insufficient stability (**3**) under catalytic conditions [103]. In light of recent evidence, however, that the molecular metal oxide ReO₃ catalyzes specific oxidation reactions (with H₂O₂), the entire class of compounds R–ReO₃ must also be considered as readily available precursors of ReO₃ groups that would normally aggregate to give the polymeric (Perovskite-type), violet, insoluble rhenium trioxide {ReO₃}_n.

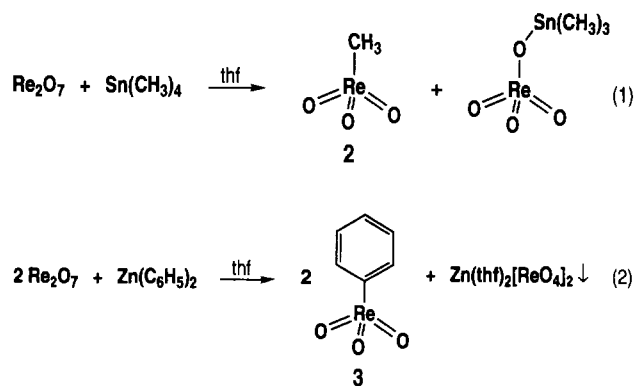


3.1. Synthesis: *impavidi progrediamur*¹

Two general routes are now available for the synthesis of organorhenium(VII) oxides.

(i) Direct alkylation (arylation) of Re₂O₇, the most common starting material, works well if the transfer reagent (e.g. SnR₄, ZnR₂) does not reduce the rhenium [27]. The drawback of this method, however, is that half of the rhenium is consumed as (relatively unreactive) perrhenate, such as the polymeric covalent trimethylstannyl-perrhenate [28] (Eq. (1)), or the poorly soluble zinc perrhenate (Eq. (2)).

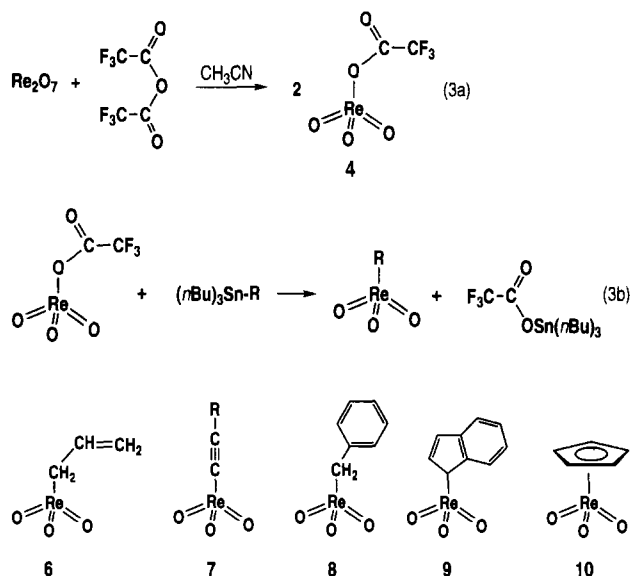
¹ Ernst Haeckel (1834–1919), German zoologist and philosopher.



(ii) No rhenium-containing by-products are formed if the alkylation (arylation) is carried out with mixed esters of perrhenic- and carboxylic acid(s), a typical example being perrhenyltrifluoroacetate **4** (Eq. (3a)). Perrhenyl carboxylates of this type are most easily obtained (> 95% yield) by treatment of Re_2O_7 with carboxylic anhydrides. They crystallize with varying numbers of solvent molecules (as donor ligands), cf. Fig. 2 [29].

Since these anhydrides contain a good leaving group, e.g. trifluoroacetate, alkylation (arylation) according to Eq. (3b) occurs under mild conditions, frequently between -80 and -20°C . Perfect selectivity for R-group transfer using tri(*n*-butyl) tin reagents ($(n\text{-Bu})_3\text{Sn-R}$) is an extra advantage of this method, and separation of the products can usually be carried out by extraction or sublimation techniques [30]. The more toxic organotin compounds (particularly tetramethyltin) can thus be avoided. An unexpected wealth of organorhenium(VII) oxides became available from the Ph.D. work of Fritz E. Kühn (1994), among them the allyl- (**6**), alkynyl- ($\text{R} = \text{H}, \text{C}_6\text{H}_5, \text{ReO}_3$; **7**), benzyl- (**8**), σ -indenyl- (**9**), and π -cyclopentadienyl (**10**) derivatives, with the last compound being much more thermally stable than pre-

viously assumed [30]. Never claim that a compound cannot exist – you may just have missed an appropriate synthetic approach! “*Impavidi progrediamur*”.



Some of the above compounds are stabilized by *N*-donor ligands, preferably quinuclidine and bipyridine bases, so raising the temperature of decomposition by 100°C relative to the parent species R-ReO_3 (Fig. 3). The indenyl complex has a fluxional geometry [31], but it is not clear why σ - is preferred over π -coordination, here and in the case of the allyl **6**.

The anhydride route shown in Eqs. 3a and 3b can be carried out as a one-pot sequence of the two reactions. Perhalogenated carboxylates are alkylated more efficiently than the parent compounds (Fig. 4). This technique is the logical exploitation of the reaction principle on which Eqs. (1) and (2) are based: Re_2O_7 undergoes a

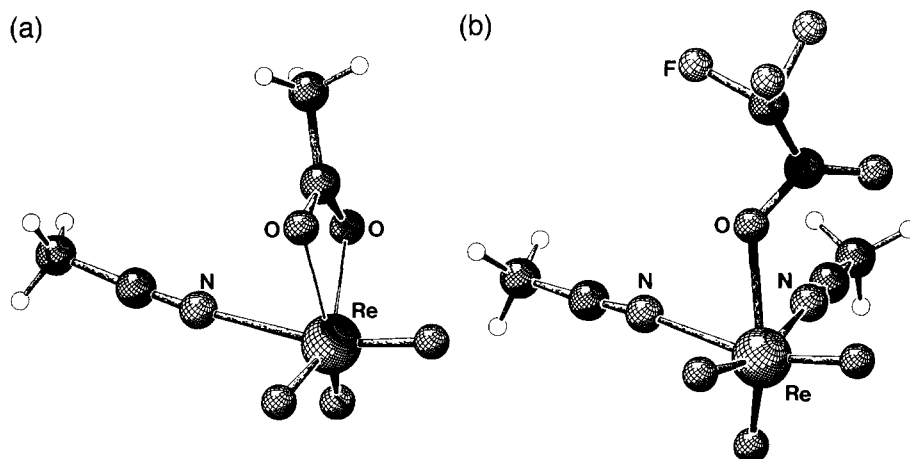


Fig. 2. Crystal structures of the mixed anhydrides of perrhenic and acetic acid (SCHAKAL representations). Left, $[\text{CH}_3\text{C}(=\text{O})\text{O}]\text{ReO}_3(\text{N}\equiv\text{C}-\text{CH}_3)$ contains a η^2 -acetate group (C.N. 5); right, $[\text{CF}_3\text{C}(=\text{O})\text{O}]\text{ReO}_3(\text{N}\equiv\text{C}-\text{CH}_3)_2$ containing two acetonitrile ligands (higher Lewis acidity at Re?) requires only η^1 -coordination for the perfluoroacetate (C.N. 6).

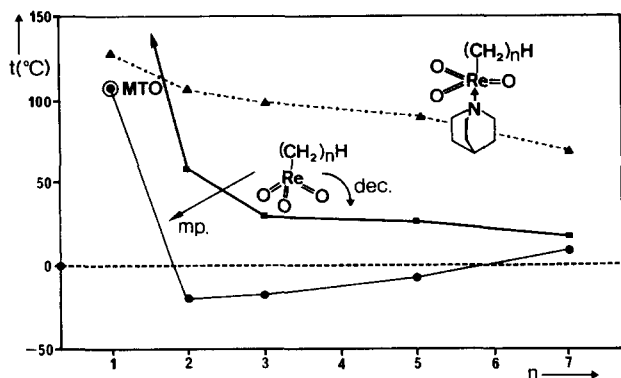
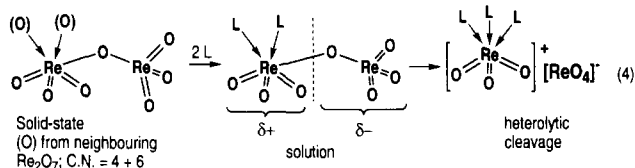


Fig. 3. Stability of organorhenium(VII) oxides $\text{H}-(\text{CH}_2)_n-\text{ReO}_3$: melting points (\circ) and dec. temp. (\blacksquare) of $\text{H}-(\text{CH}_2)_n-\text{ReO}_3$; dec. temp. (\blacktriangle) of $\text{H}-(\text{CH}_2)_n-\text{ReO}_3 \cdot \text{Quin}$ (Quin = quinuclidine).

heterolytic cleavage to form the perrhenyl cation $[\text{ReO}_3]^+$ (stabilized as CH_3ReO_3) and the perrhenate ion (Eq. (4)).



This behavior originates from the structural and solvation chemistry of Re_2O_7 : the unsymmetrical ReORe bridge situation in the solid (crystalline) Re_2O_7 is maintained upon dissolution of the compound in (donor) solvents L such as acetonitrile and THF, so nucleophiles can attack the hidden perrhenyl cation [32]. This view receives support from the fact that spontaneous hetero-

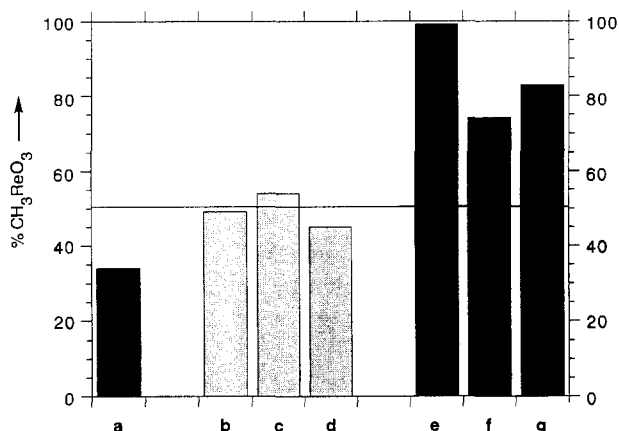
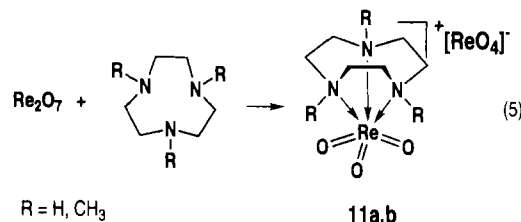
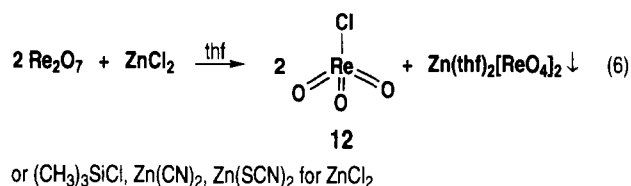


Fig. 4. Methylation of oxorhenium(VII) precursor compounds: (a) Re_2O_7 ; (b) $\text{CH}_3\text{COOReO}_3$; (c) $\text{C}_3\text{H}_7\text{COOReO}_3$; (d) $\text{ClCH}_2\text{COOReO}_3$; (e) $n\text{-C}_3\text{F}_7\text{COOReO}_3$; (f) $\text{CH}_3\text{COO}(\text{CF}_3)_2\text{COOReO}_3$; (g) $\text{CF}_3\text{COOReO}_3$. The columns show the yields obtained after 4 h reaction time at room temperature.

lysis [33] occurring with N,N,N -triazacyclononanes to give **11a** and **11b** (Eq. (5); $R = \text{H}$ or CH_3), and also with simple metal and pseudohalides [34a]; for

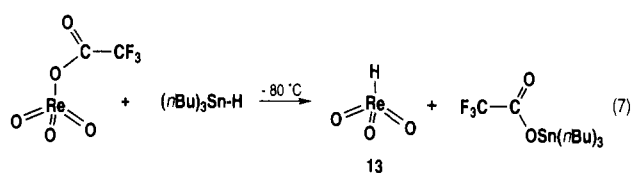


example, the hitherto difficult-to-make perrhenyl chloride, ClReO_3 **12**², and related inorganic perrhenyl compounds are now available by simply treating Re_2O_7 with ZnCl_2 or related reagents, respectively (Eq. (6)).



or $(\text{CH}_3)_3\text{SiCl}$, $\text{Zn}(\text{CN})_2$, $\text{Zn}(\text{SCN})_2$ for ZnCl_2

There is recent evidence that a hydridotrioxorhenium(VII) **13** can be formed by the same route (Eq. (7)): a high-field ^1H NMR signal at $\delta = -10.3$ ppm (THF- d_8) develops upon addition of the hydride transfer reagent $(\text{Bu}^n)_3\text{Sn-H}$ to the carboxylate at -80°C , but decomposition of **13** occurs above ca. -30°C ; trapping studies of this species are underway [35].



The “anhydride route” promises a general entry into organometallic oxide chemistry: most metal oxides (e.g. V_2O_5 , Nb_2O_5 , WO_3) are totally insoluble in organic solvents, and this precludes their direct alkylation (arylation), but they may form soluble carboxylates. The molecular oxides³ Re_2O_7 and OsO_4 , are unique excep-

² $\text{ReCl}_5 + 3 \text{Cl}_2\text{O} \rightarrow \text{ClReO}_3 + 5 \text{Cl}_2$ [34b].

³ This term is meant to signify that no significant or only weak intermolecular forces operate in the solid-state structures. OsO_4 forms strictly tetrahedral molecules (only the gas-phase structure is known); Re_2O_7 is dinuclear in the gas phase, while the crystal structure is a three-dimensional network that is easily broken up according to Eq. (4).

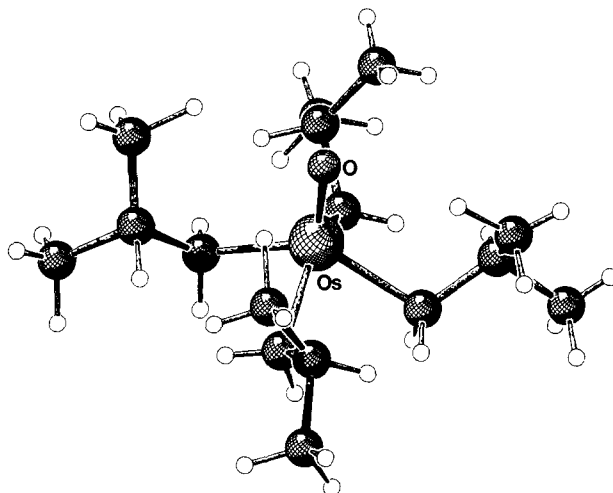


Fig. 5. Crystal and molecular structure of oxotetrakis(iso-butyl)osmium(VI) as SCHAKAL representation, taken from Ref. [37,40]. Tetragonal, C_4 -molecular symmetry, **14**; $a = 126.21(7)$, $c = 591.99(5)$ pm, $R_w = 0.018$.

tions, so facilitating our original entry into their organic chemistry. However, OsO_4 is too strong an oxidizing agent to form organic derivatives. As shown by S.J. Eder, it is necessary to turn to the easily available Os(VI) glycolates (from OsO_4 and alkenes) to synthesize organoosmium(VI) oxides such as **14**, **15** and **16** [36]. The isobutyl complex **14c**, in spite of its d^2 -Os(VI) configuration and its four β -hydrogen atoms, resists temperatures as high as $100^\circ C$ [37]. This is presumably because the β -hydrogen atoms never get into a position *trans* to the oxo group, which is necessary for the transfer of the H atom to the metal (Fig. 5). The structural chemistry depends on the coordinating σ -donor ligands and can involve tetrahedral (**16a**), trigonal-bipyramidal (**16b**), or octahedral (**16c**) geometry. A

labile trimer **15b**, with a unique *planar* Os_3O_3 ring geometry, exists only in the crystal [36a,38].

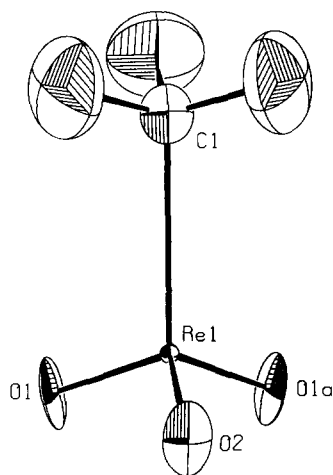
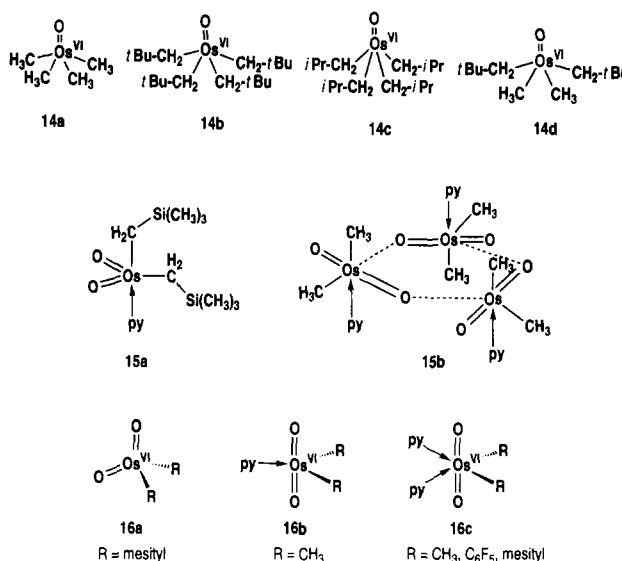


Fig. 6. Neutron powder diffraction structure (single crystal) of CD_3ReO_3 at 5 K; selected data: Re–O1, 170.2(1); Re–O2, 170.2(2); Re–C, 206.3(2); C–Re–O1, 105.9(1); O1–Re–O2, 112.8(1); O1–Re–O1a 113.2(1); Re–C–D1 108.3(1); D1–C–D2, 111.1(1); D2–C–D2a; 109.9(2). All distances are in pm and angles in degrees. Molecular C_3 symmetry.

3.2. Structure and bonding: *omnia rerum principia parva sunt*⁴

The structure of the parent MTO is known in great detail [39–42]. It was shown by neutron diffraction that the molecule adopts a staggered conformation, and that there is no close $Re \cdots H$ contact (Fig. 6). As in the above Os(VI)-series R_2OsO_2 , coordination of *N*-base ligands changes the geometry from (distorted) tetrahedral in CH_3ReO_3 (Fig. 6) to trigonal-bipyramidal for

⁴ Marcus Tullius Cicero (106–43 B.C.), Roman orator.

the species $\text{CH}_3\text{ReO}_3 \cdot \text{L}$ and octahedral for the species $\text{CH}_3\text{ReO}_3 \cdot \text{L}_2$.

However, any distorted structure seems possible, especially if ring strain is increased in chelating C,N -ligands. If the alkyl- and the N - or O -base ligands are independent, they prefer to be *trans* to each other. $\text{Re}-\text{C}$ bond lengthening by approx. 5 pm due to σ -donor ligands is significant, while the $\text{Re}-\text{O}$ distances remain within the narrow span of 169–171 pm (Fig. 7).

The addition of σ -base ligands to MTO reflects the relatively strong Lewis acidity of the metal center, a property that accounts for much of the chemistry of this compound. Oxygen exchange with ^{17}O -labeled water occurs instantaneously (but not in the case of the sterically much more crowded and presumably less Lewis-acidic **1**), giving rise to the typical ^{17}O -resonance of MTO at $\delta = 829$ ppm (CDCl_3). The latter correlates with Gutmann's donor number of the relevant solvent ($\Delta\delta = 47$ ppm [43]). ^{17}O NMR spectroscopy proved to be a useful tool in assigning structures and to detect equilibria between organorhenium(VII) oxides with other ligands and solvents [43,44].

Force constants $F(\text{ReO})$ derived from the stretching frequencies reflect the electronic influence of the organic ligands (J. Mink et al. [45]); additional Lewis bases L as well as π -bonded hydrocarbon ligands R both lower the $\text{Re}-\text{O}$ bond order, thus nicely reflecting the electron-donating effect (Table 3). Alkynyl- and alkenyl groups are thus classified as typical σ -ligands, cf. $F(\text{ReO}) = 7.38$ $\text{mdyn}/\text{\AA}$ for $\text{C}_6\text{H}_5\text{C}\equiv\text{C}-\text{ReO}_3 \cdot \text{bipy}$ [30a]. A detailed study of the vibrational spectra of MTO and higher congeners (ethyl, *n*-propyl) was published by Mink et al. [45].

Table 3
Force constants $F(\text{ReO})$ [$\text{mdyn}/\text{\AA}$] of organorhenium(VII) oxides $R-\text{ReO}_3 \cdot L$

R	L	$F(\text{ReO})$
σ -alkyl	—	8.15–8.31
σ -aryl	—	8.00–8.15
σ -alkyl	quinuclidine	7.55–7.61
π -aryl ^a	—	< 7.00

^a Cyclopentadienyl and substituted derivatives.

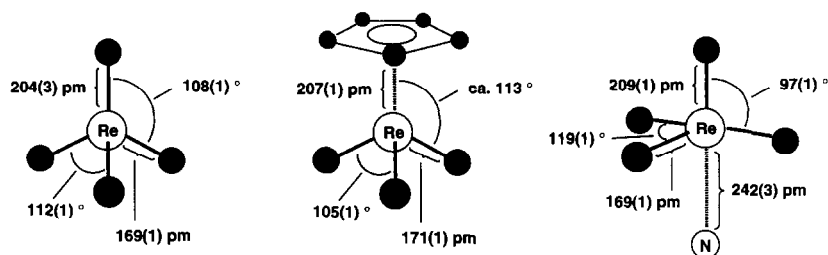


Fig. 7. Structural data of organorhenium(VII) oxides: alkyl- ReO_3 (left), $\text{Cp}-\text{ReO}_3$ (center), alkyl- $\text{ReO}_3 \cdot L$ ($L = N$ -base) right. Average bond lengths and angles are reported.

Metal oxides MO_n act as strong electron acceptor groups if the theoretical analysis for CH_3ReO_3 , supported by dipole measurements and PE spectral data [46], is generally applicable. The first ionization potential (11.8 eV) and electron affinity (3.9 eV) of the ReO_3 group are close to those of chlorine (12.8 and 2.7 eV), so the Mulliken electronegativities should also be of similar magnitude. The electron-withdrawing character of the ReO_3 group follows convincingly from the occurrence of the first ionization potential (PE spectra) of (η^1 -mesityl) ReO_3 at 9.0 eV, which in this case arises from the π -ionization of the aromatic ring ligand: free mesitylene undergoes this ionization even at 8.41 eV. SCF-calculations by Bénard et al. revealed similar electron-density maps for the three compounds CH_3ReO_3 , CF_3ReO_3 and ClReO_3 , showing a relatively uniform distribution between the metal and the ligands CH_3 , CF_3 and Cl , respectively [47a]. The bond polarities thus should be low. By way of contrast, a concentration of electron density at the fluorine is revealed by calculations for FReO_3 (Fig. 8), so the bond should be rather polar ($\text{F}^{\delta-} - \text{Re}^{\delta+}$). For all complexes an appreciable participation of the 6s-orbitals of Re is predicted, resulting in an expansion of electron density perpendicular to the metal–ligand bond axis. The Mulliken population of the respective p_z -orbitals is given at 0.94 eV (CH_3), 1.21 eV (Cl) and 1.52 eV (F). The lowest-energy ionization of MTO occurs at 11.8 eV (oxygen lone-pair) in the He-I-PE spectrum [46]. The latter was fully assigned by Bock et al. on the basis of theoretical calculations (SCF, CI, multireference-SDCI).

According to recent ab initio SCF-, two-configuration (TC) SCF and CI calculations [47a], the hypothetical $\text{O}_3\text{Re}-\text{Re}(\text{CO})_5$ should have a larger bond energy (271 kJ mol^{-1} , relaxed) than the $\text{O}_3\text{Re}-L$ molecules mentioned above. The metal–metal coupling can be expressed in terms of a σ -donation from $\text{Re}(\text{CO})_5$ to ReO_3 , but there is also evidence for some covalent character. The electronic structure of $\text{O}_3\text{Re}-\text{Re}(\text{CO})_5$ is expected to be similar to that of the known alkylrhenium(VII) oxides [47b]. Attempts to confirm this by synthetic study should be undertaken.

In a qualitative EHMO description, Mealli et al.

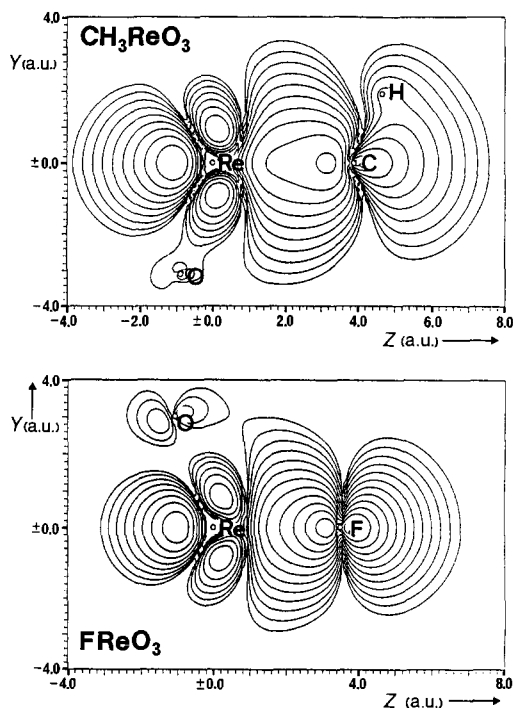


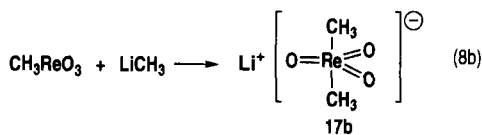
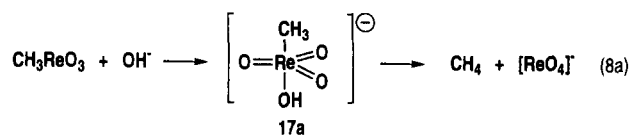
Fig. 8. Contour diagrams of the σ -population (electron density) of CH_3ReO_3 (top) and FReO_3 (bottom), according to B  nard et al., shown in the plane passing through the Re–L bond axis. The data result from SCF calculations [47a]. The outer contour line corresponds to a charge density of $0.0025 \text{ e } \text{Å}^{-3}$, with a doubling of density from line to line going towards the center.

assigned an 18e-situation to MTO (bond order of 2 2/3), contrary to the results obtained if only formal ReO double bonds are considered [48]. Re–C bond dissociation energies of 319 kJ mol^{-1} (nonrelaxed, pyramidal ReO_3 fragment) and of 237 kJ mol^{-1} (relaxed) have been calculated for MTO [48]. Density–function calculations are underway [102].

3.3. Mors sua quemque manet⁵

3.3.1. Hydrolysis

The carbon–bond strength of compounds R– ReO_3 quite obviously determines their stability. In chemical terms, only hydroxides undergo rapid degradation, as in Eq. (8a) to form perrhenate, in the case of the parent MTO an intermediate **17a** being likely to be involved. An analogous species $[\text{CH}_3\text{ReO}_3\text{Cl}]^-$ is stable, and there is X-ray crystallographic evidence for $[(\text{CH}_3)_2\text{ReO}_3]^-$ **17b** [49] (Eq. (8b)).



For this reason, alkaline media and strongly nucleophilic reagents are to be avoided in chemical transformations and in catalytic applications of MTO. However, MTO does not undergo H/D exchanges (e.g. unsuccessful attempts of deprotonation with proton sponge).

MTO is hydrolyzed rapidly in basic aqueous solutions, and more slowly in acidic media. In a collaborative project Laurency et al. [50] determined the kinetic data (at 298.2 K) for the hydrolysis in dilute solutions ($3 \times 10^{-4} \text{ M}$, 0.1 MPa) following Eq. (8a) and the rate law $-\text{d}[\text{MTO}]/\text{dt} = k_1 \cdot [\text{OH}^-][\text{MTO}]$ (UV/vis):

$$k_1 = (8.6 \pm 0.3) \cdot 10^2 \text{ mol}^{-1} \text{ sec}^{-1}$$

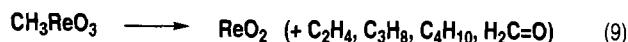
$$\Delta H_1^\ddagger = 15.9 \pm 1 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S_1^\ddagger = -135 \pm 3 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$$

$$\Delta V_1^\ddagger = -2.4 \pm 0.1 \text{ cm}^3 \cdot \text{mol}^{-1}$$

3.3.2. Thermal and plasmachemical degradation

MTO is by far the most thermally stable member of the entire class of organorhenium(VII) oxides. Decomposition to give mainly a black, lustrous, electrically conducting layer of ReO_2 occurs only well above 300°C (Eq. (9)). Higher temperatures reduce the oxygen content of the resulting rhenium oxides (e.g. $\text{Re}/\text{O} \approx 1/1$ at 450°C), indicating that the efficiency of the combustion of the hydrocarbon(s) increases with increasing temperature [39,51–53].



Simple Re–C-bond cleavage with formation of ReO_3 is not observed under such drastic conditions owing to the disproportionation $3 \text{ReO}_3 \rightleftharpoons \text{ReO}_2 + \text{Re}_2\text{O}_7$ at high temperatures. Surprisingly, at first sight, the carbon-rich oxides yield oxygen-poor residues upon thermal degradation: $(\text{C}_5\text{Me}_5)\text{ReO}_3$ (**1**) gives relatively pure rhenium at $> 500^\circ\text{C}$ ($> 98\% \text{ Re}$, $< 2\% \text{ C}$), while $(\text{C}_5\text{Me}_5)\text{Re}$

⁵ Sextus Propertius (c. 50–16 B.C.), Roman poet (lyrics, elegies).

(CO)₃ gives carbon-rich products (e.g. 67% Re, ≤ 28% C at 600°C). Similar results were obtained in plasma-enhanced chemical vapor deposition studies (PECVD) at lower temperatures: at 350°C in a hydrogen plasma, (C₅Me₅)Re(CO)₃ forms films of equimolar Re/C stoichiometry. However, MTO produces relatively pure, amorphous (X-ray) rhenium films with < 1.5% carbon contamination when heated in a H₂/Ar plasma at 300–450°C. Microcrystalline rhenium is produced when a large excess of H₂ is used in a H₂/Ar plasma at 190°C. These films are free from carbon (SIMS) and contain only small traces of oxygen and hydrogen. These and related results show that organometallic oxides may well be considered as molecular precursors for the formation of the respective metals in chemical vapor deposition (CVD) processes, if there are other ligands present to take up the oxygen (combustion).

Thermal decomposition of compounds R-ReO₃ (except MTO) in solution involves a radical-type homolytic Re–C bond cleavage with an intermolecular pathway, as revealed by the concentration-dependence of the degradation kinetics [54]; while neat C₂H₅ReO₃ (**18**), a colorless oil of m.p. –21°C, decomposes at 60°C in a sealed tube, it totally resists prolonged heating for 7 d in toluene at 80°C. However, donor solvents such as THF reduce the lifetime significantly (partial decomposition of **18** taking place in THF at 60°C during 7 d).

Ethyltrioxorhenium(VII) **18**, an ideal test-case for β-hydrogen elimination, decomposes with initial formation of butane (Fig. 9) which clearly points to a radical decomposition; only gradual formation of the C₂ hydrocarbons and (a little) methane is recorded. However, the ratio *k_c/k_d* of butane to ethylene and ethane (Eq. (10))

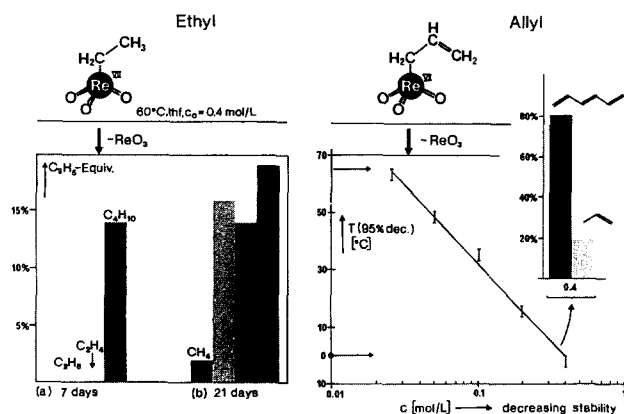
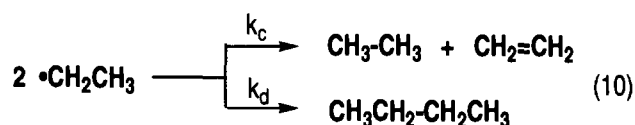


Fig. 9. Decomposition of ethyl- and allyltrioxorhenium(VII): radical- vs. β-hydride elimination? Left, mostly butane is extruded after 7 d at 60°C in THF (0.4 mol l⁻¹), while increasing amounts of C₂-products are formed subsequently; right, intermolecular decomposition is typical of the class R-ReO₃, cf. (σ-allyl)ReO₃. The temperatures (right) correspond to a ca. 95% decomposition rate.

should amount to 6.6 (gas-phase and solution) if a pure radical pathway is responsible for their formation. This is obviously not the case. However, a β-elimination mechanism is unlikely because (i) a C₄-hydrocarbon is produced in large amounts, and (ii) **18** and its congeners represent electronically “empty” d⁰-Re(VII) systems. However, when **18** is treated with triphenylphosphine (which is known to reduce the metal center, formally Re(VII) to Re(V)), a rapid decomposition occurs in toluene at 25°C with predominant formation of C₂-hydrocarbons after complete decomposition; mostly ethylene (75%) and ethane (24%) are formed (see Fig. 9).

This supports the view that a β-elimination pathway is initiated by reduction of the metal.

The results of a study of the decomposition of σ-allyltrioxorhenium(VII) (**6**) also support a radical-type decay [54]: the allyl equivalents disappear as 1,5-hexadiene, the dominant product (81% at *c*₀ = 0.4 mol l⁻¹; 58% at 0.05 mol l⁻¹), and as propylene (remainder to 100%), with the latter being *d*₁-labeled if the experiment is conducted in THF-d₈ (25°C). Only propylene is formed when **6** decomposes in the presence of water (THF solution); the inorganic product is mainly ReO₃.

3.3.3. Photolysis

Organorhenium(VII) oxides are also sensitive to photolysis [55]. The simplified MO-diagram for MTO (Fig. 10) explains a low-energy a₁ → e* LMCT excitation that both entails Re–C bond cleavage and weakens the Re–O bonds (the e*-LUMO is an antibonding π*-orbital of the rhenium–oxygen interactions). Photolysis occurs under irradiation at 200–400 nm, depending on the nature of R, and can be followed by UV/Vis spectroscopy.

Radical formation [•]R has been detected by ESR spectroscopy by using nitrosodurene as a spin-trap reagent; the [•]ReO₃ radicals formed at the same time

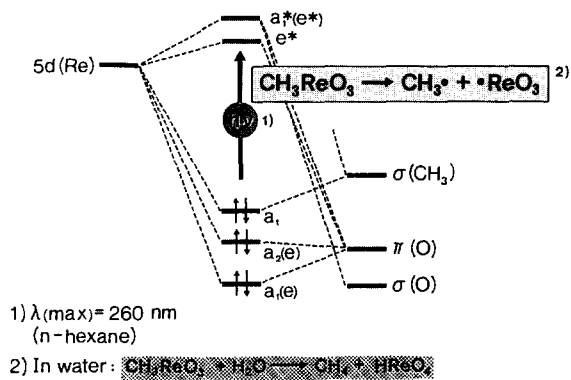
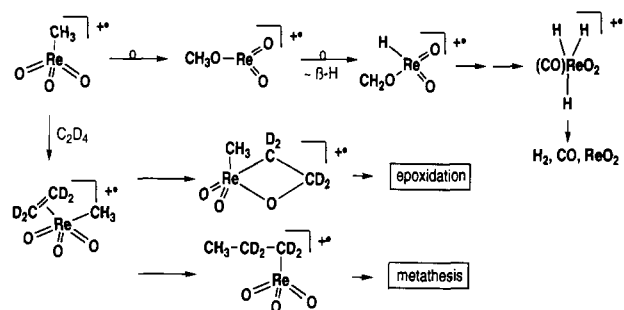


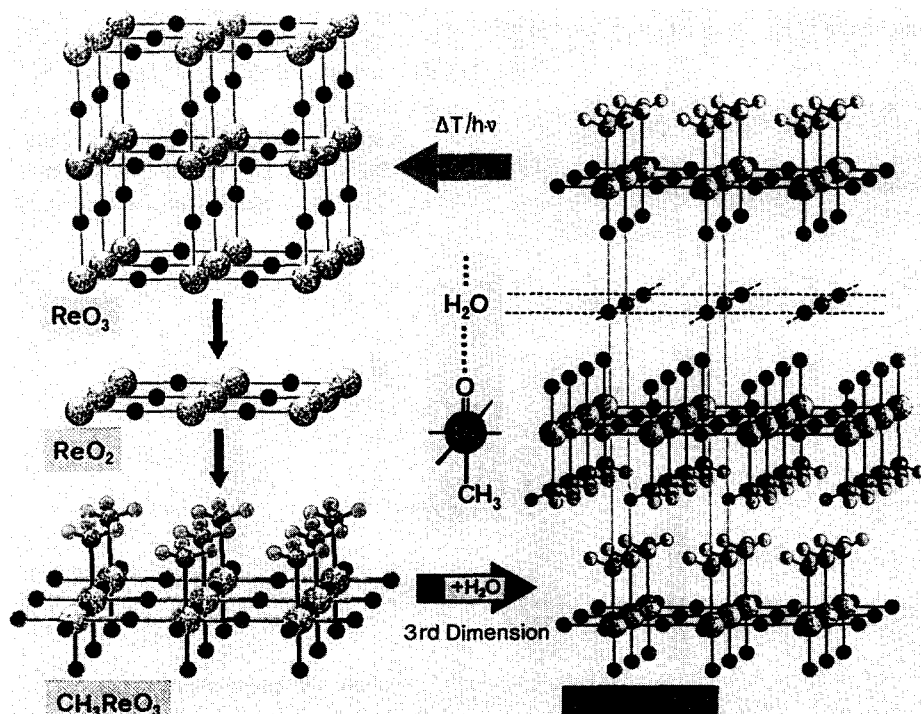
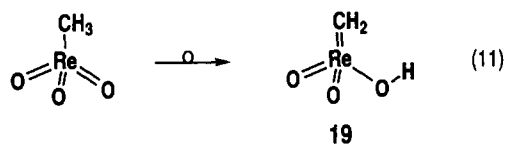
Fig. 10. Simplified MO diagram of methyltrioxorhenium(VII).

aggregate to give (colloidal) rhenium(VI) oxide. Most stable is the π -complex ($\eta^5\text{-C}_5\text{Me}_5$) ReO_3 (**1**) which does not decompose even upon prolonged photolysis ($\lambda = 313 \text{ nm}$, $\phi = 10^{-4}\%$, CH_3CN), whereas the thermally resistant MTO is the most photolabile ($\lambda = 254 \text{ nm}$, $\phi = 0.58\%$, H_2O ; $\text{C}_2\text{H}_5\text{ReO}_3$: $\lambda = 254 \text{ nm}$, $\phi = 0.53\%$, CH_3CN).

A recent low-temperature matrix-photolysis study (-5°C) does not fully fit this picture: it was shown by Maier et al. that the hydrocarbon moiety of MTO is not lost upon irradiation [56]. Instead, hydrogen migration (tautomerization in Eq. (11), enolization), as confirmed by labeling experiments employing CD_3ReO_3 occurs

Scheme 1. Gas-phase rearrangement of $[\text{MTO}]^+$ in the mass spectrometer (top) and reaction with ethylene (bottom).

(IR data). Flash photolysis of MTO generates formaldehyde. It is possible that photolysis generates a methyl radical which is trapped in the matrix cage so the enolization can successfully compete with homolysis. It is noteworthy that the resulting methylene species **19** had previously been assumed to be formed on oxidic supports in olefin metathesis (Section 3.5.5).

Fig. 11. Polymeric CH_3ReO_3 and ReO_3 are related: structural model of poly-MTO as it results stepwise from the ReO_3 lattice, see text and Ref. [60].

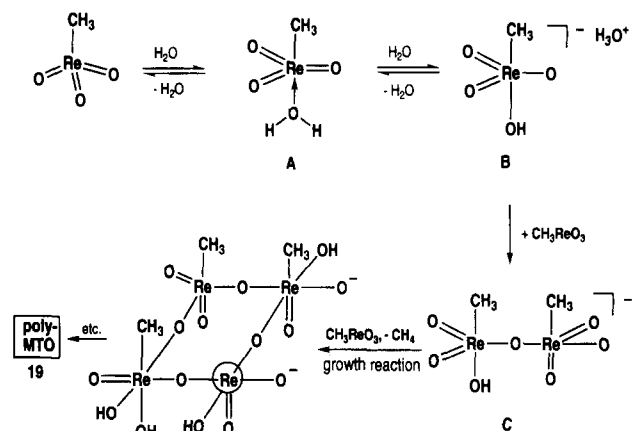
3.3.4. Degradation in the mass spectrometer

The base peak in an ordinary electron impact (EI) mass spectrum of MTO, at m/z 222 (^{187}Re), is assigned to the ion formed by loss of CO from the parent ion $[\text{CH}_3\text{ReO}_3]^+$ ($m/z = 250$) ($\rightarrow [\text{H}_3\text{ReO}_2]^+$); further loss of hydrogen is also observed [57]. If the radical cation $[\text{CH}_3\text{ReO}_3]^+$ is generated in a four-sector mass spectrometer, rearrangement to the methoxy species $[\text{CH}_3\text{O-ReO}_2]^+$ occurs, followed by multiple β -H migration (Scheme 1).

Schwarz and Schröder showed that $[\text{CH}_3\text{ReO}_3]^+$ reacts with C_2H_4 (C_2D_4) to yield a 1/1 complex that further isomerizes to give intermediates that can plausibly give rise to the metathesis and epoxidation products [58]. By use of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry, the proton affinity of MTO was measured at $174 \pm 5 \text{ kcal mol}^{-1}$, a value in the range observed for FeO_2 , $\text{Fe}(\text{O})\text{OH}$ and OsO_4 . Protonation (in the gas-phase) occurs at the oxo groups. The protonated form of MTO is inert in an ion/molecule collision with water [58], in agreement with the known stability of MTO in acidic solution.

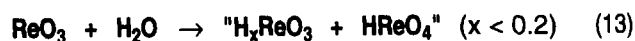
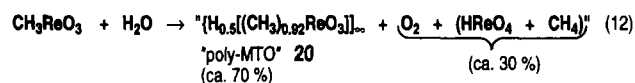
3.4. *Semper cupidus novarum rerum*⁶: two- and three-dimensional growth of methyltrioxorhenium(VII)

A phenomenon unprecedented in organometallic chemistry was encountered in a study involving the aqueous chemistry of MTO [59–61]. From the reasonable stable, colorless, acidic solutions of MTO in water ($\text{p}K_s = 3.82$, 22°C) a golden-colored, highly refractory precipitate separates very slowly at ambient temperature, or within hours at 70°C . Scherer showed that this novel material poly-MTO **20** of empirical formula $\text{H}_{0.5}[(\text{CH}_3)_{0.92}\text{ReO}_3]_x$ (Eq. (12)) has a layer-structure of methyl-deficient, corner-sharing $\text{ReO}_5(\text{CH}_3)$ octahedra (P 4 mm, tetragonal, $a = 3.728(1) \text{ \AA}$, $c = 16.516(5) \text{ \AA}$). It adopts the three-dimensional extended ReO_3 -motif in two dimensions as a $\{\text{ReO}_2\}_x$ network. Adjacent layers of corner-sharing $\text{ReO}_5(\text{CH}_3)$ octahedra (*A*) are capable of forming staggered double layers separated by intercalated water molecules *B* (monolayer) (*B*) with an ... *AA'BAA'* ... layer sequence, compatible with the structural model of Fig. 11. Interactions between the adjacent layers in this polymeric MTO are very weak (CH_3 vs. CH_3 , van der Waals forces), resulting in graphite-like macroscopic properties such as a flaky appearance, softness and lubricant character. Electric conductivity results from a CH_3 content below that expected for a 1:1 CH_3 :Re ratio (that observed being



Scheme 2. Acid-induced aggregation of CH_3ReO_3 in aqueous solution. Steps A–C are evident from the physical data of MTO in water. The CH_3 -free rhenium (8% statistically of entire metal content) is encircled in this representation.

9.2:10) and partial reduction by extra hydrogen equivalents. The presence of acidic hydrogen is typical of classical bronze-type structures such as H_xReO_3 , with $x < 0.2$ (Eq. (13)). Pressure treatment of poly-MTO slowly yields a mixture of colorless MTO and violet ReO_3 , once again indicating that the polymer is composed of these two structural units.



Consistent with $\text{p}K_s$ data of MTO, one must assume that the polymerization (polycondensation) of this compound starts from water/hydroxy equilibria like those suggested in Scheme 2, followed by nucleophilic attack of anionic species on unchanged MTO.

A minor but surprising side-product, the dinuclear complex $(\text{CH}_3)_4\text{Re}_2\text{O}_4$ of known, oxo-bridged structure, was detected (X-ray diffraction analysis), indicating the existence of methyl radicals in aqueous solutions of MTO. (As a matter of fact, water is the solvent best suited for reactions involving free radicals owing to the strength of its O–H bonds.) Preparation of new types of intercalation compounds would appear to be possible by replacement of the layer-interconnecting water molecules, and work in this area is in progress.

The new polymeric organometallic oxide undergoes thermal degradation at 230 – 290°C (Fig. 12), with a weight loss of ca. 6% (TG/MS). This exothermic step ($\Delta H = -8.21 \text{ kJ mol}^{-1}$; DSC) corresponds to the clean formation of (crystalline, violet) ReO_3 without any C,

⁶ Gaius Julius Caesar (100–40 B.C.), Roman emperor.

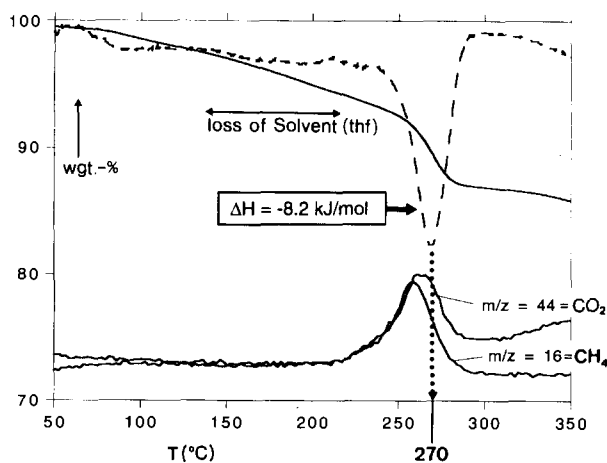


Fig. 12. TG/MS spectra of poly-MTO, see text.

H-contamination [59]. The formation of phase-pure ReO_3 as powders or films suggests that this polymer route may have potential as an alternative to MOCVD techniques, that depend on volatile precursor compounds. (Note that the cell dimensions of (cubic) ReO_3 are close to the data for poly-MTO $a = 3.748(1) \text{ \AA}$; $Pm3m$.)

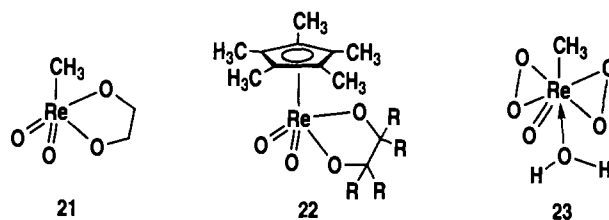
3.5. Catalysis: *ex paucis multa, ex minimis maxima*⁷

In a number of reactions the parent MTO (properties and data see Table 3) has revealed a far better catalytic performance than the previously investigated $(\eta^5\text{-C}_5\text{Me}_5)\text{ReO}_3$. Much of what we had learned about the reactivity of $(\eta^5\text{-C}_5\text{Me}_5)\text{ReO}_3$ was used to develop catalytic applications of MTO. These have attracted attention from industry and various journals [62,63].

3.5.1. Epoxidation

It was in particular the intellectual and experimental contributions of Richard W. Fischer that brought about successful oxidation catalysis of MTO in the period 1991–1994. His efforts are being continued by Monika Rauch and João Correia.

MTO is an efficient, probably the most efficient, epoxidation catalyst known [64,65]. Had we originally expected that MTO would react with olefins just like its isoelectronic congener OsO_4 , to form metallacycles **21**, we should have been aware that such species only exist in equilibria with $(\eta^5\text{-C}_5\text{Me}_5)\text{ReO}_3$ at high temperatures. However, no catalytic activity is observed for the glycolate complexes **21** and **22**. It was recognized instead that the peroxy complex **23**, formed from MTO and H_2O_2 , cleanly epoxidizes olefins even at low temperatures.



An X-ray structural analysis of the isolated catalyst (showing it to be the hydrogen-bridge stabilized diglyme-adduct, Fig. 13) was performed by Wolfgang Scherer [66] and Georg Artus has recently isolated the related inorganic peroxoperrhenium acid $\text{H}_4\text{Re}_2\text{O}_{13}$, again as a diglyme-adduct [67]. A detailed UV/vis kinetic study revealed the catalytic cycle outlined in Scheme 3, showing that the bis(peroxy) complex **23** is far more reactive towards olefins than the monoperoxo species **24**.

MTO-catalyzed *S*-oxidations were reported by Adam et al. [68], and its mechanistic aspects by Espenson and coworkers [69].

Epoxidations with MTO/ H_2O_2 attracted interest from industry (e.g., Hoechst AG, Arco Chemicals) for a number of good reasons. First, MTO is readily available (it is now even available from Fluka and Aldrich); second, it is active at very low concentrations of both MTO and H_2O_2 (the latter is used at < 5 wt.%); third, the catalytic system works over a large temperature range and is relatively stable towards water (formed in olefin epoxidation from H_2O_2).

Furthermore, selectivities can be adjusted by use of certain additives; for example, epoxide ring-opening is

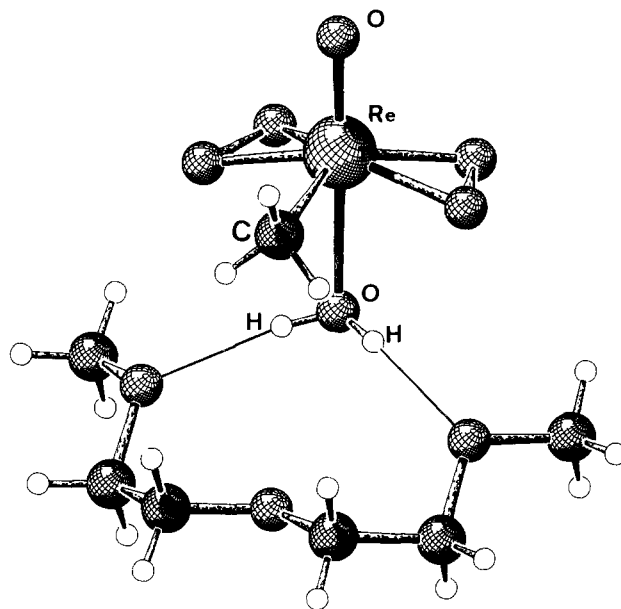
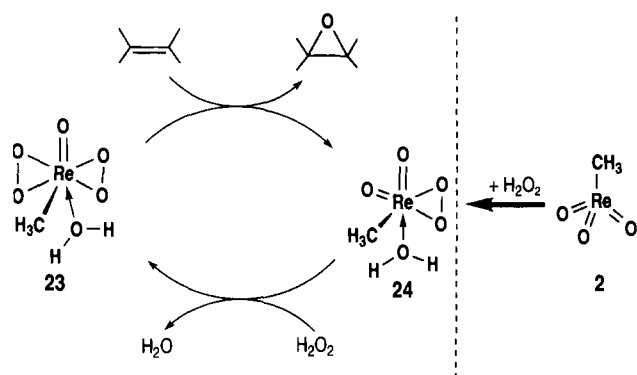


Fig. 13. Crystal structure of the bis(peroxy)rhenium(VII) complex $\text{CH}_3\text{Re}(\text{O}_2)_2\text{O} \cdot \text{H}_2\text{O}$ as a diglyme adduct (SCHAKAL representation), the active species in MTO-catalyzed oxidations.

⁷ Erasmus von Rotterdam (1469–1536), humanist and philologist (“Adagia”, 1500).

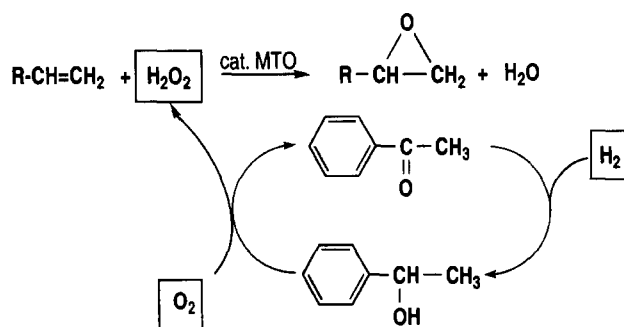


Scheme 3. MTO-catalyzed epoxidation by H_2O_2 : reaction mechanism.

fully suppressed in the presence of *N*-donor ligands such as 2,2'-bipyridine. The catalyst has been used to epoxidize olefins on a scale up of to 1 kg. Turnover numbers (TON) up to 2000 [mol/mol cat.] and turnover frequencies (TOF) of ca. 1200 [mol/mol cat. per hour] have been reached. Typical MTO concentrations are 0.2–0.4 mol%. Advantages are the low H_2O_2 concentrations needed for rapid epoxidation. Furthermore, most other epoxidation catalysts are sufficiently effective only at room temperature or above (normally at 40–80°C) while MTO/ H_2O_2 is effective even at –30°C. The solvent in which the highest yields are obtained is *t*-butanol.

Arco has patented a process involving use of MTO as catalyst for the epoxidation of propylene by oxygen [63]; a secondary alcohol (e.g. α -methyl benzylalcohol) serves as the auxiliary reductant for the in situ generation of hydrogen peroxide (Scheme 4).

The catalytic cycle for the epoxidation has been established by UV/vis and ^1H NMR spectroscopic



Scheme 4. Catalytic epoxidation by MTO: the ARCO process (US patent no. 5.166.372).

kinetics. Of key mechanistic importance is the formation of the bis(peroxo) rhenium(VII) complex **23** from MTO and two equivalents of H_2O_2 in a clean reaction (Scheme 3). Although it is explosive when pure, Richard Fischer managed to isolate this compound. An X-ray diffraction study of its crystalline and less dangerous diglyme adduct (H-bonding with coordinated H_2O) revealed it to have a trigonal bipyramidal structure if each peroxo ligand is considered as a structural unit (Fig. 13). A distorted tetrahedral (gas-phase) structure is found for **23*** which compound results by removing the coordinated water from **23** under low pressure, cf. Eq. (14) and Fig. 14 ($d_{\text{ReC}} = 204(1)$ pm, Haaland and coworkers [39,40,70]).

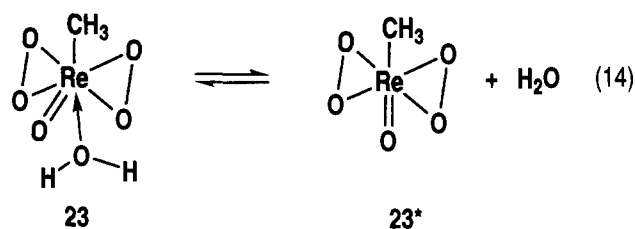


Table 4

Experimental data for methyltrioxorhenium(VII)

Colorless needles (gradual development of a greyish tint upon prolonged storage in light)

Soluble in all common organic solvents (especially in polar solvents) and in water

(ca. 50 g L^{-1} in $\text{H}_2\text{O} \approx 20$ mol l^{-1} ; $\text{p}K_s$ (25°C) = 7.53 (saturated solution, pH \approx 4)

M.p. 111°C (without decomp.), sublimable at 25°C/1 mmHg, no decomposition in the gas-phase < 300°C

$\rho = 4.103$ g cm^{-3}

Dipole moment $\mu_{\text{eff}} = 2.6$ Db (C_6H_6 , 25°C), $\chi = 55 \times 10^{-6}$ cm^3 mol^{-1}

IR (cm^{-1}): $\nu(\text{ReO})$ 1001w, 965vs (CS_2)

$\nu(\text{CH})$ 2989m, 2986vw, 2900m (CH, str.)

UV/Vis (diethylether): $\lambda_1(\text{max}) = 260$ nm ($\epsilon_1 = 1400$ L mol^{-1} cm^{-1}), $\lambda_2(\text{max}) = 232$ (1900)

NMR (CDCl_3 , 25°C): $\delta\text{H} = 2.61$, $\delta\text{C} = 19.03$ [$^2J(\text{CH}) = 138$ Hz], $\delta\text{O} = 829$ ppm

NMR (solid-state, 25°C): $\delta\text{H} = 2$ ppm (ext. H_2O), $\delta\text{C} = 36$ ppm (ext. adamantane)

MS: $m/z = 250$ (M^+ ; ^{187}Re), 220 ($[\text{M} - \text{H}_2\text{CO}]^+$; 100%)

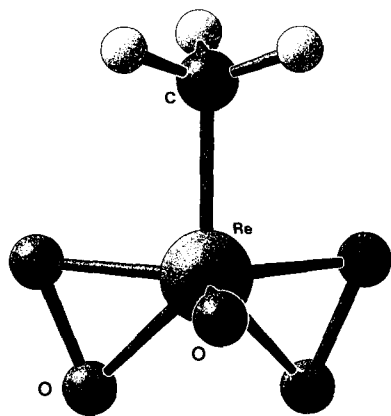
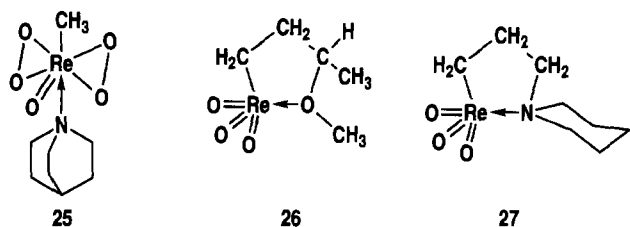


Fig. 14. Gas-phase structure of the peroxo complex $\text{CH}_3\text{Re}(\text{O}_2)_2\text{O}$: electron-diffraction study. Selected data: Re–O, 167(1); Re–C, 204(1); O–O, 145.1(6); C–H, 113(2); O–Re–C 99(4); Re–C–H 110(4). All distances are in pm and angles in degrees.

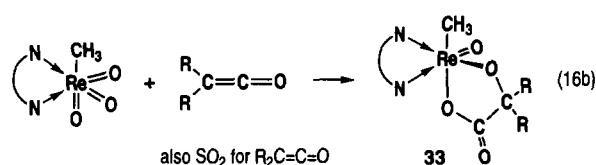
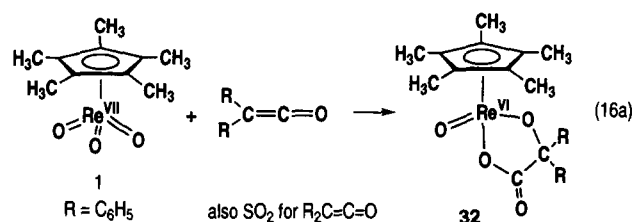
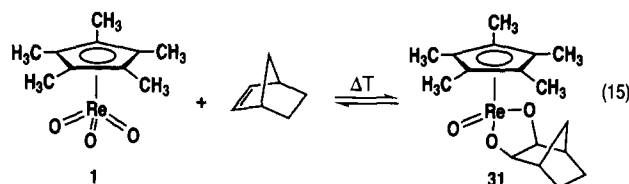
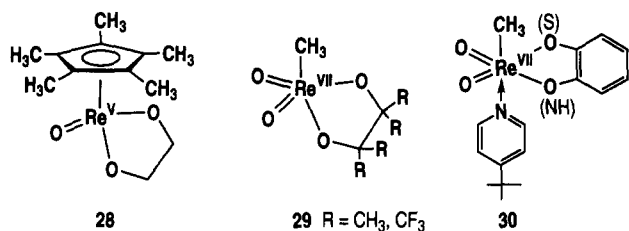
Compound **23** is a weak Brønsted acid in aqueous solution ($\text{p}K_s \approx 6$ at 8°C) but there is relatively fast decomposition in the absence of an excess of hydrogen peroxide. Only the bis(peroxo) intermediate **23** reacts fast with the olefin. The Re–C bond is of pivotal importance for the catalytic activity: if it is cleaved, for example by addition of hydroxide (Eq. (8a)), epoxidation immediately stops. This shows that formation of the (inactive) perrhenic acid must be avoided in oxidation reactions involving MTO. However, **23** seems to be one of the most reactive peroxo metal complexes for epoxidations known, as shown by stoichiometric reactions. The much lower activities of other rhenium oxides, e.g. Re_2O_7 , is due to subsequent hydrolysis ($\rightarrow \text{H}[\text{ReO}_4]$) that does not occur with MTO under the conditions of catalysis (cf. Ref. [67] for aromatic oxidations).



Donor ligands such as quinuclidine are compatible with peroxide species. Thus the adduct **25**, an orange-colored, stable compound (dec. 95°C), was isolated [39]. *O*- and *N*-functionalized derivatives such as the structurally characterized examples **26** and **27**, respectively, are also efficient catalysts, opening a possible new route to chiral modifications for enantioselective epoxidations (Fig. 15).

As recently reported by Russian chemists, MTO also catalyzes the selective oxidation of anisol to *o*- and *p*-methoxyphenol by means of hydrogen peroxide; the reaction proceeds without a solvent [25p]. Yields of 80–95% were reported.

In contrast to what was originally expected, the oxidation chemistry of CH_3ReO_3 (MTO) does not resemble that of the isoelectronic neighbor: OsO_4 adds directly to olefins in cycloaddition reactions to give the long-known osmium(VI) 1,2-diolates. Similarly constituted derivatives have been obtained for **1** and **2**, with compounds **28–30** being typical examples (X-ray structures). However, these are only accessible by condensation reactions from 1,2-diols, and not from olefins. In spite of being an excellent epoxidation catalyst metal, rhenium seems not to form *cis*-hydroxylation catalysts. The equilibrium of Eq. (15) depends on the ring-strain in the olefin (e.g. the cycloaddition of norbornene yields 49% of **31** [71]).



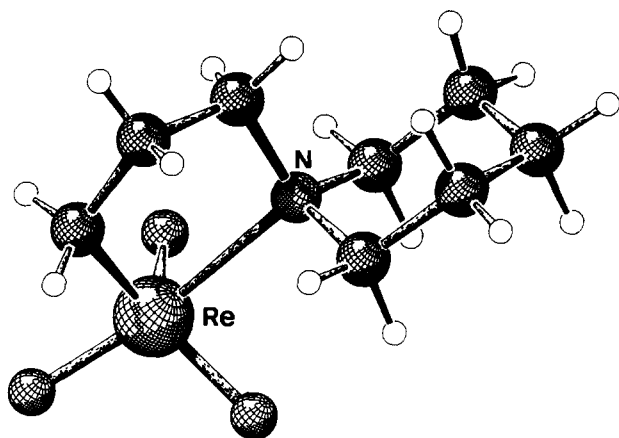


Fig. 15. Crystal structure of the piperidyl-functionalized propylrhenium(VII) oxide **27**, data taken from Ref. [44].

MTO is even less reactive. Whereas **1** reacts with ketenes in a [2 + 3]-cycloaddition to give **32** (Eq. (16a) [72]), MTO is inert towards ketenes unless it is activated by a base-ligand such as 2,2'-bipyridine, in which case a regioselective cycloaddition of the same kind occurs immediately (Eq. (16b) [73]). There is no straightforward explanation for the failure of MTO to react with olefins. Other heterocumulenes (e.g. SO_2) show the same trend: no reaction with MTO, fast cycloaddition with $\text{MTO} \cdot \text{bipy}$ and with $(\text{C}_5\text{Me}_5)\text{ReO}_3$. It is noteworthy that the congener CH_3TcO_3 does react with olefins, thus giving the *cis*-1,2-diol from cyclohexene [74].

An MTO-catalyzed alkoxylation of cyclohexene-epoxide was reported by Russian workers [101b].

3.5.2. Baeyer–Villiger oxidation

The oxidative conversion of cyclic ketones into lactones (Baeyer–Villiger oxidation) and of open-chain ketones into esters (Dakins reaction) is normally performed with percarboxylic acids. This reaction involves nucleophilic oxidation (at the carbonyl group), in contrast to the electrophilic nature of both epoxidation and aromatic oxidation. Little is known about metal-catalyzed alternatives to the Baeyer–Villiger reaction even though there is a great industrial demand for them.

MTO is surprisingly active (Eq. (17)): cycloketones ($n = 1–3$) can be converted into lactones even at 15°C by means of diluted hydrogen peroxide (10 wt.%) in acetonitrile or *t*-butanol [75]. Turnover frequencies up to 18000 [mol/mol cat. per hour] were obtained for the easy case of cyclobutanone. Other cycloketones are admittedly less reactive (TON 50–100). A comparison of oxidizing agents for cyclobutanone reveals the efficiency of MTO (Fig. 16). The peroxy complex **23** has been shown to be the active species, and there is spectroscopic evidence of initial formation of an adduct with the cycloketone. Once again, only one peroxy group takes part in the oxidation of the substrate. Regarding the mechanistic aspects of the reactions of **23**, one has to take into account that according to Adam's $\chi(\text{SO})$ data it has both electrophilic and nucleophilic character. Donor solvents such as acetonitrile seem to enhance the nucleophilicity of the peroxy groups, thus

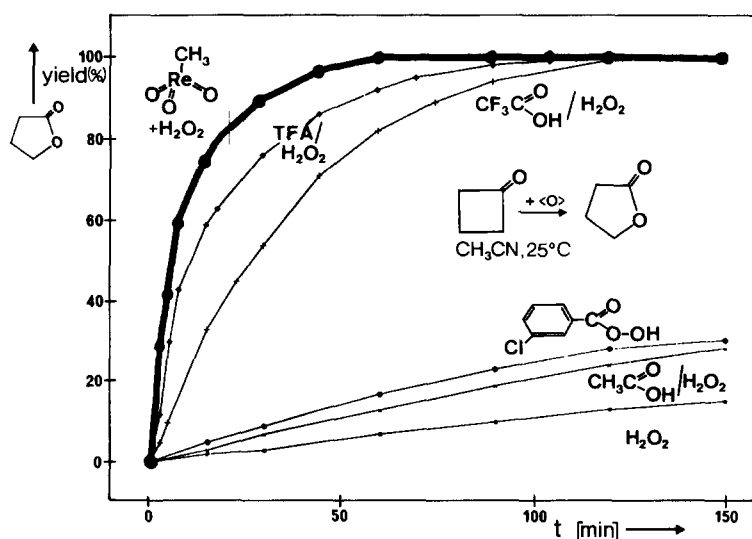
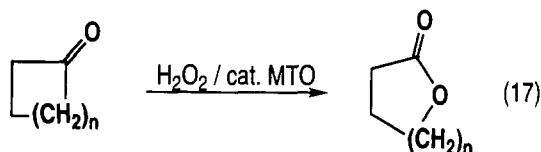


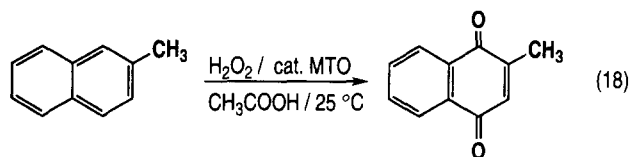
Fig. 16. Efficiency of MTO in the catalytic Baeyer–Villiger oxidation of cyclobutanone. A number of conventional, non-catalytic versions are shown in comparison with $\text{MTO}/\text{H}_2\text{O}_2$.

explaining the observed reactivity in the Baeyer–Villiger oxidation. This explanation correlates with $^1\text{H}/^{17}\text{O}$ NMR data [43,44].



3.5.3. Aromatic oxidation

Yet another catalytic application of MTO has been recognized in the oxidation of aromatic compounds. In a joint effort with Adam's group of Würzburg university, we developed a new, easy synthesis of 1,4-quinones [76], among them the industrially-important Vitamin-K₃ (2-methyl-1,4-naphthoquinone, menadione) of Eq. (18).



The success of this reaction, however, depends on use of high H_2O_2 concentrations (usually 85 wt.%) and on a strongly acidic medium, but conversions of 81% and selectivities up to 86% toward the required rather than the undesired isomer, 2-methyl-5,8-naphthoquinone have been achieved. The new procedure for making this vitamin could replace the industrially applied chromic acid process (32%–60% yield) which involves use of stoichiometric amounts of the oxidant, and yields 18 kg of toxic chromium-containing waste per kilogram of product [77]. A special Pd(II)-catalyst is also inferior

to MTO [78]. Electron-donating groups in the aromatics increase the efficiency of oxidation.

From a mechanistic point of view, it should be noted that the $\text{MTO}/\text{H}_2\text{O}_2/\text{CH}_3\text{CO}_2\text{H}$ system primarily hydroxylates the aromatic compound. For example, hydroxymesitylene is formed in 75% yield from mesitylene at 25°C. Trimethyl-1,4-hydroquinone, an important intermediate in the synthesis of Vitamin E [79], can now be made by the same method in 75% yield [80]. Further aromatic oxidations have been reported by Yamazaki [101a].

3.5.4. Metal carbonyl oxidation

The above-mentioned catalytic intermediates of peroxo rhenium(VII) complexes are involved in the oxidation of metal carbonyls [67,81]. The first quantitative conversion of a metal carbonyl into a metal oxide has been achieved by use of MTO and higher congeners (e.g. $\text{C}_5\text{H}_5\text{ReO}_3$) as catalysts (Eq. (19)). H_2O_2 alone reacts slowly even at room temperature and does not yield clean products [82]. Perrhenic acid and perrhenates are once again inactive. The mild conditions of the new method seem well-suited for making organic oxides of other metals, since metal carbonyls constitute a most abundant class of starting materials. Strong L–M bonds in the precursor metal carbonyl are necessary to avoid oxidation of the ligand L other than CO (e.g. $\text{L} = \text{C}_5\text{Me}_5$).

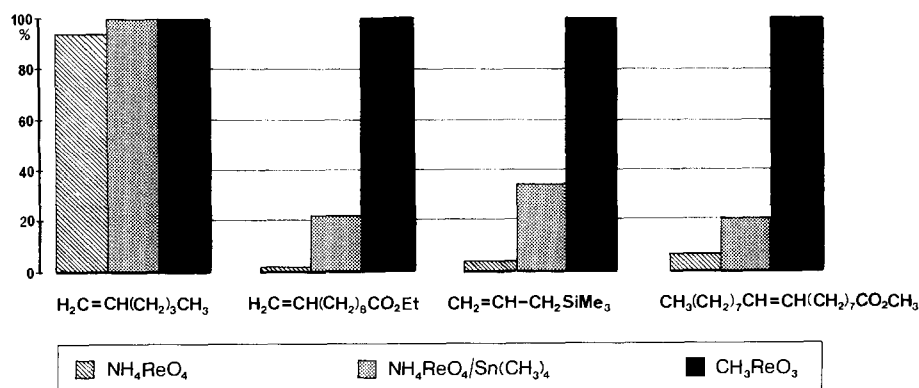
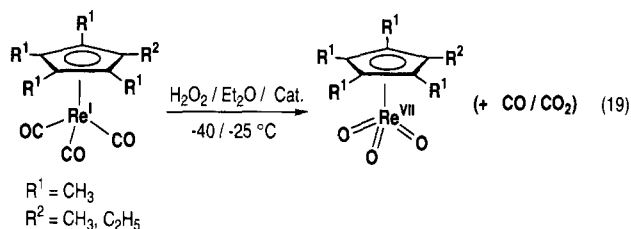
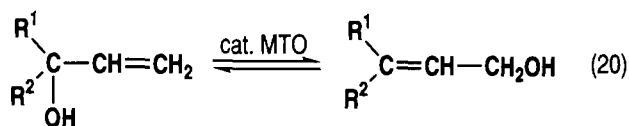


Fig. 17. Olefin metathesis: comparison of Re-catalysts (3 wt.% Re on $\text{Al}_2\text{O}_3\text{-SiO}_2$; 25°C).

3.5.5. Olefin isomerization and olefin metathesis

According to a patent by BASF AG, certain olefins undergo (secondary/primary) double-bond isomerization under the catalytic influence of MTO (Eq. (20)). Equilibrium is reached in 65 min at 60°C with an olefin:MTO ratio of 150:1 [83]. More importantly, olefin metathesis is effected by MTO, with functionalized olefins being particularly attractive as starting compounds.



Although it has long been known that rhenium oxides, e.g. Re_2O_7 , are activated for olefin metathesis by alkylating agents such as tetramethyltin, it was left to Werner Wagner of our group to recognize the activity of the structurally well-defined (pre-)catalyst MTO, even for difficult olefins such as allyl bromide and CC-unsaturated carboxylic esters [84], cf. Fig. 17. The best results are obtained by immobilizing the catalyst on acidic supports, especially Nb_2O_5 (work in collaboration with Jean-Marie Basset, Lyon). None of the structural proposals can be taken as certain, but models like **34** are reasonable on chemical and structural grounds. The possible active form **19** (Eq. (11)) could result from a tautomerization process on the surface. Better experimental evidence is needed to resolve conflicting mechanisms [85] and could perhaps be obtained from molecular models based on (condensation) reactions of silanols with MTO.

The new catalytic system works at room temperature and includes the whole range of metathesis from ring-opening polymerization to ethenolysis of internal olefins. Identical catalyst loadings are more efficient for MTO than for the industrially employed two-component system $\text{NH}_4[\text{ReO}_4]/\text{Sn}(\text{CH}_3)_4$ (which chemically corresponds more to $\text{Re}_2\text{O}_7/\text{Sn}(\text{CH}_3)_4$).

The molecular structure of the (surface) species seems to determine the quality of the catalytic performance: if during the metathesis of 2-pentene catalyst degradation by Re–C bond cleavage (formation of methane) is induced by raising the temperature, the rate of product formation is lowered (Fig. 18). It is therefore important to note that a maximum of only 2% of the methyl groups are lost when MTO is immobilized on $\text{SiO}_2/\text{Al}_2\text{O}_3$ (calcinated, 550°C). Puls-microreactor experiments performed by Flessner provided evidence that a π -allylic intermediate occurs, perhaps without engagement of the Re-methyl group. The Re(V)-cyclobutanes

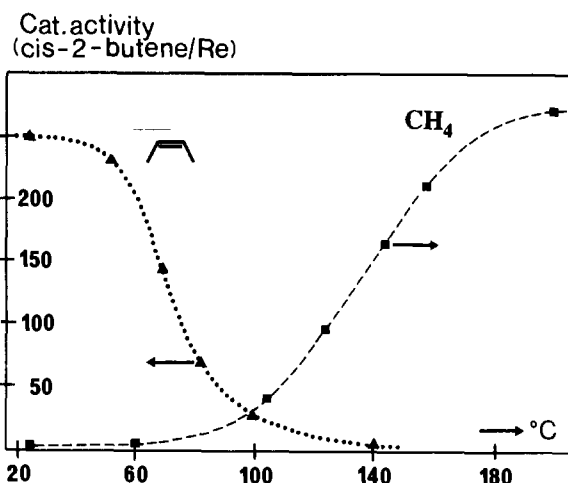
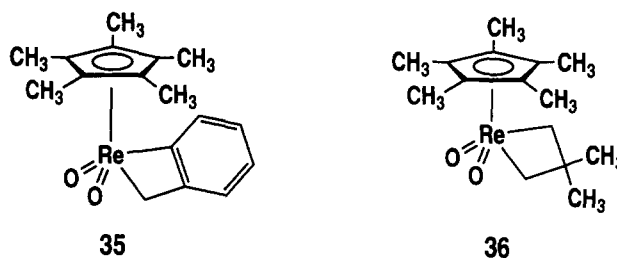


Fig. 18. Activity vs. methane elimination (at higher temperatures) during the metathesis of 2-pentene, monitored by the formation of *cis*-2-butene (according to the equilibrium $2 \text{CH}_3\text{CH}=\text{CH}_2 \rightleftharpoons \text{CH}_2=\text{CH}_2 + \text{CH}_3\text{CH}=\text{CHCH}_3$) and methane formation. Conditions: 2-pentene:MTO = 1000:1, MTO/ Nb_2O_5 [300] 1 wt.%.

35 and **36** of Flöel et al. [86] are reasonable models for (surface-attached) catalytic intermediates.

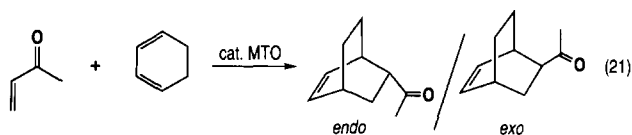


Bein and coworkers recently reported on the metathesis activity of zeolite-encapsulated MTO. They concluded from IR and EXAFS data that MTO is anchored via hydrogen bridges to the zeolite oxygens, without significant changes in the MTO structure [87].

3.5.6. Diels–Alder reactions

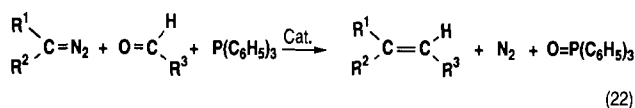
Although the effect has been little studied, it is known that MTO enhances the Diels–Alder reactivity of unsaturated CC compounds. The standard case of Eq. (21) can be combined with a subsequent epoxidation step, demonstrating a rather unique property of MTO. However, MTO is not a unique catalyst for the Diels–Alder reaction. Any Lewis-acidic metal compound is a likely candidate, and it was not surprising that Re_2O_7 also displayed marked activity: 0.05 mol% of this catalyst suffices to effect quantitative reaction of methacrolein with cyclohexadiene(1,3) in 30 min at 25°C (TOF = 4 000 [mol/mol cat. per hour]; TOF = 300 at 0°C with 98% *endo*-selectivity). It seems likely that

these rhenium(VII) catalysts are activated by addition of the conjugated carbonyl group through the oxygen to the Lewis-acidic metal centers. It is possible to use MTO as catalyst in the tandem Diels-Alder/epoxidation reaction sequence [88]. Work on improving the catalyst performance is underway.

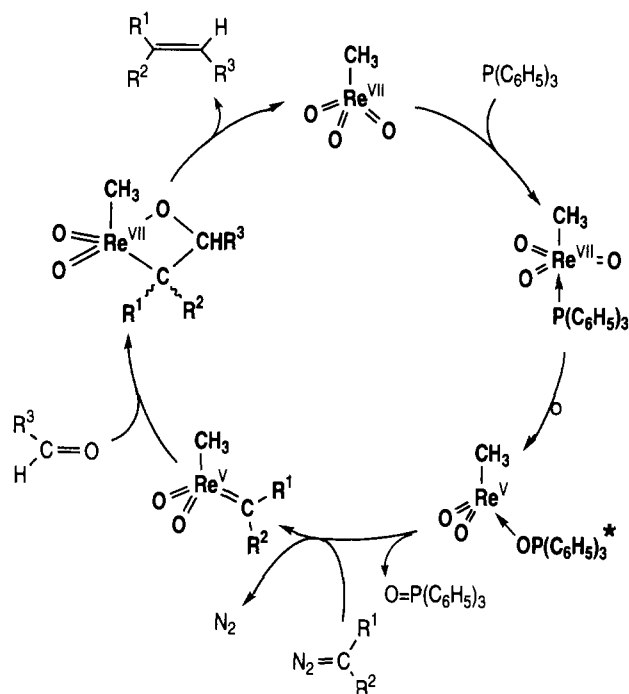


3.5.7. Olefination of aldehydes

Mei Wang of our group showed the catalytic influence of MTO on a CC-coupling reaction having great potential: aliphatic diazoalkanes react with aldehydes (or strained cycloketones) to form olefins according to Eq. (22), if catalytic amounts of MTO and stoichiometric amounts of phosphines, e.g. $\text{P}(\text{C}_6\text{H}_5)_3$, are present [89].

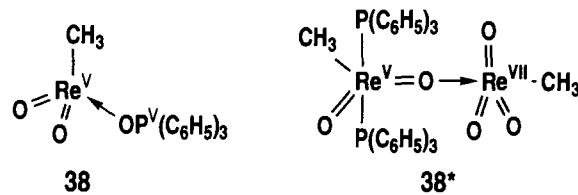
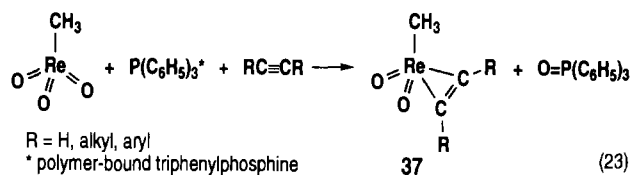


The reaction involved in this simple catalytic route to olefins from readily available starting compounds (diazoacetates and -malonates are particularly reactive) can be regarded as Wittig-type reactions. It has the advantage over Tebbe–Grubbs coupling since it does not require use of a *stoichiometric* amount of an organometallic coupling reagent. This arises from the fact that the Re–O bond is weaker than the Ti–O bond [90], with only the former being amenable to reductive elimination by phosphines (as phosphine(V) oxides). A typical model reaction is the synthesis of the Re(V)–alkyne-complexes **37** by Felixberger [91] via the (postulated) intermediate **38** (Eq. (23)). A related intermediate of formula **38*** (X-ray diffraction structure) is also formed from MTO and $\text{P}(\text{C}_6\text{H}_5)_3$ according to Peter Roesky et al. [89b]. In any case, phosphines seem to first attack the Lewis-acidic Re(VII) center of MTO and then migrate to the oxo ligand. The mechanistic model suggested in Scheme 5 takes account of the presently available evidence. Both of the suggested Re(V)–carbene and the Re(V)–oxetane intermediates are reasonable in



Scheme 5. Suggested mechanistic model of the MTO-catalyzed olefination of aldehydes by diazoalkanes in the presence of phosphines. The main catalytic species is probably the $\text{Re}^{\text{V}}/\text{Re}^{\text{VII}}$ -complex **38***.

light of related known chemistry, but the synthesis of independent model compounds is still desirable.

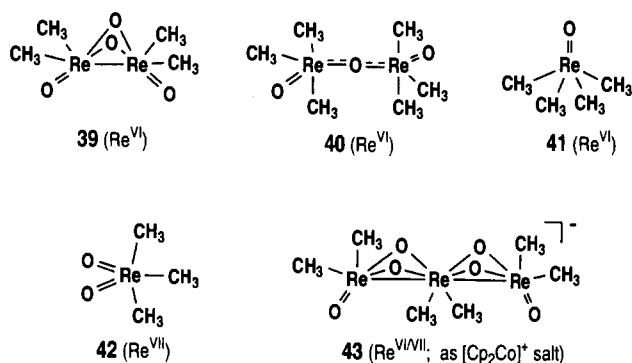


3.5.8. Multi-alkylated complexes as catalysts

Although the catalytic oxidation is by far the most developed use of MTO, there is also significant potential in the case of other reactions mediated by this molecule and its congeners. Some of the catalytic prop-

erties depend to a large extent on the Lewis-acidity of the heptavalent rhenium, but it is also the low coordination state that makes MTO a molecular catalyst sterically accessible to various reagents (e.g. H_2O_2 , phosphines). In many cases, catalytic activities fall dramatically if the methyl (alkyl) group is absent, clearly demonstrating the special nature of MTO. The olefination of aldehyde does not occur with simple oxides such as Re_2O_7 .

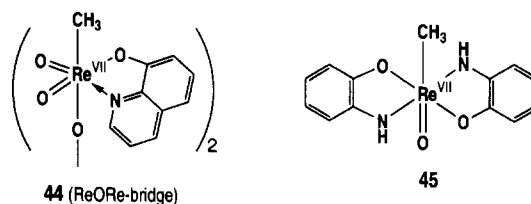
Multiple alkylation of certain oxorhenium precursor compounds gave mono- and dinuclear oxoalkyls **39–42** of simple composition and relatively straightforward structures [40,92]. Some of these are active as catalysts in olefin epoxidation (similar activities for CH_3ReO_3 and $(\text{CH}_3)_4\text{Re}_2\text{O}_4$) and olefin metathesis [39]. The paramagnetic d^1 -Re(VI) species **41** is square-pyramidal (like the d^2 -Re(V) complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CH}_3)_4$), the d^0 -Re(VII) compound **42** is trigonal-bipyramidal with the two oxo groups in equatorial positions, as expected from simple valence shell electron pair repulsion (VSEPR) considerations (gas-phase structure: Arne Haaland, Wolfgang Scherer et al.). A trinuclear oxoalkyl complex **43** with a linear sequence of metal atoms became available through work by Rolf Albach involving controlled treatment of the intermediate deep-green radical anion $[\mathbf{39}]^{\cdot-}$ (ESR) with oxygen [93]. This method of forming metal–metal bonds should also be applicable to the preparation of heteronuclear clusters.



3.6. Plus potest qui plus valet.⁸ Functionalization of methyltrioxorhenium — further aspects

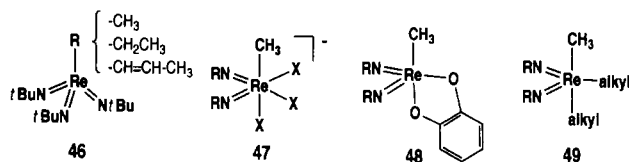
Since the electron-deficiency in the low-coordinate metal is likely to open a number of reaction routes, this

topic was investigated in a separate study by Takacs [94]. Condensation reactions involving the oxo groups were found to dominate the scene. Takacs synthesized a plethora of both Re(VII)- and Re(V)-complexes by treating MTO with protic reagents such as alcohols, thiophenols and amines. Compounds **28–30** and **44–49** are typical, showing that *N*-donor ligands may be required to stabilize the condensation products sufficiently to allow isolation. The Re–CH₃ bond is retained in all these cases.



3.6.1. Condensation reactions

Similar *O,N*-, *S,N*- and *S,S*-chelate complexes have been made. Since MTO is resistant to even strong Brønsted acids, the first step in these condensation reactions can only be nucleophilic attack at the metal, as is known to be the case for chloride ($\rightarrow [\text{CH}_3\text{ReO}_3\text{Cl}]^-$ and $[\text{CH}_3\text{ReO}_3\text{Cl}_2]^{2-}$). The same statement applies to aminolysis, which provides a simple route to imido derivatives. Examples are the remarkably thermally stable complexes of type **46**, of which even the ethyl- and σ -allyl complexes (R) survive temperatures far above 100°C [95]. There is no π -coordination of the allyl complex, presumably because of the much stronger donor capacity of imido-ligands compared with the oxo-ligands. The stable hydride $\text{HRe}(=\text{N}^t\text{Bu})_3$ has been synthesized by an independent route from the anion $[\text{Re}(=\text{N}^t\text{Bu})_3]^-$ [96].

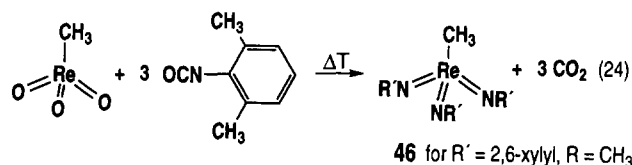


3.6.2. Isocyanate reactions

Another route to imido complexes (Rocco Paciello, Malcom Cook) involves the reaction of MTO with isocyanates in boiling toluene (Eq. (24)). Instead of H_2O (see above) CO_2 is formed in this case, so hydrol-

⁸ Publius Vergilius Maro (70–19 B.C.), Roman poet.

ysis of the Re–N bond cannot be occurring during the synthesis [95].

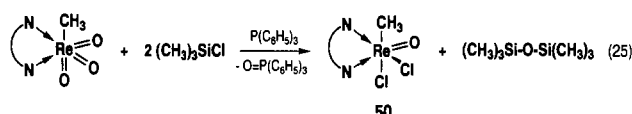


3.6.3. Imido complexes

In the $(C_5Me_5)ReO_3$ -series, imido derivatives can be made from silylamines [99]. The imido derivatives of MTO made available by these two major routes include the thermally extraordinarily stable ethyl (!) and allyl species of type **46**. Acidolysis with hydrogen halides yields **47**, and condensation with catechol gives **48**. This latter compound undergoes clean alkylation to give, for example, the first mixed-alkyl complex **49** in this series [94c].

3.6.4. Halide derivatives

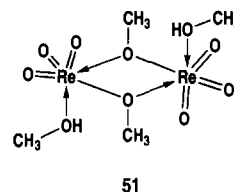
A number of Re(V)-derivatives of MTO can be obtained by chlorination to give the reactive intermediate **50** (Roesky). Alkylation once again occurs smoothly without redox side reactions [73].



3.6.5. Alkoxides

Some of the related complexes show properties somewhat different from those of MTO. Upon replacement of the methyl- by stannoxy-, siloxy-, and methoxy ligands, the hydrolytic instability increases, and eventually structural aggregation occurs to give dimers or polymers. Examples are the dimeric “ CH_3OReO_3 ”, for which a structure analogous to that of MTO was originally proposed [97]. The dimeric, solvated structure of **51** (X-ray diffraction study) serves to emphasize the importance of the Lewis-acidity in all these Re(VII)-complexes [98]. The ^{17}O NMR data point to a perrhenate $[ReO_4]^-$ character for $R_3SnOReO_3$ while the others resemble perrhenyl $[ReO_3]^+$ species. Siloxyrheni-

um(VII) amides of type $(CH_3)_3SiORe(NR)_3$ are available directly from the corresponding oxide [100].



3.7. Epilogue: why organometallic oxides? Plus ultra⁹

After ten years of systematic research, organorhenium oxides are a well-established class of compounds in respect of synthesis, structure and bonding, as well as their catalytic properties. General principles applying to the synthetic routes and the mechanisms of the catalyses have been revealed through numerous isolated examples that now come together to form a rather complete picture. It proved particularly beneficial to use the stoichiometric chemistry of **1** (not covered in the present account) to develop catalytic activity in the case of the normally more reactive derivatives of MTO. The main advantages of this latter, structurally very simple compound derive from the stability of the Re–C bond that prevents the molecule from undergoing aggregation to three-dimensional (polymeric) ReO_3 and other degradation products. However, numerous reactions take place at the Re–O bonds, that convert MTO into highly reactive (catalytic) species, one notable example being the explosive peroxo complex $CH_3Re(O_2)_2O \cdot H_2O$. After starting as laboratory curiosities¹⁰, organometallic oxides are now fully established on the basis of known synthetic methodology (cf. Eqs. (3a, 3b) and serve in new catalytic applications. Special emphasis should be given to the relatively little explored electrochemistry of these systems in order to investigate, understand and exploit the redox processes. As a catalysis-related topic of general interest, comparison of epoxidation and *cis*-hydroxylation using molecularly defined metal oxides should be made by both experimental and theoretical studies. For example what are the prerequisites for a

⁹ Karl V (1500–1558), Roman–German Emperor.

¹⁰ The first reported attempts at making $(C_5H_5)ReO_3$ in 1963 were unsuccessful (A. Riedel, *Diploma Thesis*, Technische Hochschule München) and after the discovery of $(C_5Me_5)ReO_3$ R. Dagoni stated, “It is also surprising that as good an oxidant as rhenium(VII) must be, it doesn’t chew up the organic ligand”, (*Chem. Eng. News*, 62 (1984) 28).

metal oxide L_nMO_x that enable it to react with an olefin under cycloaddition? Answering this question will pave the way to a switchable catalyst through tailored design, a constant goal in molecular catalysis.

Acknowledgments

The report of a full decade (1984–1994) of research summarized in this review covers the work of many experimentally skilled young coworkers. Most of them received their Diploma and Ph.D. degrees during their time with me. Others were welcomed as research fellows through the most generous Alexander von Humboldt Foundation: Roger Alberto, João Correia, Ian Degnan, Veronique Dufaud, Mei Wang, Claude de Mèric de Bellefon, Kazushi Mashima, Rocco Paciello, Rinaldo Poli, Ricardo Serrano, Marc Taillefer, Janos Takacs, Hoa Tran Huy, Claire Whitacker and Bill Wojtczak. The Royal Society of London supported Malcolm R. Cook through the award of a postdoctoral fellowship. All these coworkers deserve my respectful thanks for being both dedicated, careful researchers and good comrades in our Munich laboratory. Not all of them can be mentioned here but their names are quoted in the text and references. The technical and scientific personnel of our institute are acknowledged for continued reliable services, with Manfred Barth (Microanalytical Laboratory), Prof. Fritz Kreißl (mass spectrometry), Dr. Peter Härter (NMR spectroscopy), Dr. Eberhardt Herdtweck (crystallography), Dr. Dimitris Michalios (project coordination) and Dr. Karl Öfele (general administration) deserving special mention. Excellent research facilities have been provided by our alma mater, Freistaat Bayern, Bayerische Forschungsförderung (through the ‘‘Bayerische Forschungsverbund Katalyse’’, FORKAT), Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Stiftung Volkswagenwerk, Bundesministerium für Forschung und Technologie (BMFT), and by the European Community (Network Selective Processes and Catalysis involving Small Molecules). Additional support came from German chemical industry whose willingness to take part in collaborative studies (Hoechst AG) and to provide other support (Degussa AG, H.C. Stark GmbH, Chemetall GmbH) deserve special mention. Ph.D. fellowships were obtained from the Herrmann Schlosser Foundation of Degussa AG (U. Küsthardt, F.E. Kühn, W. Wachter), the Merck'sche Gesellschaft für Kunst und Wissenschaft e.V. (J. Felixberger), the Dr. Karl Wamsler Foundation (A. Stumpf, Ph.D. student in Lyon), and the Fonds der Chemischen Industrie (R.A. Fischer, P.W. Roesky, Morawietz, Eder M. Mattner). The Max-Planck Research Award jointly granted to the author and to Jean-Marie Basset (CNRS Lyon) led to an extensive

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¹¹ This list is not comprehensive with regard to our work. However, the key references given here should facilitate a rapid entry into the various aspects discussed in this essay.

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