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Organorhenium Oxides[†]

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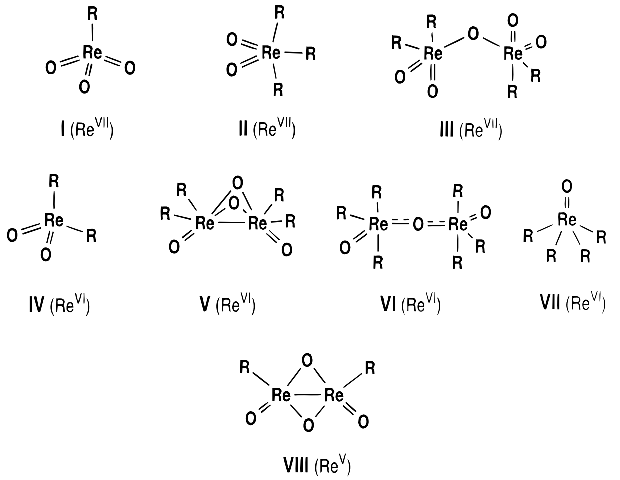
Introduction

Less than 20 years ago the entire class of organorhenium oxides was completely unknown, but today an amazing wealth of these complexes exists. In the last decade many new facts about organorhenium oxides were published, and not only the knowledge about their preparation, structures, and chemical behavior has significantly grown. It is now well established that organorhenium oxides have interesting applications in both catalysis and material sciences. The field of organorhenium oxide chemistry is thus still in rapid progress. It is prototypal for organometal oxides in general.

The first attempt to synthesize an organorhenium oxide was performed in 1963 in the group of E. O. Fischer. His diploma student A. Riedel reacted $ClReO_3$ with $Na(C_5H_5)$ to receive $(C_5H_5)ReO_3$, which was expected to be a half-sandwich complex in piano stool configuration.[2a] However, the reaction only led to the oxidation of cyclopentadiene, and nearly 30 years passed before the desired compound was synthesized.[2b] The first organorhenium oxides, namely, $(CH_3)_4ReO$ and $((CH_3)_3SiCH_2)_4ReO$, were prepared by G. Wilkinson and co-workers in 1974.[2c,d] During the following 10 years some more derivatives were reported, but in most cases the yield was low and the synthetic access to these "exotic" compounds not easy.

We came in contact with this chemistry in 1984 when W. A. Herrmann and R. Serrano managed to synthesize η^5-$(C_5(CH_3)_5)ReO_3$, the first half-sandwich complex of the type $(\eta^5$-$C_5R_5)MO_x$.[2e] During the following years we became more and more interested in this chemistry, fascinated by the manifold reaction chemistry of η^5-$(C_5(CH_3)_5)ReO_3$ and its application as a model for oxidation catalysts. A second important step was the improvement of the synthesis of methyltrioxorhenium, first detected in tiny amounts upon reaction of $(CH_3)_4ReO$ with air in 1979 by R. J. Beattie and P. Jones.[2f,3] Methyltrioxorhenium is now one of the best examined organometallic compounds.

Chart 1



The results of the organotrioxorhenium(VII) chemistry up to 1990 have already been reviewed in several papers.[4c,h,i,j] We now give a brief overview on the developments in organorhenium oxide chemistry in the recent years and describe our own contributions to this fast growing field.

Eight different types of neutral molecules containing only Re, terminal oxo ligands, oxo bridges, and organic groups (R = alkyl, aryl) are known (compounds **I**−**VIII** (Chart 1)), in total approximately 70 complexes. The formal oxidation states of these molecules are VII, VI, and V. A significantly greater variety of derivatives can be deduced from these eight basic types, also mainly in the oxidation states VI and VII.

Wolfgang A. Herrmann was born in Kelheim on April 18, 1948. He studied chemistry at the Technische Universität München (Diploma Degree 1971 in the group of Professor E. O. Fischer). He received his Ph.D. in 1973 at the University of Regensburg under the direction of Professor H. Brunner and carried out his postdoctoral research with Professor P. S. Skell (Pennsylvania State University). He finished his Habilitation in 1978 at the University of Regensburg, was appointed Associate Professor at the University of Regensburg in 1979, and was appointed full Professor at the University of Frankfurt/Main in 1982. Since 1985 he has held a chair of Inorganic Chemistry at the Technische Universität München. He is author of more than 400 publications and has earned numerous awards, among them the Leibniz-award (1986), the German-French Alexander von Humboldt-award (1990) and the Max-Planck research award (1991). Since October 1995 he has been President of the Technische Universität München.

Fritz E. Kühn was born in Freising on Oct 27, 1965. He studied chemistry at the Technische Universität München and received his Ph.D. in 1994 under the direction of Professor W. A. Herrmann as a fellow of the Hermann-Schlosser-foundation (Degussa A.G.). He carried out his postdoctoral research in 1995−1996 with Professor F. A. Cotton (Texas A & M University) as a Feodor Lynen fellow of the Alexander von Humboldt-foundation. In April 1996 he returned to Munich and started a Habilitation.

[†] Multiple Bonds between Transition Metals and Main-Group Elements. 162. Part 161: see ref 1.

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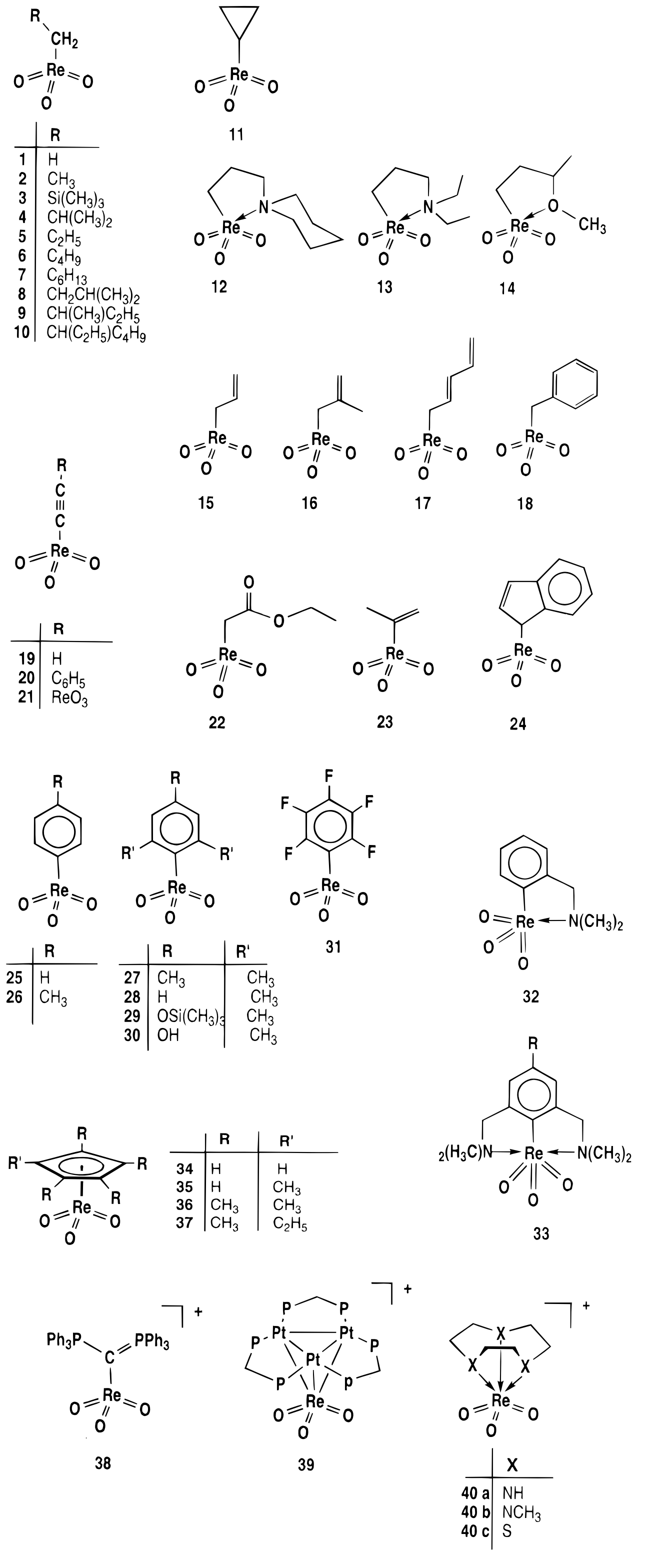
Chart 2



	R
1	H
2	CH_3
3	$Si(CH_3)_3$
4	$CH(CH_3)_2$
5	C_2H_5
6	C_4H_9
7	C_6H_{13}
8	$CH_2CH(CH_3)_2$
9	$CH(CH_3)C_2H_5$
10	$CH(C_2H_5)C_4H_9$

	R
19	H
20	C_6H_5
21	ReO_3

	R
25	H
26	CH_3

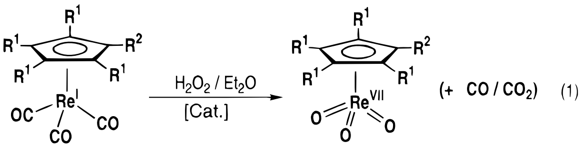
	R	R'
27	CH_3	CH_3
28	H	CH_3
29	$OSi(CH_3)_3$	CH_3
30	OH	CH_3

	R	R'
34	H	H
35	H	CH_3
36	CH_3	CH_3
37	CH_3	C_2H_5

	X
40 a	NH
40 b	NCH_3
40 c	S

Synthesis

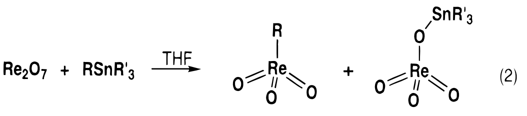
Organorhenium(VII) Oxides. By far the most thoroughly examined organorhenium oxides are those of type **I**. The type **I** organorhenium(VII) oxides known to date are given as compounds **1**−**38** (Chart 2). Nowadays two major ways to prepare organorhenium oxides of type **I** exist: (1) Precursor compounds of rhenium in low oxidation states, such as organorhenium carbonyls, can be oxidized by a variety of oxidants, but the available synthetic methods can only be used in the preparation of a few organorhenium(VII) oxides (namely, **36** and **37**) (eq 1).[4] Only compounds with an oxidatively stable electron-donor ligand can be derived by oxidation of Re(I) to Re(VII).[4k] In our experience the best method yet developed is the catalytic oxidation of organorhenium carbonyls with H_2O_2 and **1** as catalyst below room temperature.[4g] The oxidation method, starting with a rhenium carbonyl compound and an oxidizing agent, is also successful for the preparation of some inorganic Re(VII) trioxides (compounds **39** and **40**).[5] The σ-aryl derivative $(Mes)ReO_3$ (**27**) can be synthesized by the oxidation of $ReO_2(Mes)_2$ with NO_2.[6] In contrast to compounds **36** and **37** the product yields in these cases are often comparatively low. (2) The best method to synthesize organorhenium(VII) oxides nowadays is the reaction of a rhenium precursor complex already in the oxidation state VII with an alkylating or arylating agent.[7−11] For the success of this reaction type, a $[ReO_3]^+$ synthon and a good leaving group have to be present. For several years we considered Re_2O_7 as the ideal starting material.[8] Reactions with certain tin(IV) and zinc(II) organyls leads to the formation of organorhenium(VII) oxides according to eqs 2 and 3 without reduction. However, the most important drawback of this



$R^1 = CH_3$
$R^2 = CH_3, C_2H_5$

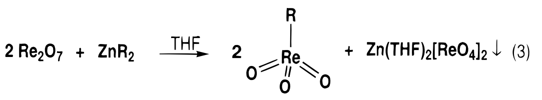
36, 37

Cat. = $(CF_3C(O))_2O$,
CH_3ReO_3,
$C_2H_5ReO_3$,
$(C_5H_5)ReO_3$,
$[C_5H_4(CH_3)]ReO_3$,
$ClReO_3$,
Re_2O_7,
ReO_3



$$Re_2O_7 + RSnR'_3 \xrightarrow{THF} RReO_3 + R'_3SnOReO_3 \quad (2)$$

1, 15 - 24, 34, 35



$$2\,Re_2O_7 + ZnR_2 \xrightarrow{THF} 2\,RReO_3 + Zn(THF)_2[ReO_4]_2\downarrow \quad (3)$$

2 - 14, 25 - 30, 34, 35

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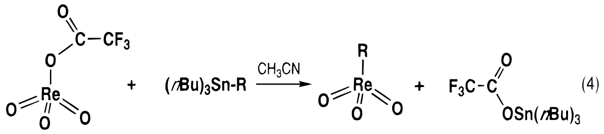
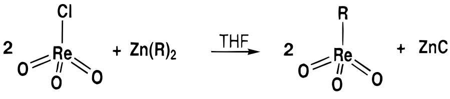
method is the formation of an equimolar amount of tin or zinc perrhenate, thus waisting half of the rhenium. Especially with regard to the catalytic interest in some $RReO_3$ compounds, this situation seemed very disadvantageous to us.

A few years ago we found that chlorotrioxorhenium(VII)[9] and perrhenyl carboxylates[10] are much more useful precursors for the perrhenyl synthon. Both compounds are easily and quantitatively available from Re_2O_7 and can be used *in situ* for the reaction with the organylating reagents without rhenium loss (eqs 4 and 5).[9,10] Covalent perrhenates such as $Me_3SiOReO_3$ and $Me_3SnOReO_3$ are also suitable precursor compounds of $R-ReO_3$ complexes.[11]



(4)

1, 2, 15 - 30, 34, 35



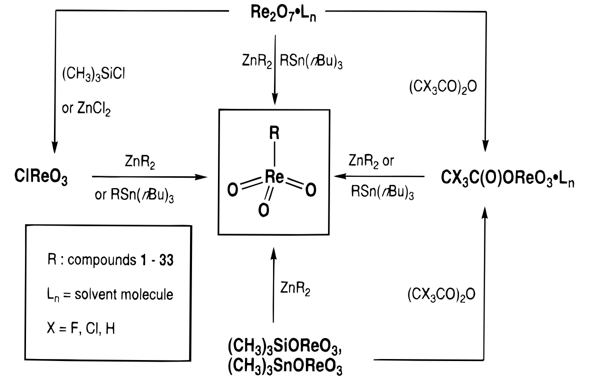
(5)

2 - 14, 25 - 35

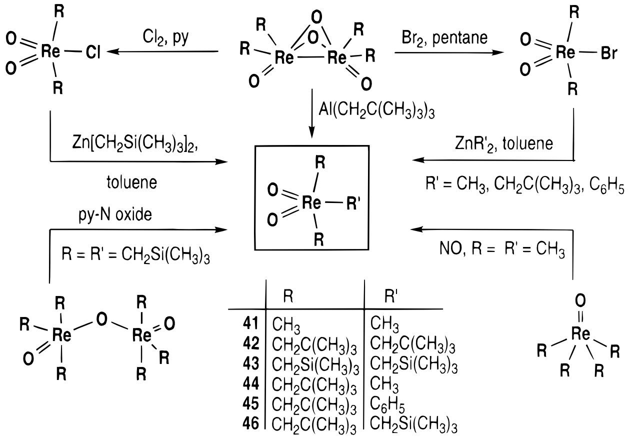
It has been shown that organozinc precursors are useful for the preparation of long-chain alkylrhenium oxides (**2**−**14**)[12] and σ-arylrhenium oxides (**25**−**33**)[13] while methyl- (**1**), alkenyl- (**15**−**18**, **22**−**24**), and alkynyl- (**19**−**21**) rhenium(VII) oxides and nonperalkylated cyclopentadienylrhenium(VII) oxides (**35**, **36**) are available with organotin precursors.[14] Some derivatives such as (η^5-cyclopentadienyl)trioxorhenium (**35**) and (η^1-phenyl)-trioxorhenium (**25**) are accessible by both methods. Derivative **38** is synthesized by reaction of Re_2O_7 with carbodiphosphorane, $Ph_3P{=}C{=}PPh_3$.[15] The success of a certain synthesis depends on the transferability of the organic group and the redox potential of the precursors.[4k,2b] Scheme 1 summarizes the synthetic pathways to organotrioxorhenium(VII) derivatives of type **I**, starting from Re(VII) precursors.

In stark contrast to compounds of type **I** only very few examples of type **II** are known (compounds **41**−**46**).[16−20] These molecules are synthesized according to Scheme 2 and subsequently purified by chromatography or sublimation. Compounds **41** and **42** were the first organorhenium(VII) oxides to be synthesized. They were prepared by the reaction of $(CH_3)_4ReO$ with NO at −78 °C as early as 1975.[16a] The best accessway to these complexes uses $R_4(\mu\text{-}O)_2O_2Re_2$ derivatives as starting material (see Scheme 2) and has been developed by D. Hoffman and coworkers.[16e] Nevertheless, the total yield over all steps is quite low.

Scheme 1



Scheme 2



	R	R'
41	CH_3	CH_3
42	$CH_2C(CH_3)_3$	$CH_2C(CH_3)_3$
43	$CH_2Si(CH_3)_3$	$CH_2Si(CH_3)_3$
44	$CH_2C(CH_3)_3$	CH_3
45	$CH_2C(CH_3)_3$	C_6H_5
46	$CH_2C(CH_3)_3$	$CH_2Si(CH_3)_3$

Even less is known about molecules of type **III**. Only one complex of this type, namely, $(\mu\text{-}O)[((CH_3)_3CCH_2)ReO_2]_2$ (**47**), has been reported.[17] The three ways of its preparation are presented in Scheme 3. Again, the reaction starting from $R_4(\mu\text{-}O)_2O_2Re_2$ gives the best yield. We tried to repeat this reaction by using $Me_4(\mu\text{-}O)_2O_2Re_2$

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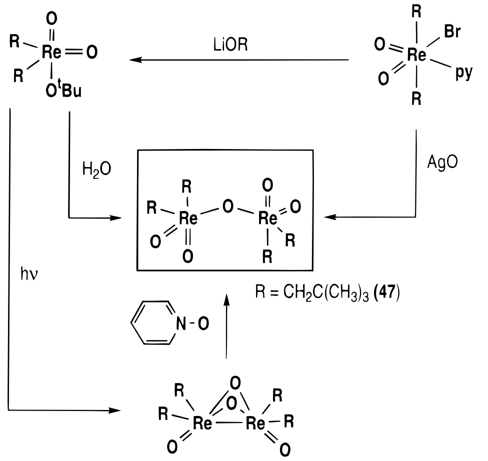
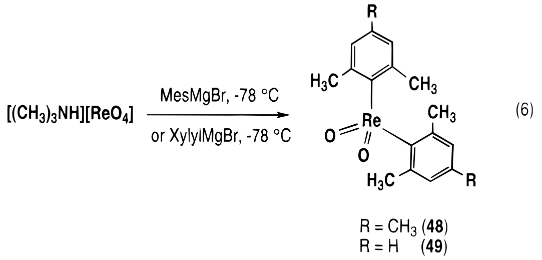
Scheme 3



42

as starting material to get the sterically less crowded methyl derivative but were only able to isolate it after stabilization with two pyridine molecules per molecule of product.[20b] Obviously only bulky ligands R allow the existence of donor free derivatives. This may be an important hint for the synthesis of further derivatives and is not uncommon in this chemistry.

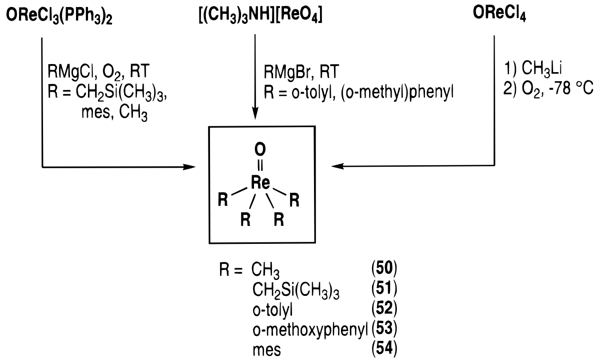
Organorhenium(VI) Oxides. In comparison to the organorhenium(VII) oxides where *ca.* 45 derivates of types **I**−**III** are known, not more than 20 different organorhenium(VI) oxides of types **IV**−**VII** have been published. This is mainly due to relatively inefficient and inconvenient synthetic strategies which are far less developed than in the case of the type I family. In most cases a certain amount of undesired byproducts is formed which sometimes cause problems during the purification processes.

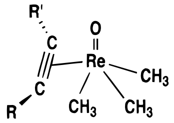


(6)

Interaction of trimethylammonium perrhenate or dirhenium heptaoxide with excess arylmagnesium bromide in THF leads to a complex of stoichiometry $[(aryl)_2ReO_2]_2$-$Mg(THF)_2$ (aryl = mesityl (mes), xylyl) (eq 6). These compounds are easily oxidized to $(mes)_2ReO_2$ (**48**) and $(xylyl)_2ReO_2$ (**49**). The oxidation can be achieved by oxygen or aqueous H_2O_2.[18b] These molecules are the only examples of type **IV**. In the case of aryl = *o*-tolyl and *o*-methoxyphenyl, compounds of type **VII** are formed under the same reaction conditions.[18a] Again, the steric bulk of the ligands is important for the stability of type **IV** molecules. As already mentioned, molecules of type **VII** were the first organorhenium oxides that have been prepared.[2c] $ORe(CH_3)_4$ (**50**) has been prepared by the reaction of $OReCl_3(PPh_3)_2$ and $(CH_3)Li$ with subsequent oxidation by O_2. Today only three more derivatives of type **VII** are known (compounds **52**−**54**).[18] Synthetic pathways leading to molecule type **VII** according to G. Wilkinson et al. are summarized in Scheme 4.[18−20] It is also possible to synthesize compounds of type **VII** with mixed alkyl groups. $ORe(CH_3)_3(CHCHP(CH_3)_3)$ (**50a**) and $ORe(CH_2Si(CH_3)_3)(CHCHP(CH_3)_3)$ (**51a**) can be prepared by reaction of the rhenium(V) oxo alkyl phosphine complexes $OReR_3(P(CH_3)_3)$ (R = CH_3, $Si(CH_3)_3$) with ethyne, a formal insertion of ethyne into the Re−P bonds.[18c] Substituted alkynes react with $ORe(CH_3)_3(P(CH_3)_3)$ to give the adducts $ORe(CH_3)_3(RC{\vdots}CR')$ (compound type **50b**) (R = R′ = CH_3, C_2H_5, Ph; R = CH_3, Ph, and R′ = H).[18c]

Scheme 4





50b

The best examined types of organorhenium(VI) oxides with respect to their synthesis are **V** and **VI**.[20,21] Alkylation of $OReCl_4$ with RMgX proceeds through Re(V) intermediates, *e.g.*, $[R_2ReO_2]_2Mg(THF)_2$, which can be oxidized with H_2O_2 or O_2 to give paramagnetic R_4ReO (type **VII**; see above).[2c,18a,20a] Simultaneously to the formation of type **VII** compounds, also diamagnetic dimers of type **VI** are formed.[20] Further oxidation of compound **50** with NO or O_2 at higher temperatures leads to *cis*-Me_3ReO_2 (type **II**). At low temperatures (−78 °C) type **V** derivatives are formed.

Type **VI** molecules are accessible in better yields by the reduction of $(CH_3)_3SiOReO_3$ with aluminum organyls or by heating of type **V** derivatives in the presence of excess ZnR_2.[20b] Another pathway is the reaction of organorhenium trioxides (type **I**) with excess ZnR_2 above room temperature.[20b] Yet only two different compounds of type **VI** are known (R = CH_3 (**55**) and R = $CH_2Si(CH_3)_3$ (**56**)). Molecules of general type **V** are accessible by the reaction of Re_2O_7 with $RTi(o\text{-}iPr)_3$ or much more conveniently by the reaction of Re_2O_7 or $RReO_3$ with stoichiometric amounts of ZnR_2 at low temperatures.[20,21] With these methods several derivatives (compounds **57**−**63**) are available.[20,21] We recently found that reduction of CH_3ReO_3 (**1**) with ZnR_2 leads to mixed derivatives $[(\mu\text{-}O)Re(O)(CH_3)R]_2$, R = C_2H_5 (**64**), *i*-C_3H_7 (**65**).[21c] Selected synthetic pathways toward type **V** and **VI** compounds are given in Scheme 5. As already mentioned, type **V** com-

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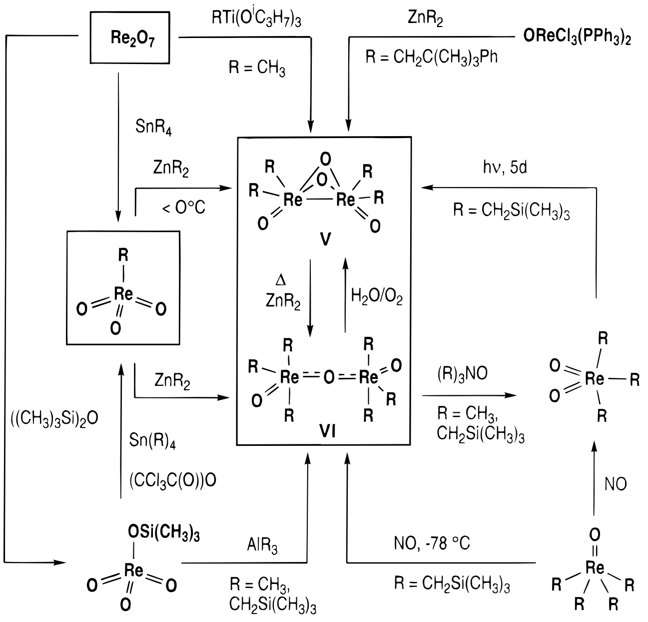
(21) (a) Huggins, J. M.; Whitt, D. R.; Lebioda, L. *J. Organomet. Chem.* **1986**, *312*, C15. (b) Cai, S.; Hoffman, D. M.; Huffman, J. C.; Wierda, D. A.; Woo, H.-G. *Inorg. Chem.* **1987**, *26*, 3693. (c) Kühn, F. E.; Mink, J.; Herrmann, W. A. *Chem. Ber.* **1997**, *130*, 295.

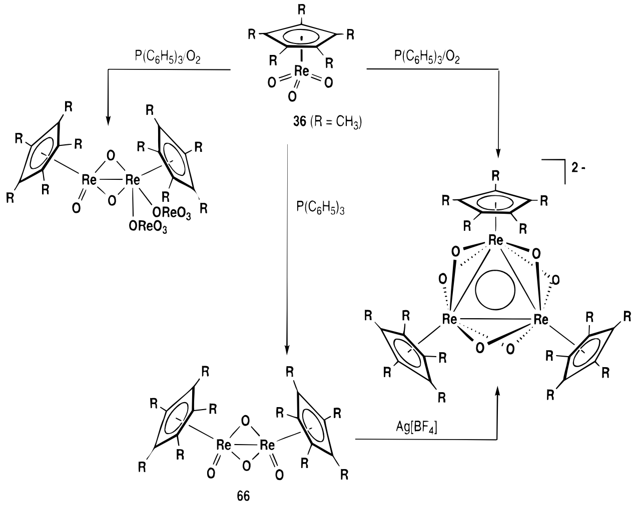
Scheme 5



V: R = $CH_2C(CH_3)_2Ph$ **(57)**
$CH_2Si(CH_3)_3$ **(58)**
$CH_2C(CH_3)_3$ **(59)**
CH_3 **(60)**
C_2H_5 **(61)**
c-C_3H_5 **(62)**
i-C_3H_7 **(63)**
CH_3/C_2H_5 **(64)**
CH_3/i-C_3H_7 **(65)**

VI: R = CH_3 **(55)**
$C_2Si(CH_3)_3$ **(56)**

Scheme 6

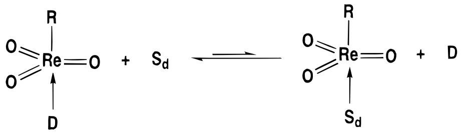


pounds are the most useful starting materials for the synthesis of type **II** and **III** complexes. A high-yield access to these complexes is therefore important.

Organorhenium(V) Oxides. Organorhenium(V) oxides are not known without additional donor stabilization. The only exception of this statement is derivative **66** and related compounds (Scheme 6). **66** is the only known compound of type **VIII**. The stability of this molecule is probably again due to the steric bulk and also the donor capability of the pentamethylcyclopentadienyl ligand. Alkyl and σ-aryl derivatives have not been synthesized up to now. Compound **66** is accessible from **36** and triphenylphosphine under oxygen free conditions.[2e,4] The reaction chemistry of **66** and related complexes was summarized elsewhere.[4]

Structures and Properties

Crystallography and Spectroscopy. Selected structural features of complex types **I**–**VII** are given in Table 1.[5,12,14–27] In general small changes in the donor capability or the steric bulk of ligands R do not affect the bond distances and angles of the molecules significantly. Spectroscopic results, *e.g.*, NMR and IR spectroscopy, are much more sensitive to small electronic changes than X-ray crystallography. ^{17}O NMR studies show strong ligand effects (Scheme 7) and a strong solvent dependence of the chemical shifts.[28a,29] Unfortunately more detailed ^{17}O NMR investigations have only been undertaken with type **I** molecules.[4k,27c,29] In solution organorhenium(VII) oxides $R{-}ReO_3{\cdot}(S_d)$ and their Lewis base adducts show both oxygen and ligand (D) exchange. The exchange rates depend strongly on the donor capability of the solvent and the temperature (eq 7).[29] In our experience IR


(7)

$$R{-}ReO_3{\cdot}D + S_d \rightleftharpoons R{-}ReO_3{\cdot}S_d + D \qquad (7)$$

S_d = donor solvent
D = Lewis base

spectroscopy is another very useful tool to examine the donor capability of the ligands R and L, respectively, in $R{-}ReO_3{\cdot}(L_n)$ complexes. Typical wavenumbers of ν_{sym}(ReO) and ν_{asym}(ReO) are given in Scheme 8.[4k,30] Typical IR shifts of Re=O and Re–O stretching frequencies of the general types **I**–**VII** are summarized in Table 2.[4k]

The dipole moments of $R{-}ReO_3$ reflect the strong electron-withdrawing character of the ReO_3 fragment.[4j,31a] Theoretical calculations confirmed the strong electron-withdrawing properties of the ReO_3 moiety. Calculations also indicate a partial triple bond character in the terminal

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(22) (a) Felixberger, J. K.; Kuchler, J. G.; Herdtweck, E.; Paciello, R. A.; Herrmann, W. A. *Angew. Chem.* **1988**, *100*, 975; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 946. (b) Herrmann, W. A.; Serrano, R.; Ziegler, M. L.; Pfisterer, H.; Nuber, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 50.

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(25) (a) Kiprof, P. Ph.D. Thesis, Technische Universität München, 1992. (b) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (c) Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899. (d) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 57.

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(27) (a) Herrmann, W. A.; Kuchler, J. G.; Weichselbaumer, G.; Herdtweck, E.; Kiprof, P. *J. Organomet. Chem.* **1989**, *372*, 351. (b) Herrmann, W. A.; Weichselbaumer, G.; Herdtweck, E. *Ibid.* **1989**, *372*, 371. (c) Roesky, P. W. Ph.D. Thesis, Technische Universität München, 1994. (d) Herrmann, W. A.; Correia, J. D. G.; Geisberger, M.; Mattner, M.; Artus, G. R. J.; Kühn, F. E. *J. Organomet. Chem.*, in press.

(28) (a) Herrmann, W. A.; Kühn, F. E.; Rauch, M. U.; Correia, J. D. G.; Artus, G. R. J. *Inorg. Chem.* **1995**, *34*, 2914. (b) Rietveld, M. H. P.; Nagelholt, L.; Grove, D. M.; Veldman, N.; Spek, A. L.; Rauch, M. U.; Herrmann, W. A.; v. Koten, G. *J. Organomet. Chem.*, in press.

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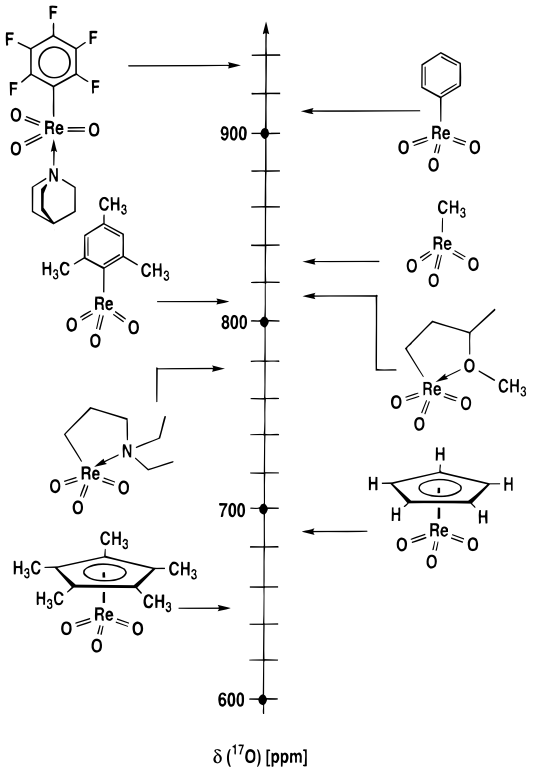
Table 1. Selected Structural Data of Organorhenium Oxides[a]

structure type	Re—O—Re	Re═O	Re—O_{br}	Re—C
I, σ-R, distorted tetrahedral		169(1)		209(1)
I, π-R, distorted tetrahedral		172(2)		207(1)
II, distorted trigonal bipyramidal		172(5)		215(3)
III, corner-sharing trigonal bipyramids (distorted)	166(1)	169(1)	192(3)	not given
IV, distorted tetrahedral		168(1)		206(1)
V, distorted edge-sharing tetragonal pyramidal	85(2)	166(2)	192(4)	213(4)
VI, distorted corner-sharing trigonal bipyramidal	180(0)	172(4)	184(2)	219(8)
VII, distorted tetragonal pyramidal		167(2)		216(4)

[a] Mean values of bond distances are given in picometers, bond angles in degrees. Standard deviations are given in parentheses.

Scheme 7



ReO bonds to get more electron density to the electron deficient rhenium core.[31,32]

Cyclic voltammetric measurements of type **I** derivatives are in good agreement with theoretical stability calculations. Electron-donating substituents, *e.g.*, R = $CH_2Si(CH_3)_3$, and Lewis base ligands, *e.g.*, quinuclidine and 2,2′-bipyridine, enhance the redox stability.[4j,k,26b,33] Alkylrhenium(VI) oxides show mainly one-electron redox chemistry.[33] Monomeric complexes, *e.g.*, $(CH_3)_4ReO$, are reduced to the corresponding anion, dimeric complexes to mixed valence dimers.[33,34] In the case of $[(\mu\text{-}O)(CH_3)_2ReO]_2$ a one-electron reduction and the presence of oxygen lead immediately to the formation of a trimeric compound, a cluster anion of formula $[(CH_3)_6Re_3O_2(\mu\text{-}O)_4]^-$ (**67**).[34] It

Scheme 8

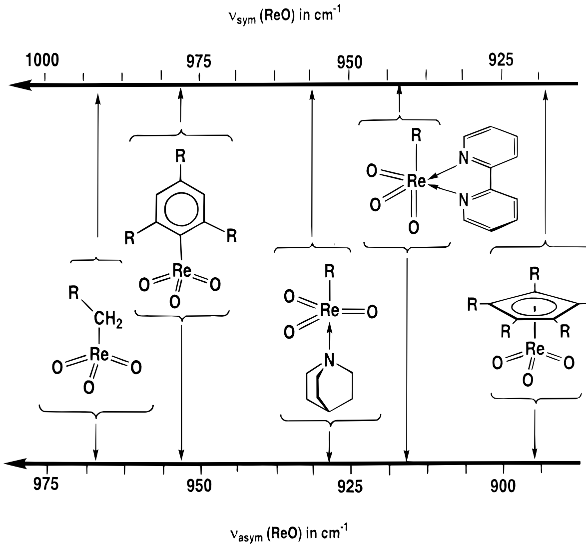
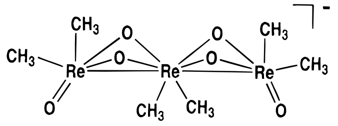


Table 2. IR Vibrations ν(ReO) (cm^{-1}) of Organorhenium Oxides

compound	structure type	$\nu_{sym/asym}$(Re═O)	ν(Re—O—Re)
$RReO_3$ (R = alkyl)	**I**	1000−990 965−955	
$RReO_3$ (R = σ-aryl)	**I**	990−975 960−950	
$RReO_3$ (R = π-cyclopentadienyl)	**I**	925−915 895−880	
R_3ReO_2	**II**	990−985 940−950	
μ-O$[R_2ReO_2]_2$	**III**	980−975 950−940	700−690
R_2ReO_2	**IV**	975−970 935−925	
$[(\mu\text{-}O)R_2ReO]_2$	**V**	1030−1000	760−740
μ-O$[R_3ReO]_2$	**VI**	1030−1000	850−750
R_4ReO	**VII**	1010−990	
$[(\mu\text{-}O)RReO]_2$	**VIII**	930	635, 615



67 (Re$^{VI/VII}$; as $[Cp_2Co]^+$ salt)
linear Re_3-framework

represents an example of an acyclic organometallic oxide framework with metal−metal bonding. Ligands bulkier than the methyl group, *e.g.*, cyclopropyl or neopentyl ligands, do not allow such a trimerization.[33] The neopentyl derivative can be reduced electrochemically to $[R_2ReO_2]^-$ and in a preparative way with Na/Hg as reducing agent (see below).[20a]

Behavior in the Presence of Water. We were rather surprised when we examined the behavior of **1** in the presence of water. Heating this compound in aqueous solution for several hours at 70 °C leads to the formation of a gold-colored, polymeric compound of empirical

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(31) (a) Köstlmeier, S.; Häberlen, O. D.; Rösch, N.; Herrmann, W. A.; Solouki, B.; Bock, H. *Organometallics* **1996**, *15*, 1872. (b) Wiest, R. T.; Leininger, T.; Jeung, G. H.; Benárd, M. *J. Phys. Chem.* **1992**, *96*, 10800. (c) Costas, M.; Poblet, J. M.; Rohmer, M. M.; Benárd, M. *Inorg. Chem.* **1995**, *34*, 176. (d) Szyperski, T.; Schwerdtfeger, P. *Angew. Chem.* **1989**, *101*, 1271; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1128.

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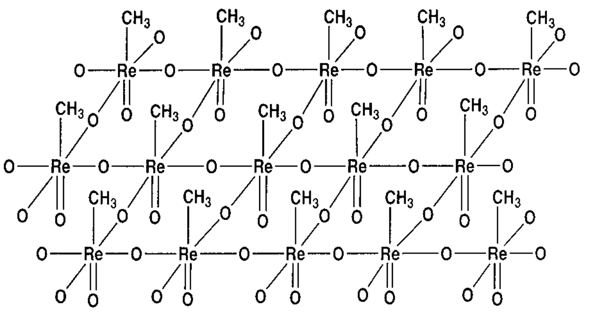


(1a)

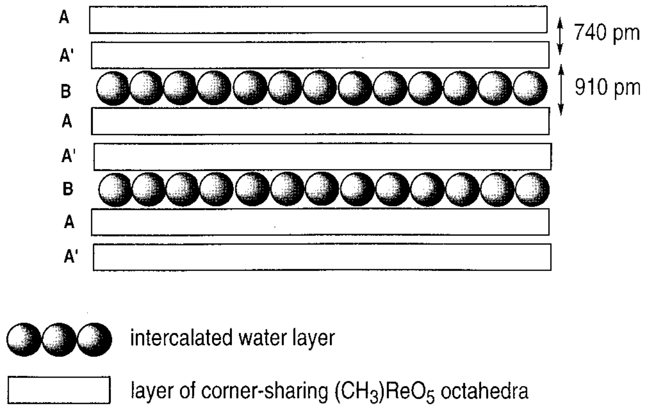
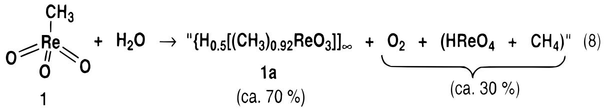


FIGURE 1. Stacking model for crystalline areas of "poly(methyltrioxorhenium(VII))" (1a).

formula $\{H_{0.5}[(CH_3)_{0.92}ReO_3]\}$ (**1a**) in high yield (eq 8).[35,36]

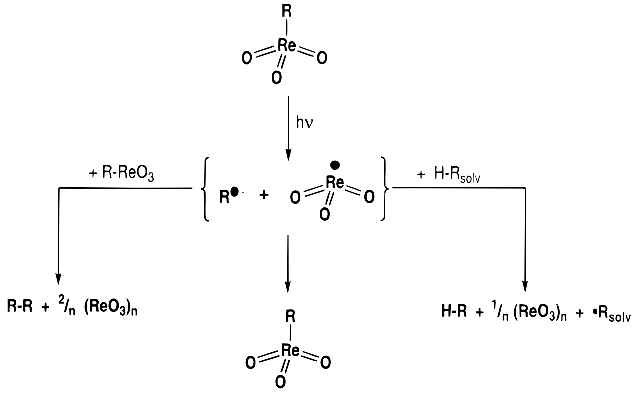


$$\underset{1}{CH_3ReO_3} + H_2O \rightarrow \text{"}\underset{\substack{1a \\ (ca.\ 70\ \%)}}{\{H_{0.5}[(CH_3)_{0.92}ReO_3]\}_\infty} + \underbrace{O_2 + (HReO_4 + CH_4)\text{"}}_{(ca.\ 30\ \%)} \quad (8)$$

This is the first example of a polymeric organometal oxide. The structure of the crystalline domains of **1a** can be described as double layers of corner-sharing CH_3ReO_5 octahedra (AA′) with intercalated water molecules (B) in a ...AA′BAA′... layer sequence (Figure 1). Therefore, the oxo groups of two adjacent layers are vis-à-vis with the intercalated water layer. Hydrogen bridges are formed between the oxo groups and the water molecules, enhancing the structure of the polymer. The double layers are interconnected by van der Waals attractions generated by the nonpolar methyl groups which are orientated inside the double layer. These structural features explain the observed lubricity of **1a**. Substoichiometry with respect to the CH_3/Re ratio of 4.6:5 and partial reduction by extra hydrogen equivalents are responsible for a high electric conductivity of **1a**.[26,35] For the amorphous areas of **1a** a model with turbostatic and 001 defect stacking of double layers of corner-sharing $(CH_3)ReO_5$ octahedra with smaller water content has been proposed.[26,35]

Up to now we did not find a similar behavior of another organorhenium oxide. Longer chain alkylrhenium(VII) oxides and especially alkenyl and alkynyl derivatives decompose slowly under formation of ReO_4^- and hydrocarbons in the presence of water.[4k,37] π-Organylrhenium(VII) oxides are not soluble in water. All organorhenium(VII) oxides of type **I**, including **1a**, are sensitive to OH^- ions. In basic solutions they decompose quickly under formation of perrhenate.[37] The decomposition in an acidic medium is very slow.[38] Organorhenium(VI) oxides of types **V** and **VI** are water stable.[20,21,35a]

Scheme 9



Photochemical Behavior. Organorhenium(VII) oxides of type **I** undergo homolytic decomposition of the C–Re bond as shown by ESR and UV/vis experiments (Scheme 9).[39] Light in the range of $\lambda = 200-400$ nm is very efficient for homolysis; in the daylight most of the compounds decompose slowly.[39a] We first made this observation when we compared UV/vis spectra of solutions of compound **1** which have been stored in drawers or in daylight, respectively. The most light stable derivatives (lowest quantum yield) are the π-aromatic complexes; the most sensitive compounds are the σ-alkyl derivatives. The photochemical behavior of types **II**–**VIII** was not yet examined in great detail, but quite a few of compounds **41**–**65** show light sensitivity.[16–21]

Thermal Behavior. Thermal stability of organorhenium oxides varies in a large temperature range. While CH_3ReO_3 (**1**) decomposes only above 300 °C[35,37,40] and $[\eta^5\text{-}C_5(CH_3)_5]ReO_3$ (**36**)[2b,40] is stable up to *ca.* 210 °C, (indenyl)ReO_3 (**24**)[14b] is not stable above −30 °C and (benzyl)ReO_3 (**18**)[15a] decomposes below −40 °C. As is known from gas phase analyses and TG/MS experiments, the hydrocarbon ligand reacts with the oxo ligands mainly under formation of CO_2 and H_2O, if a temperature-triggered intramolecular redox reaction can take place.[40] The higher the hydrocarbon content of the organorhenium oxide, the lower is the oxygen content of the resulting residue. If **1** is tempered at 130 °C in a sealed tube, a red-colored, amorphous, polymeric compound is formed which closely resembles **1a** in its characteristics, and we interpret it as

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(35) (a) Herrmann, W. A.; Fischer, R. W.; Scherer, W. *Adv. Mater.* **1992**, *4*, 653. (b) Herrmann, W. A.; Fischer, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 3223. (c) Mattner, M. R.; Herrmann, W. A.; Berger, R.; Gerber, C.; Gimzewski, J. M. *Adv. Mater.* **1996**, *8*, 654.

(36) Genin, H. S.; Lawler, K. A.; Hoffmann, R.; Herrmann, W. A.; Fischer, R. W.; Scherer, W. *J. Am. Chem. Soc.* **1995**, *117*, 3244.

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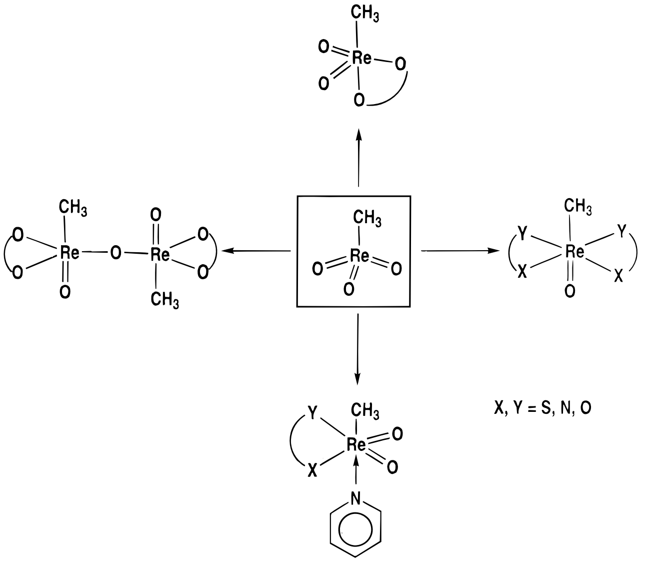
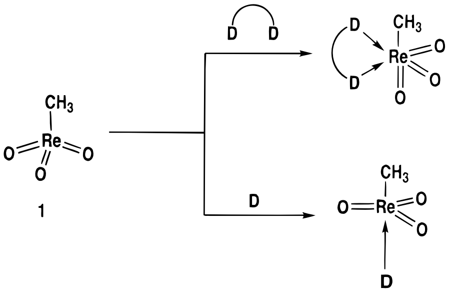
Scheme 10



Scheme 11



the water free form of **1a**. In contrast to **1a** it is much more hygroscopic and less stable.[40b,41]

Most of the thermally unstable organorhenium(VII) oxides are much more stable in (diluted) organic solutions (especially in noncoordinating solvents, *e.g.*, benzene).[4k] In solution thermal decomposition follows mainly radical pathways. The decomposition rate depends both on the concentration and on the temperature.[4k,14a]

Derivatives of Organorhenium(VII) Oxides

Interestingly, the chemistry of **1** is quite different from the chemistry of **36** which has already been summarized in other reviews.[4,42] It has been assumed that this is due to both electronic and steric reasons.[4,31,42] Four main types of reactions of **1** are known to date:

Condensation Reactions. Up to two of the oxo ligands of **1** are replaced by chelating ligands (*e.g.*, alcohols, thiophenols, amines) under formation of O,N-, S,N-, and S,S-chelate complexes.[43] N donors are sometimes required to stabilize the products. Furthermore, the reaction of **1** with epoxides also leads to glycolate complexes under mild conditions.[44] In some cases (e.g., with glycols) a dimerization and reduction of the Re(VII) centers take place.[43] Scheme 10 summarizes this reaction type.

Adduct Formation with Electron Donors. (η^1-Organo)rhenium(VII) trioxides are Lewis acids with two free coordination sites. Reaction with Lewis bases leads to electronic and steric saturation of the Re center (Scheme 11). Both oxygen and nitrogen bases have been used.[27] Monodentate ligands usually lead to trigonal bipyramidal products, bidentate bases to (distorted) octahedral coordination. Nucleophilic attack which causes the formation of these complexes may also be the first step in condensation reactions are described above. Special attention has been paid to these adducts because they have proven to be highly selective oxidation catalysts (see below). In solution these Lewis base adducts show fluctional geometry, due to the comparatively weak Re–L bond.[28a] Compound **1** also forms quite sensitive adducts with hexacyanoferrate(II) and even with heterocyclic carbenes.[45,46] Compound **36** does not form Lewis base adducts. The chemistry of **36** is governed by reductive processes, no matter whether Lewis bases or Lewis acids are used as reagents.[42] With amines or *N*-oxides **36** does not react at all.[4k,42] Interestingly, the 2,2′-bipyridine adduct of **1** (**1b**) shows a reaction behavior similar to that of **36**.[27c,47] This is clearly an effect of its electronic saturation in combination with the steric demand of the base ligand.[27c,47] Some typical reactions of **1b** are summarized in Scheme 12. Regioselective reactions take place because of the two different types of oxygen atoms, present in complex **1b**.[28b,48]

Reduction. In the presence of trimethylchlorosilane and triphenylphosphine, **1** undergoes reductive chlorination to form $[(CH_3(Ph_3PO)ReCl_2(O)]_2O$.[49] This is in remarkable contrast to the behavior of **36**, which forms (η^5-$C_5(CH_3)_5)ReCl_4$ under analogous conditions.[50] Reaction of **1** with alkynes in the presence of polymer bound triphenylphosphine leads to reductive substitution according to Scheme 13.[51] **36** undergoes cycloadditions not only with certain olefins, *e.g.*, norbornadiene,[52] but also with SO_2 and diphenylketene.[42,53] The latter reactions do not work with **1**, but with **1b** (see above). Reaction of **1** with triphenylphosphine causes partial reduction of Re(VII) to Re(V), thus leading to a noteworthy mixed Re(V)/Re(VII)

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(45) Kunkely, H.; Vogler, A. *J. Organomet. Chem.* **1996**, *506*, 175.

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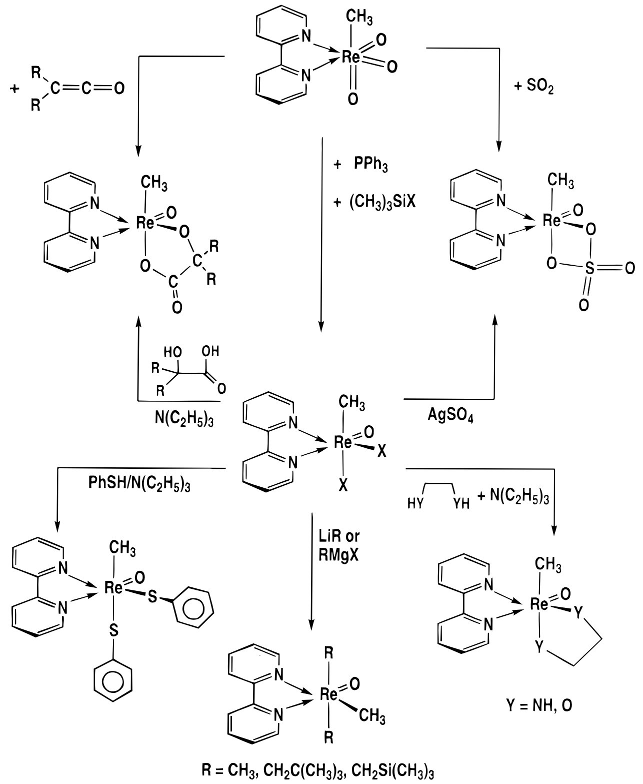
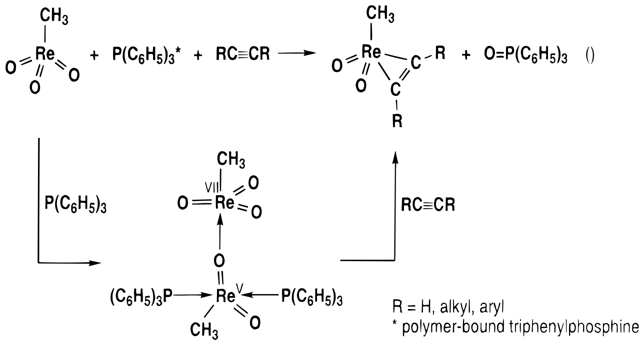
(53) (a) Herrmann, W. A.; Küsthardt, U.; Ziegler, M. L.; Zahn, T. *Angew. Chem.* **1985**, *97*, 857; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 860. (b) Küsthardt, U.; Herrmann, W. A.; Ziegler, M. L.; Zahn, T.; Nuber, B. *J. Organomet. Chem.* **1986**, *311*, 163.

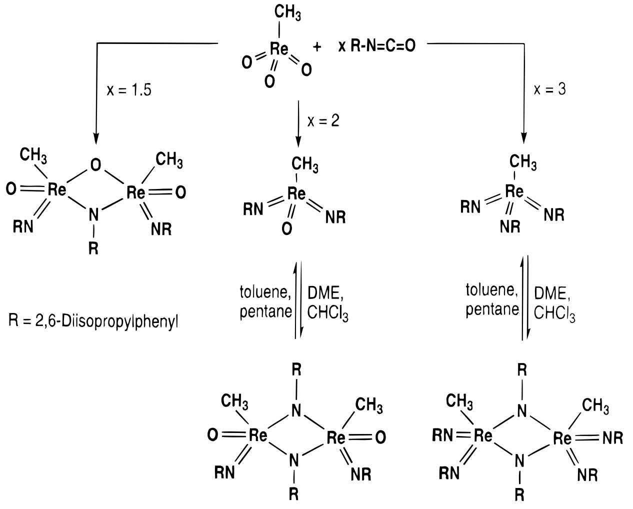
Scheme 12



Scheme 13



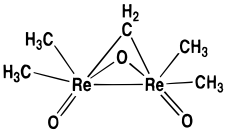
Scheme 14



compound, namely, $(Ph_3P)_2(O)(CH_3)ReO \rightarrow Re(O_3)CH_3$ (Scheme 13). We consider this derivative as an intermediate in the catalytic olefination of aldehydes (see below).[54]

Reaction with Isocyanates. Complexes of type $CH_3Re(NR)_3$ are formed by the reaction of **1** with isocyanates according to Scheme 14. Organotrisimidorhenium(VII) derivatives are also available by aminolysis.[55] Some imido derivatives are thermally significantly more stable than the corresponding oxo complexes, most prominently the allyl and the hydrido derivatives.[55a] The pronounced stability of these complexes may be due to the much stronger donor capability of imido ligands in comparison to oxo ligands. The chemistry of these interesting compounds is described elsewhere.[55]

Reactions of Other Organorhenium(VII) Oxides. The chemistry of molecules of general type **III**, namely, of the light sensitive compound **47**, has not been examined in detail.[17] The chemistry of type **II** compounds is better known. Derivatives **41**–**46** are thermally quite stable. Photolysis of **42** in pentane or pyridine yields the alkylidene complex $O_2Re(CHC(CH_3)_3)(CH_2C(CH_3)_3)$ (**68**), which has been structurally characterized as a distorted tetrahedral molecule, thus resembling complex type **I**.[16e,56] Complex **68** was the first rhenium(VII) oxo alkylidene complex characterized by X-ray crystallography.[56] We regard compounds like this as possible intermediates in the aldehyde olefination. A closer examination of **68** and similar compounds may therefore bring new insight to the mechanism of this important process. Another noteworthy oxo alkylidene complex, an analog of complex type **V**, is the dimeric rhenium(VI) oxo methylidene derivative of composition $(\mu\text{-}O)(\mu\text{-}CH_2)[(CH_3)_2)ReO]_2$ (**70**) which can be derived from the Re(V) starting material $(CH_3)_3ReO(P(CH_3)_3)$.[57] Derivative **68** reacts with quinuclidine to form a Lewis base adduct of composition $O_2Re(CHC(CH_3)_3)(CH_2C(CH_3)_3)\cdot$(quinuclidine) (**69**).[16e] Thermolysis of complex **45** in pyridine gives $O_2Re(CH_2C(CH_3)_3)(py)_3$ and neopentylbenzene under reductive elimination. Complex **45** reacts with $(CH_3)C{\equiv}C(CH_3)$ and $PhC{\equiv}CH$ to form $O_2Re(CH_2C(CH_3)_3)$(alkyne) compounds.[16e] These reactions are summarized in Scheme 15.



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Derivatives of Organorhenium(VI) Oxides

Derivatives of organorhenium(VI) oxides also have not yet been examined very systematically. The reason may be the relative inefficient accessways to some of the compounds. Nevertheless, several noteworthy details are known which surely will trigger further research in this field. The reactions of $(mes)_2ReO_2$ (**48**, type **IV**)

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(54) Herrmann, W. A.; Roesky, P. W.; Wang, M.; Scherer, W. *Organometallics*, **1994**, *13*, 4531.

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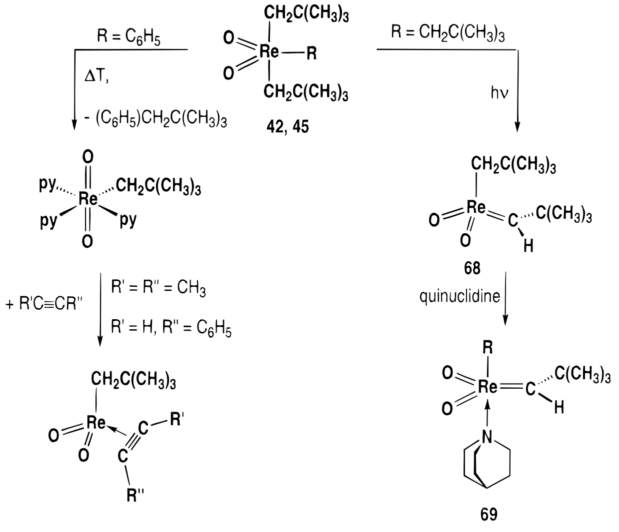
Scheme 15



with oxides of nitrogen have been studied.[6,18] With NO, **48** gives the dimesitylamido compound, $ReO_3[N(mes)_2]$; with NO_2 (N_2O_4) it reacts quantitatively to give the mesityl trioxo complex **27**. Nitromesitylene and 2,4,6-trimethylbenzene diazonium nitrate are formed as byproducts. Thus, both reactions with NO and NO_2 involve oxygen transfer to the metal compound, which is oxidized to Re(VII).[6]

Compounds of type **V** can be easily reduced by means of cyclic voltammetry or with reducing agents, *e.g.*, cobaltocene (see above). Compound **59** is reduced with Li/Hg or Na/Hg to give diamagnetic $M[ReO_2(CH_2C(CH_3)_3)_2]$, M = Li, Na.[20,21] **59** can be oxidized with Cl_2, Br_2, and $AgBF_4$ to $O_2Re(CH_2C(CH_3)_3)_2X(py)$ (X = Cl, Br, F). In the resulting trigonal bipyramidal complexes the halogenato ligand occupies an equatorial position.[21] Oxidation of **60** under comparable conditions cannot be observed.[20b] Reaction with pyridine *N*-oxide in toluene and pyridine leads to the formation of an orange Re(VII) complex of composition (μ-O)$[Re_2(CH_3)_2O_2(py)_2]_2$. An X-ray crystal structure analysis showed a distorted octahedral geometry around the Re centers, which are linked by a bent Re−O−Re bridge.[20b]

The reaction of excess $P(CH_3)_3$ with **58** leads to the formation of $ORe(P(CH_3)_3)(CH_2Si(CH_3)_3)_3$. The latter compound reacts rapidly with CO to give purple $ORe(P(CH_3)_3)(\eta^2\text{-}C(O)CH_2Si(CH_3)_3)(CH_2Si(CH_3)_3)_2$. An analogous pyridine complex, $ORe((py)(\eta^2\text{-}C(O)CH_2Si(CH_3)_3)(CH_2Si(CH_3)_3)_2$, is prepared by adding CO to a solution of **58** in pyridine.[16c] Complex **58** also reacts with O_2, DMSO, or pyridine *N*-oxide to yield **43**.[16c,20] Reaction of derivative **59** with stoichiometric amounts of H_2S leads to replacement of one bridging oxygen by a bridging sulfur atom.[20c] With 2 equiv of H_2S, both bridging oxygens are replaced by sulfur.[20c]

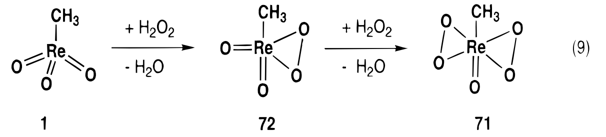
50 reacts with trialkylaluminum under formation of the explosive, green, paramagnetic d^1-complex $Re(CH_3)_6$.[16a] Interaction of hexamethylrhenium with methyllithium forms the octarhenate(VI) ion, which can be isolated as *N,N,N′,N′*-tetramethylethylenediamine salt $Li_2[Re(CH_3)_8]\cdot$tmed.[16a,2c,19] $Re(CH_3)_6$ reacts with O_2 to give **50**, with nitric oxide to give **41**.[16a,2c,19]

Applications

The high catalytic activity of several organorhenium oxides is one of the most important driving forces for the research in this field. Especially methyltrioxorhenium has proven to be an excellent catalyst in important organic reactions. Alone this aspect would cover an extra paper,[7] but a few key results should be given in the present context, too.

Oxidation Catalysis. Only a few years ago the importance of rhenium compounds in oxidation catalysis was not considered worth mentioning.[58] This picture has changed drastically during the recent five years. Organorhenium oxides, especially methyltrioxorhenium(VII) (**1**), have proven to be excellent oxidation catalysts. In the last few years dozens of papers appeared on the catalytic applications of **1** and related derivatives, and the field is still in full progress.[59−71]

An important breakthrough in the use of organorhenium oxides of type **I** in oxidation catalysis was the isolation and characterization of the reaction product of **1** with H_2O_2. According to eq 9a bisperoxo complex of stoichiometry $(CH_3)Re(O_2)_2O$ (**71**) is formed. Our coworkers managed to isolate crystals of this explosive



(9)

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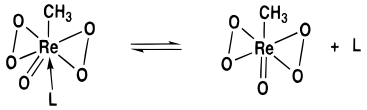
compound as adducts with a donor ligand L (L = H_2O (**71a**), $O{=}P(N(CH_3)_2)_3$ (**71b**)).[59] If each peroxo group is considered a coordinative unit, the molecular structure of complex **71a,b** can be described as a trigonal bipyramid. In the gas phase the molecule is not coordinated with an additional ligand L (**71**).[60] ^{17}O NMR experiments showed that **71a,b** exchange their ligand L rapidly in solution[4k,61] and are in equilibrium with the noncoordinated form **71** (eq 10). The ligand free complex **71** has a trigonal pyramidal structure, with significant shorter Re−O and Re−C bond distances than in **71a,b**. This is very likely due to the enhanced Lewis acidity of the free complex **71**. Experiments with the isolated complex **71a** have shown that it is an active species in oxidation catalysis, *e.g.*, in the oxidation of olefins.[59,60] *In situ* experiments indicated that the reaction of **1** with 1 equiv of H_2O_2 leads to a monoperoxo complex (**72**) according to eq 9. This complex is also catalytically active in certain oxidation processes.[62−71] Unfortunately it has not been possible to isolate complex **72**. Several mechanistic studies have been published, describing the coordination of hydrogen peroxide to **1**, the behavior of **71** in the gas phase, the photochemical and photophysical behavior of **71**, and the decomposition of **71** and **72**.[62c−e]



(10)

L = H_2O (**71a**)
L = $OP(N(C_2H_5)_2)_3$ (**71b**)

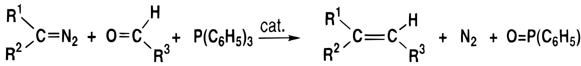
71

Compounds **71** and **72** are responsible for the catalytic oxidation of alkenes,[64] alkynes,[65] aromatic compounds,[66] sulfur compounds,[67] phosphines, arsines, and stibines,[68] amines and other organonitrogen compounds,[69] halide ions,[70] and oxygen insertion in C−H bonds.[71] This has been shown by *in situ* UV/vis, NMR, GC/MS, and IR spectroscopy.[64−71]

Other methylrhenium oxides, *e.g.*, $(CH_3)_4ReO$ (**60**), also form **71** in the presence of excess H_2O_2.[64b] Alkyl- and alkenylrhenium oxides of type **I** form similar active species, but they are not as stable as **71**.[61,64b] Lewis base adducts of **1** and intramolecular base adducts (*e.g.*, **14**) show catalytic activity in the olefin oxidation.[1,64b] Their activity is lower than in the case of **1**/**71**, but the selectivity toward epoxides is higher.

It has been shown that **71** also act as an active species in the Baeyer−Villiger oxidation and in the Dakins reaction.[66c,72] These reactions involve nucleophilic oxidation at the carbonyl group in contrast to the electrophilic nature of the above-mentioned oxidations, *e.g.*, in the olefin epoxidation. This reversed behavior, which was surprising to us on the first glance, may be due to substrate binding to rhenium.[72]

Aldehyde Olefination and Related Reactions. Aldehydes, treated with diazoalkane in the presence of an equimolar amount of a tertiary phosphine and **1** as catalyst, afford an olefinic coupling product in good yields already at room temperature according to eq 11.[73a]



$$R^1R^2C{=}N_2 + O{=}C(H)R^3 + P(C_6H_5)_3 \xrightarrow{cat.} R^1R^2C{=}C(H)R^3 + N_2 + O{=}P(C_6H_5)_3 \quad (11)$$

It has been shown by *in situ* spectroscopy and isolation and crystallization of the reaction product of **1** with tertiary phosphines (see Scheme 12) that Re(V) species act as catalysts in this process. Ligand- or solvent-stabilized methyldioxorhenium(V) seems to be the key compound.[51,54,73] *In situ* generated methyldioxorhenium is also able to successively abstract oxygen atoms from the notorious sluggish oxidation agent perchlorate.[73c] The deoxygenation of epoxides, sulfoxides, *N*-oxides, triphenylarsine oxide, and triphenylstilbene oxide at room temperature is also catalyzed by **1** with triphenylphosphine as oxygen acceptor.[73b]

Other organorhenium oxides form less active catalysts for aldehyde olefination. Starting with the results gained with **1** as catalyst precursor and a Re(V) species as active catalyst, it was found that trichlorooxorhenium(V) and derivatives are very active aldehyde olefination catalyst precursors, even more active than **1**.[27c,74] In contrast to the oxidation catalysis with organorhenium oxides, the presence of a rhenium−carbon bond seems not to be crucial for this process.

Olefin Metathesis. The system Re_2O_7/Al_2O_3 is an effective heterogeneous catalyst for carrying out olefin metathesis under mild conditions. Its activity can be further increased by the addition of tetraalkyltin compounds.[75] Tin-containing cocatalysts are essential for the metathesis of functionalized olefins.[75] These observations triggered the synthesis of methyltrioxorhenium (**1**) *via* eq 2 in our group. It was then discovered that **1** and other organorhenium oxides of formula (η^1-R)ReO_3 on an acid metal oxide support form metathesis catalysts that are active without additives even for functionalized olefins.[76] Standard supports are $Al_2O_3{-}SiO_2$ or Nb_2O_5. The activity is related to the surface acidity.[77] A high metathesis activity is observed when **1** is chemisorbed on the surface. No evidence for a surface carbene species was obtained, but there appears to be a correlation between the catalytic

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activity and the presence of an alkyl fragment on the surface.[76,77] The carbene species whose presence is implied in the catalytic cycle seems not to originate from the methyl group of **1**,[77b] but new experimental evidence is needed to clarify the remaining questions, such as the oxidation state of the Re center after heterogenization. It was also possible to encapsulate **1** in zeolite, maintaining its metathesis activity. IR and EXAFS data indicate that the structure of **1** remains unchanged while it is anchored by hydrogen bridges to the zeolite oxygens.[78a,b] There is evidence that the loading level of **1** corresponds to four molecules per supercage of zeolite Y.[78c]

Ring-opening polymerization is catalyzed by the homogeneous catalyst **1**/R_nAlCl_{3-n} ($R = CH_3$, C_2H_5, $n = 1$, 2). As in the case of the heterogeneous olefin metathesis, the reaction can be performed at room temperature.[76]

Beneath the above-mentioned type **I** molecules, other alkylrhenium oxides and related inorganic compounds catalyze the olefin metathesis, too.[79] $(CH_3)_4(\mu\text{-}O_2)O_2Re_2$ (**60**) can be activated by $AlCl_3$ and forms an active catalyst system for the homogeneous metathesis of unfunctionalized olefins. $(CH_3)_6Re_2O_3$ (**55**) is active only in the presence of both $AlCl_3$ and $Sn(CH_3)_4$. $(CH_3)_3ReO_2$ (**41**) is active in both the homogeneous and heterogeneous phases, but as in the case of **55** and **60** it is more stereoselective and less active than **1**. In homogeneous reactions this behavior is even more pronounced. The lower activity and higher selectivity may be due to greater steric problems in the case of **41**, **55**, and **60** and the lower Lewis acidity of the Re(VI) centers.[79a]

Other Applications. There are some other catalytic applications of organorhenium oxides, mainly of compound **1**, which have not yet been examined in great detail. Complex **1** enhances the Diels–Alder reactivity of unsaturated CC compounds.[80a] Furthermore, in the presence of **1** catalytic alkoxylation of cyclohexene with secondary and tertiary alcohols can be performed. The catalyst can cause disproportionation of epoxides, yielding unsaturated compounds and diols.[80b] A third new application is that catalytic amounts of **1** with ethyl diazoacetate convert aldehydes and ketones to epoxides and aromatic imines to aziridines. The presence of an oxyethylidene type active species, analogous to **72**, is proposed.[80c]

Conclusions

Organorhenium oxides can now be regarded as one of the best examined classes of organometallic compounds. Chemical examinations supported by a broad variety of spectroscopic, analytic, and structural methods helped to uncover the multitude of chemistry and properties of these complexes. The results clearly show the strong interdependence of properties, applications, and seemingly small physical and structural changes of closely related derivatives. The knowledge which has been accumulated in the field of the organorhenium oxides is also fruitful ground for the whole high-oxidation-state transition-metal chemistry. Our broad knowledge on methyltrioxorhenium(VII) (**1**) will not only pave the way into the chemistry of other metals, *e.g.*, $O{=}Os(CH_3)_4$,[81] but also fertilize the development of related compounds with "bare" (thus sterically unpretentious) ligands like nitrogen. As a matter of fact, only very few organometallic nitrides are known, *e.g.*, $N{\equiv}Mo(CH_2{}^tBut)_3$,[82] with the latter being promising candidates in the preparation of novel catalysts for ammoxidation.[83] It appears that the structurally most simple organometallic compounds still warrant intense efforts to become known and understood.

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