

Rhenium(VII) Oxo and Imido Complexes: Synthesis, Structures, and Applications

Carlos C. Romão,^{*†} Fritz E. Kühn,[‡] and Wolfgang A. Herrmann[‡]

Instituto de Tecnologia Química e Biológica, Quinta do Marquês, EAN, Apartado 127, 2780 Oeiras, Portugal, and Anorganisch-Chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching bei München, Germany

Received March 20, 1997 (Revised Manuscript Received July 18, 1997)

Contents

I. Introduction	3197	1. The Imido–Alkyne $\text{XR}(\text{NAr})_x(\eta^2\text{-C}_2\text{R}_2)_{3-x}$ Complexes	3239
II. LReO_3 Compounds and Derivatives	3199	2. The Imido–Alkydene and Imido–Alkyidyne Complexes	3240
A. Inorganic XReO_3 Compounds and Derivatives	3199	I. Structural Studies	3241
1. Dirhenium Heptaoxide, Re_2O_7 , and Derivatives	3199	VII. Conclusions	3243
2. Halides and Pseudohalides of Type XReO_3 and Their Adducts	3200	VIII. Abbreviations	3243
3. R_3EOReO_3 Compounds and Their Adducts ($\text{E} = \text{C}, \text{Si}, \text{Sn}, \text{Ge}, \text{Sn}, \text{Pb}$)	3202	IX. Acknowledgments	3243
4. The Amido R_2NReO_3 , the Phosphiniminato Complexes, and Their Adducts	3204	X. References	3243
5. The Carboxylato Complexes (RCOO)- ReO_3 and Their Adducts	3204		
6. The $[\text{L}_3\text{ReO}_3]^+$ and $[\text{L}_3\text{ReO}_3]$ Complexes	3205		
7. Miscellaneous Inorganic LReO_3 Derivatives	3206		
8. Structural and Spectroscopic Characterization	3206		
9. Reactions of Re_2O_7 and XReO_3 Compounds	3208		
B. Organic RReO_3 Compounds and Derivatives	3209		
1. The Alkyl RReO_3 Derivatives	3209		
2. The Methyl(vinyl) ReO_3 Complex	3212		
3. Allyl, Benzyl, and Pseudoallylic Compounds	3212		
4. The Alkynyl RReO_3 Derivatives	3212		
5. The Aryl Derivatives	3213		
6. The Cyclopentadienyl Derivatives	3213		
7. The Indenyl Derivative	3214		
8. Structural and Spectroscopic Characterization	3215		
9. Reactions of Organic RReO_3 Compounds	3220		
10. Applications	3223		
III. The L_3ReO_2 Compounds and Derivatives	3230		
A. Inorganic X_3ReO_2 Derivatives	3230		
B. Organic and Mixed Derivatives	3231		
IV. The $\text{L}_4\text{Re}_2\text{O}_5$ Compounds and Derivatives	3234		
V. The L_5ReO Compounds and Derivatives	3234		
VI. The Re(VII) Imido Compounds and Derivatives	3234		
A. The Inorganic $\text{XRe}(\text{NR})_3$ Derivatives	3235		
B. The Organic $\text{RRe}(\text{NR})_3$ Derivatives	3236		
C. The Inorganic $\text{X}_3\text{Re}(\text{NR})_2$ Derivatives	3236		
D. The Organic $\text{R}_3\text{Re}(\text{NR})_2$ Derivatives	3237		
E. Miscellaneous Polynuclear and Mixed Imido and Oxo–Imido Derivatives	3238		
F. The $\text{X}_5\text{Re}(\text{NR})$ Derivatives	3238		
G. Reactions of $\text{XRe}(\text{NR})_3$ Complexes	3238		
H. Reactions of $\text{X}_3\text{Re}(\text{NR})_2$ and Derivatives	3239		

I. Introduction

The first examples of organometallic derivatives of metal oxides appeared in a syncretic fashion and were merely regarded as laboratory curiosities in a time where low oxidation state chemistry dominated organometallic chemistry as a whole. However, the development of high oxidation state organometallic chemistry, mainly due to the pioneering efforts of G. Wilkinson, started to unravel a number of such species. Their importance as actual catalysts and/or catalyst precursors was also established in several processes particularly so in olefin metathesis. In this respect, rhenium, a metal otherwise devoid of catalytic importance,¹ was found to play a key role by providing the first catalysts capable of metathesizing functionalized olefins. Moreover, the variety of transformations of organic compounds that are catalyzed by metal oxides certainly suggests the existence of organometallic derivatives as elusive, albeit decisive intermediates.

Upon this highly interesting and unexplored ground, serendipity opened the way to a rapidly growing research activity that has produced a vast amount of chemical and physicochemical data on rhenium oxide derivatives gathered in an increasingly consistent and rationalized fashion. This effort overcame the field of organometallic chemistry inasmuch as it originated a reappraisal of some very basic inorganic chemistry of Re(VII) oxides, *e.g.*, the coordination chemistry of Re_2O_7 , and produced a remarkable row of useful active and selective catalysts the most important of which is methyltrioxorhenium(VII) (MTO).

The following work deals with all the synthetic, structural, spectroscopic, and other relevant studies of the inorganic and organometallic Re(VII) oxides in sections II–V.

[†] Instituto de Tecnologia Química e Biológica.

[‡] Technische Universität München.



Carlos Crispim Romão was born in Lisbon, Portugal. He graduated in Chemical Engineering at the Instituto Superior Técnico, Technical University of Lisbon (1971) where he received his Ph.D. under the supervision of Professor A. R. Dias (1979) and was successively appointed Assistant Professor, Associate Professor, and later obtained his *Agregação* degree (1993). In 1989 he was appointed research leader at the Instituto de Tecnologia Química e Biológica, Oeiras, where he recently became Associate Professor (1997). He carried out research at the University of Oxford with Professor M. L. H. Green, FRS (1974) and was a postdoctoral research fellow of the Alexander von Humboldt Foundation, at the Max-Planck Institut f. Kohlenforschung, Mülheim a.d. Ruhr, Germany, with Professor P. W. Jolly (1982/84) and at the Technische Universität München, with Professor W. A. Herrmann with whom he has collaborated on rhenium oxide chemistry since 1990.



Fritz Elmar Kühn was born in Freising, Bavaria. He studied chemistry at the Technische Universität München in Garching 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 1995–1996 with Professor F. A. Cotton (Texas A & M University) as a Feodor Lynen fellow of the Alexander von Humboldt Foundation. He also spent several months at the Instituto de Tecnologia Química e Biológica in Oeiras, Portugal (DAAD grant and Alexander von Humboldt Fellowship) to carry out research projects with Professor C. C. Romão. In 1996 he started a Habilitation at the Technische Universität München.

These sections are defined by the cores of the known organic and inorganic Re(VII) oxide species, namely $[\text{ReO}_3]^+$, *cis*- $[\text{ReO}_2]^{3+}$, $[\text{O}_2\text{Re-O-ReO}_2]^{4+}$ and $[\text{ReO}]^{5+}$. The rich chemistry of the Re(VI) and Re(V) oxides is not considered in this review.

Providing the largest number of examples, section II was divided in two large subchapters dealing separately with inorganic and organic $[\text{ReO}_3]^+$ complexes.

Particular emphasis is given to the synthetic aspects since, in our opinion, the systematization and mastering of these routes was decisive for the understanding of all this chemistry and will be instru-



Wolfgang Anton Herrmann was born in Kelheim, Bavaria. 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 1975–1976 with Professor P. S. Skell (Pennsylvania State University) as a DFG Fellow. He finished his Habilitation 1978 at the University of Regensburg, was appointed Associate Professor at the University of Regensburg 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 (succession of E. O. Fischer). He is author of more than 450 publications and has earned numerous awards, among them the Leibniz Award (1986), the German–French Alexander von Humboldt Award (1990), the Max-Planck Research Award (1991), and the Bundesverdienstkreuz of the Federal Republic of Germany (1997). Since October 1995 he has been President of the Technische Universität München.

mental for the development of the future steps particularly those requiring “tailored” molecular catalysts.

The inorganic complexes in sections II and V have been known for a long time and are mentioned in previous reviews on the chemistry of rhenium.^{2–4} However, their inclusion gives a more thorough perspective of the existing achievements and limitations and reveals several barely touched areas of Re oxide chemistry needing to be explored and/or reexplored. The renewal of the inorganic chemistry of $[\text{ReO}_3]^+$ complexes (section II.A) provides an appropriate example.

Due to the recent synthetic improvements most of the organometallic derivatives are not covered in older comprehensive works on organorhenium chemistry,^{5a} but some are mentioned in more recent encyclopedic reviews.^{5b,c}

More recently, condensed personal accounts by some of the authors surveyed the organometallic RReO_3 chemistry and some of its applications.⁶

The rapid achievements in the field of catalysis are summarized for the first time in section II.B.10 covering results mostly reported in the last three years.

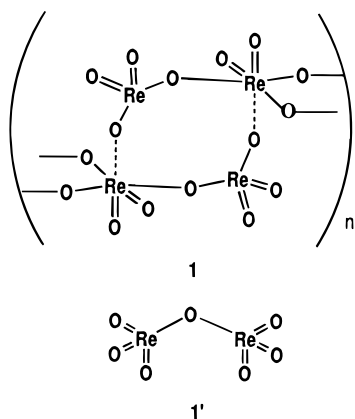
Being isoelectronic with the oxo ligand, the imido group (NR) produces similar types of complexes as far as general structural and electronic patterns are concerned.⁷ However, their higher electronic richness combined with a tunable stereochemical bulk lead to a flexible and rich chemistry discussed in section VI. Their isoelectronic carbene and carbyne derivatives which play a role in the context of alkene and alkyne metathesis are presented also in section VI.

II. $L\text{ReO}_3$ Compounds and Derivatives

A. Inorganic $X\text{ReO}_3$ Compounds and Derivatives

1. Dirhenium Heptaoxide, Re_2O_7 , and Derivatives

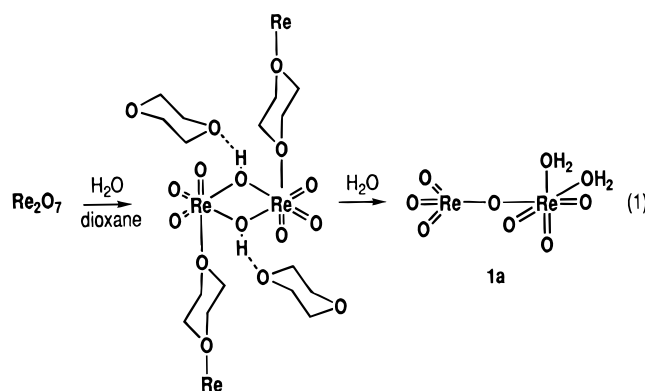
This key compound in all the chemistry of Re(VII) oxides is prepared by burning the metal in an atmosphere of oxygen at 400 °C.⁸ Re_2O_7 belongs to a small group of binary metal oxides which are soluble in certain organic solvents, other examples being Mn_2O_7 , Tc_2O_7 , RuO_4 , and OsO_4 . While these oxides keep strictly molecular structures in the crystal,⁹ Re_2O_7 exhibits an infinite polymeric solid-state structure like most insoluble metal oxides, *e.g.*, MoO_3 and WO_3 . However, this solid-state structure of Re_2O_7 is unique: an equal number of nearly regular ReO_4 tetrahedra and of (highly distorted) ReO_6 octahedra share corners through oxygen bridges as drawn in **1**.¹⁰ Important in this context is that the bridging Re–O bonds (172.5–216.0 pm) are longer than the terminal ones (165.0–174.2 pm). Also, the four different oxygens bound to a tetrahedrally coordinated Re center differ from each other only about 10 pm in length (168–180 pm) while the octahedrally coordinated Re atoms form three longer (205–216 pm) and three significantly shorter (165–175 pm) Re–O bonds.



In the gas phase, the structure determined by electron diffraction, **1'**,¹¹ shows two perfectly equivalent Re atoms, each one with a tetrahedral environment and both connected by a symmetric, bent Re–O–Re bridge, with a Re–O–Re angle of 143.6(9)°, thereby confirming earlier assumptions based on spectroscopic data.²

The solubilization of Re_2O_7 in organic solvents has provided some conflicting reports. At a certain stage several studies described Re_2O_7 as being insoluble in any organic solvent in the strict absence of water.^{2,12} Solubility was then attributed to the formation of soluble perrhenic acid from residual water in the solvent. As a matter of fact, Re_2O_7 dissolves freely in water to give perrhenic acid (formally HReO_4 ; $\text{p}K_a = -1.25$),² which can be crystallized out of these solutions as the bis(aqua) adduct of Re_2O_7 , *i.e.*, $\text{Re}_2\text{O}_7 \cdot (\text{H}_2\text{O})_2$ (**1a**).^{13a,b} Both water molecules are coordinated to the same rhenium atom which becomes octahedral. The other Re atom remains tetrahedral and the Re–O–Re bond is nearly linear (bond angle = 179.3°).¹³ Careful studies on the

hydrolysis of Re_2O_7 have, however, shown that the first product of the interaction of Re_2O_7 with water, in 1,4-dioxane, can actually be considered as a dimer of $\text{ReO}_3(\text{OH})$, namely $\text{Re}_2\text{O}_6(\text{OH})_2 \cdot 3(1,4\text{-dioxane})$ which adds water to give the bis(aqua) adduct **1a**, as drawn in eq 1.^{13c} This very sensitive molecule is stabilized in the crystal by coordination of one solvent molecule to the Re atom and by hydrogen bonding of the other 1,4-dioxane molecules to the bridging OH groups.^{13c} The central Re_2O_2 ring is planar and symmetric. A similar structure has been found for the corresponding methoxide dimer $[\text{ReO}_3(\text{OMe})(\text{HOMe})]_2$ (see below).



Two recent structures of supramolecular adducts of **1a** (Chart 1) with 1,4-dioxane^{13d} and diglyme^{13e} have been reported. In both cases there is no coordination of the dioxane or diglyme molecules to the Re atoms. Instead, they are associated to the coordinated H_2O molecules by hydrogen bonds.

A reinvestigation of this solubility problem was recently carried out in order to establish the true nature of the species existing in the solutions of Re_2O_7 used as the starting material for the synthesis of many other Re(VII) oxide derivatives, namely the organometallic ones.

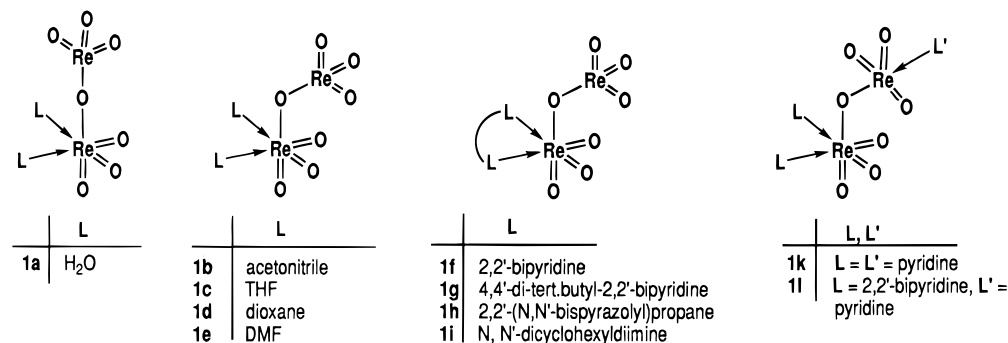
If bulk Re_2O_7 is dissolved in aprotic, organic donor solvents such as MeCN, THF or DME, solvent adducts of Re_2O_7 are obtained, $\text{Re}_2\text{O}_7 \cdot (\text{Solv})_2$ (**1b–d**) (Solv = solvent), which were shown by crystallography to be structurally similar to **1a**.^{11,14}

Therefore, it is clear that the species existing in solutions of Re_2O_7 are solvates of the type $\text{Re}_2\text{O}_7 \cdot (\text{Solv})_2$. $\text{Re}_2\text{O}_7 \cdot (1,4\text{-dioxane})_2$ (**1e**) could also be isolated in the absence of water.^{11a} The polymeric solid-state structure of Re_2O_7 breaks down at the expense of the newly formed Re–(Solv) bonds. Nondonating or weakly donating solvents are, therefore, incapable of dissolving Re_2O_7 as experimentally observed.

Addition of other bidentate ligands to solutions of Re_2O_7 in THF or MeCN produced a number of adducts **1f–i**.

With only two exceptions, the structures are always of the same type, both with mono (L) and bidentate (L–L) ligands, *i.e.*, two donor atoms bind the same Re atom which becomes octahedral with the three oxo ligands in a *fac* configuration while the other Re atom remains tetrahedral with shorter Re=O bonds.¹⁴ The exceptions are $\text{Re}_2\text{O}_7 \cdot \text{py}_3$ (**1k**) and $\text{Re}_2\text{O}_7 \cdot \text{py} \cdot \text{bipy}$ (**1l**). Here, one of the Re atoms has the usual octahedral coordination while the other becomes

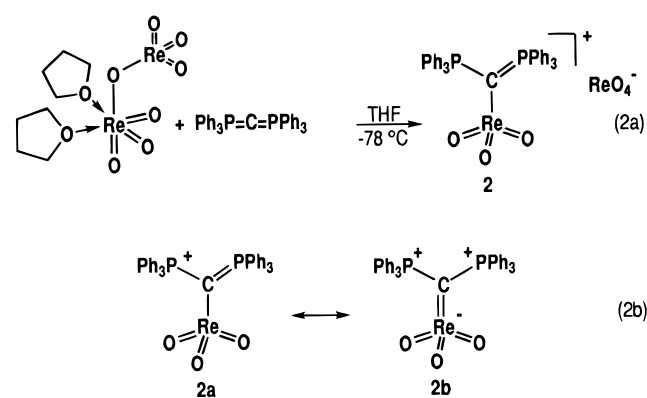
Chart 1



5-coordinated (TBP).^{15a} All the $\text{Re}_2\text{O}_7 \cdot \text{L}_2$ and $\text{Re}_2\text{O}_7 \cdot (\text{L}-\text{L})$ complexes are nonelectrolytes in nitromethane showing that the bridging $\text{Re}-\text{O}-\text{Re}$ bond remains intact in solution.^{14b} This has also been confirmed by ¹⁷O NMR studies (see section II.A.8.b).

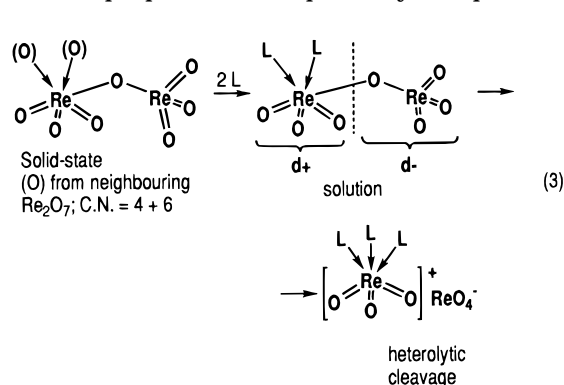
However, when Re_2O_7 in THF, is treated with tridentate N or S ligands (L_3), this $\text{Re}-\text{O}-\text{Re}$ bond is broken and the ionic complexes $[\text{L}_3\text{ReO}_3][\text{ReO}_4^-]$ which are 1:1 electrolytes in MeNO_2 , are formed. These complexes are further dealt with in section II.A.6.

Besides tridentate ligands, the very good donor carbodiphosphorane also cleaves Re_2O_7 as in eq 2a.¹⁶

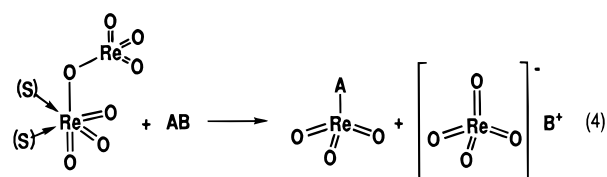


Charge stabilization via resonance hybrids **2a** and **2b** is held responsible for the remarkable stability of this complex as seen in eq 2b.

Two important conclusions were drawn from these facts. First, the fragment ReO_3^+ can be stabilized by a number of appropriate ligands which will modulate its reactivity. Second, Re_2O_7 can be easily broken into two ionic fragments along the redox neutral disproportionation pathway of eq 3.



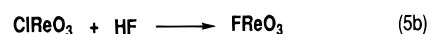
This allowed for reactions of the generalized type given in eq 4 to be devised for the preparation of inorganic and organic perrhenyl derivatives which resulted in the rapid expansion of this chemistry. In these reactions ReO_4^- acts as a leaving group and Re_2O_7 may be simply described as a type XReO_3 derivative with $\text{X} = \text{ReO}_4^-$.



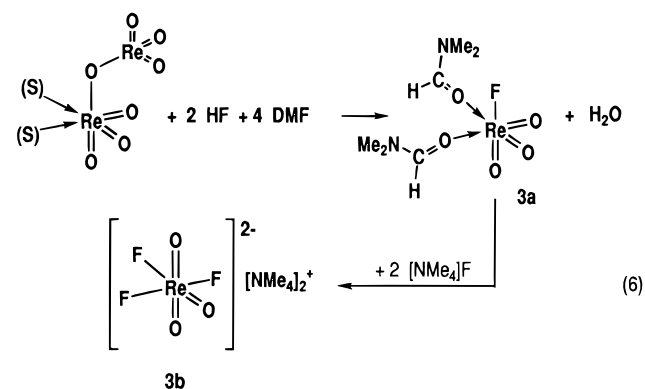
2. Halides and Pseudohalides of Type XReO_3 and Their Adducts

The halides XReO_3 ($\text{X} = \text{F}$, **3**; Cl , **4**; Br , **5**) represent the simplest perrhenyl derivatives and have been known for a long time.²⁻⁴ They have been mainly prepared by halogenation of ReO_3 , Re_2O_7 , and ReO_4^- although some solution routes are known for the chloride.

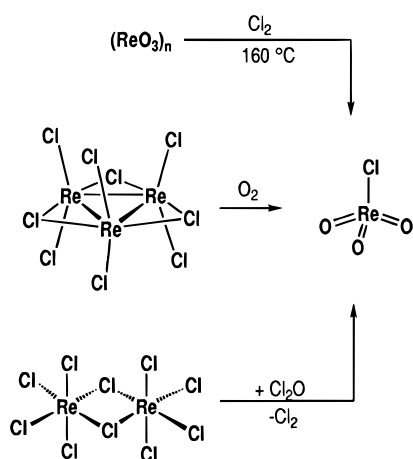
The fluoride is prepared by fluorination of perrhenate by IF_5 as in eq 5a,¹⁷ or by reaction of HF with Re_2O_7 , KReO_4 ,^{18a} or, more conveniently, from ClReO_3 as in eq 5b.



This extremely reactive, volatile yellow powder hydrolyzes in air to HF and perrhenic acid. Its only chemistry known, so far, is the formation of an adduct with DMF **3a** and fluoride **3b**, described in eq 6.¹⁹



Scheme 1



The green complex $(\text{F}_5\text{TeO})\text{ReO}_3$ is a fluoride analogue which is prepared by reaction of FReO_3 with $\text{B}(\text{OTeF}_5)_3$ and is characterized by IR, MS, and ^{19}F NMR.^{19b} Indeed, all the high oxidation state Re(VII) oxo fluorides have the corresponding OTeF_5 derivatives characterized, as can be seen in the sections III and V.

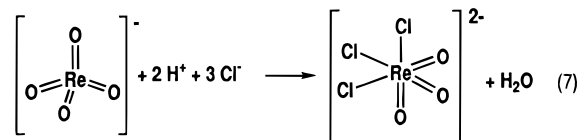
The bromide, BrReO_3 , is best prepared by bromination of Re_2O_7 with ReBr_3 ,^{20a} but bromination of ReO_3 ^{20b} or oxidation of ReBr_4 with O_2 at 100–120 °C^{20c} has also been used. The compound is a low melting (39.5 °C) colorless solid which readily decomposes above melting point to give ReO_3 . Its only derivative known is the adduct $\text{fac}[\text{Br}(\text{DMF})_2\text{ReO}_3]$ which has a chloride analogue (see below).^{21b}

A few “dry” preparations of the extremely aggressive and reactive liquid, ClReO_3 , have been reported (Scheme 1).²² The safer method seems to be chlorination of ReO_3 ,^{22a} since reaction of Re_3Cl_9 with O_2 may be dangerously explosive^{22b} and reaction of ReCl_5 with Cl_2O ^{22c} also involves the manipulation of rather dangerous materials.

Due to its aggressive reactivity and the difficulties found in its preparation, the chemistry of ClReO_3 has also remained very limited. ClReO_3 hydrolyzes in air to HReO_4 and HCl and, as expected from such a ligand environment, ClReO_3 is a strong Lewis acid, forming adducts with donor ligands. The octahedral complexes $\text{fac}[\text{L}_2\text{ClReO}_3]$ ($\text{L} = \text{DMF}$, DMSO ,^{21a,b} dimethylacetamide, tetramethylurea, HMPT ,^{21c} py , $1/2$ bipy,^{21d} $1/2$ 8-oxyquinoline,^{21e} are readily formed when the ligands are reacted with ClReO_3 in chlorinated solvents such as CCl_4 . The same $\text{fac}\text{-ReO}_3$ arrangement is present in the chloride complexes, $\text{fac}[\text{Cl}_3\text{ReO}_3]\text{A}_2$ ($\text{A} = \text{Me}_4\text{N}^+$, pyH^+ , and other ammonium ions) isolated upon ACl addition to solutions of ClReO_3 in similar solvents.²³ This geometry contrasts with the *mer* arrangement of **3b** (eq 6). Solvolysis of $\text{fac}[\text{Cl}_3\text{ReO}_3]\text{A}_2$ (**4a**) in DMF has allowed the preparation of $\text{fac}[\text{Cl}_2(\text{DMF})\text{ReO}_3]\text{A}$ and $\text{fac}[\text{Cl}(\text{DMF})_2\text{ReO}_3]$.¹⁹ The structures were mostly derived from IR and Raman data and a few X-ray crystallography studies.²⁴ The 5-coordinate $[\text{Cl}_2\text{ReO}_3]\text{-}[\text{PPh}_4]$ was isolated from ClReO_3 and ClPPh_4 in $\text{CH}_2\text{-Cl}_2$ but its structure remains unclear.²⁵

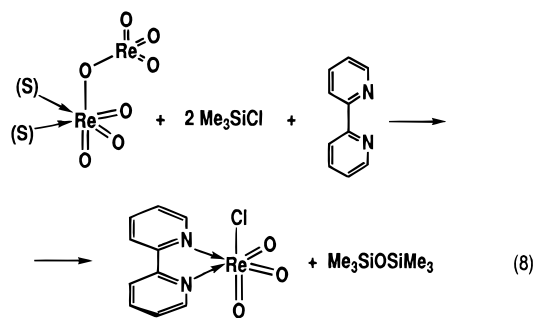
Another way of generating ClReO_3 is by protonation of KReO_4 . This can be done in DMF and DMSO,

by means of dry gaseous HCl , whereby KCl precipitates and the complexes $\text{fac}[\text{Cl}(\text{Solv})_2\text{ReO}_3]$ can be isolated. The same method allows the preparation of $\text{fac}[\text{Br}(\text{DMF})_2\text{ReO}_3]$, the only known derivative of BrReO_3 .^{21b} A similar chemistry takes place in water solution. In fact, when CsCl is added to ReO_4^- in 10 M aqueous HCl , $\text{fac}[\text{Cl}_3\text{ReO}_3]\text{Cs}_2$ is formed according to eq 7.²⁶ Its structure was later determined by X-ray crystallography.^{24a}



If bipy or phen are added to these solutions, the complexes L_2ClReO_3 ($\text{L}_2 = \text{bipy}$, phen) precipitate in high yield, revealing the intermediate formation of ClReO_3 .²⁷

However, in spite of their interest for the characterization of the XReO_3 complexes, all the methods named so far, have their practical value limited by the difficult synthesis and handling of all XReO_3 complexes ($\text{X} = \text{F}$, Cl , Br) or by the use of strongly coordinating solvents and ligands. Furthermore, the preparation of other pseudohalide derivatives was difficult to envisage by such methods. This situation changed with the simple reaction of eq 8 which is conveniently carried out in THF or MeCN and has been shown to be quantitative by ^{17}O NMR. Addition of bipy leads to $\text{XReO}_3(\text{bipy})$ ($\text{X} = \text{Cl}$, Br) in 93% isolated yield.^{28,29}

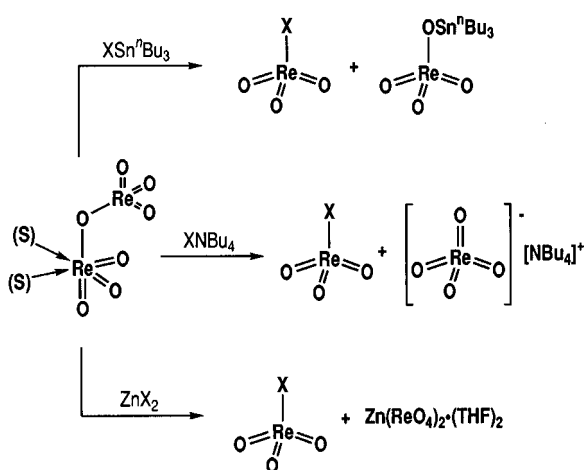


If pyridine is substituted for bipy, a much lower yield (86%) of the more soluble $\text{ClReO}_3(\text{py})_2$ is recovered. Quinuclidine, only gives the monoadduct, $\text{ClReO}_3(\text{quinuc})$ in 69% yield.²⁹ Due to their high insolubility, bipy adducts have played an important role in the identification of the presence of XReO_3 and RReO_3 complexes in solution, by precipitation as $\text{XReO}_3(\text{bipy})$ or $\text{RReO}_3(\text{bipy})$, as will be seen in many other forthcoming examples.

This type of reaction was further explored in the quantitative preparation (^{13}C NMR) of a solution of the cyanide derivative NClReO_3 using NCSnBu_3 .²⁹

As already suggested by eqs 2–4, nucleophilic substitution of the good leaving group ReO_4^- by other nucleophiles occurs easily. As described in Scheme 2 several halides and pseudohalides of type XReO_3 ($\text{X} = \text{F}$, Cl , Br , CN , SCN) have been prepared according to this principle. The compounds were isolated as their bipy adducts.

Scheme 2

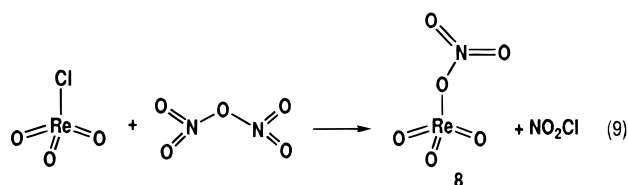


Another very useful method for the *in situ* preparation of ClReO_3 in THF solution uses ZnX_2 . In this case the equilibrium is driven to the right by the insolubility of $\text{Zn}(\text{ReO}_4)_2 \cdot (\text{THF})_2$. The disadvantage is that only 50% conversion of initial Re is possible. On the other hand, ClReO_3 is the only product remaining in solution and can be used for further reactions. It can even be extracted from the THF solution into CCl_4 .²⁹

The bromide derivative, BrReO_3 can be quantitatively prepared *in situ* by the same procedure, using ZnBr_2 , but the iodide derivative does not exist because I^- is oxidized by ReO_3^+ .

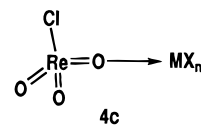
A somehow unexpected characteristic of the THF solutions of ClReO_3 and other XReO_3 compounds is their mild reactivity, namely toward several alkylating agents. This moderation is most certainly due to the weak coordination of THF and opens a convenient way to develop the incipient chemistry of these compounds which is still limited to the adducts XReO_3L and XReO_3L_2 .

The nitrate derivative $(\text{NO}_3)\text{ReO}_3$ (**8**) was prepared by an entirely different method as depicted in eq 9.³⁰



It hydrolyzes to HReO_4 and HNO_3 but is stable at room temperature under a dry atmosphere. It decomposes above 70–75 °C to give Re_2O_7 , NO_2 , and O_2 . X-ray powder data and other spectroscopic studies seem to exclude the alternative ionic formulation as nitronium perrhenate, $[\text{NO}_2]^+[\text{ReO}_4]^-$.

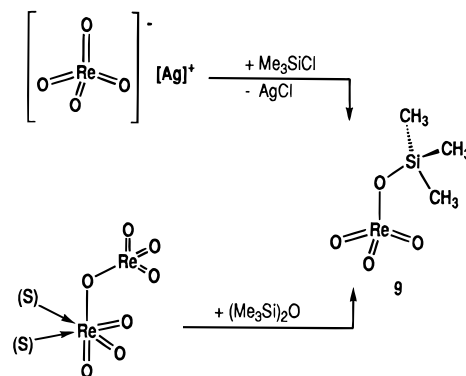
In spite of the Lewis acidity of its Re center, ClReO_3 has been shown to behave as a Lewis base, forming adducts with other metal salts. This behavior was first detected in the crystal structure of the adduct $\text{ClReO}_3 \cdot \text{ReOCl}$ where the Re–O–Re bridge observed comes from ClReO_3 . The latter interacts with other Lewis acids, MX_n , e.g., AlCl_3 , NbCl_5 ,^{31a} SbCl_5 ,^{31b} and ReOCl_4 ^{31c} under formation of the adducts **4c**.



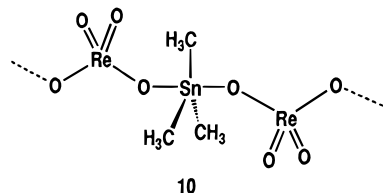
3. R_3EOReO_3 Compounds and Their Adducts (E = C, Si, Sn, Ge, Sn, Pb)

The first representative of this general class of alkoxide analogues was the volatile, hexane soluble siloxy derivative $\text{Me}_3\text{SiOReO}_3$ (**9**) prepared by Schmidt and Schmidbaur in 1959, according to the reactions in Scheme 3.^{32a,b}

Scheme 3

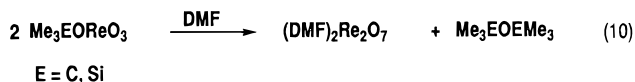


The second process is practically quantitative and very convenient for the preparation of a compound that has been an important starting material in the Re oxide chemistry namely for a series of Re(VI) alkoxides. This species is hydrolytically sensitive but thermally stable melting without decomposition at 79.5–80.5 °C. Its crystal structure reveals a bent Si–O–Re angle (164°) and not very different “Re–O” and “Re=O” distances.^{32c} This might suggest a “perrhenate”-like structure and reactivity which, however, is confirmed neither by chemistry nor by spectroscopy. Indeed, $\text{Me}_3\text{SiOReO}_3$ usually reacts as a “perrhenyl” synthon $[\text{ReO}_3]^+$ and not as a “silyl perrhenate”, as judged from mechanistic studies on the preparation of MeOReO_3 and other similar derivatives as well as IR and ¹⁷O NMR studies.³³ The tin analogue **10** is produced in quantitative yield, together with MeReO_3 , in the reaction of Re_2O_7 with Me_4Sn (see section II.B.1). In the solid state it has a polymeric structure with 5-coordinated Sn atoms.³⁴



A lead analogue, $\text{Ph}_3\text{PbOReO}_3$, was isolated from the reaction of Re_2O_7 with Ph_4Pb .³⁴ More recently, it was shown that the reaction of Re_2O_7 with R_3SiOH , R_3GeOH , and Ph_3SnOH gives R_3EOReO_3 complexes, like $\text{Ph}_3\text{SiOReO}_3$, $\text{Mes}_3\text{GeOReO}_3$, and the dimer $(\text{O}_3\text{ReOSn}(\text{Ph})_2\text{OSn}(\text{Ph})_2\text{OH})_2$,^{35a} and ${}^t\text{Bu}_2\text{Si}(\text{OReO}_3)_2$.^{35b} Reaction of Re_2O_7 with ${}^t\text{BuSi}(\text{OH})_3$ gave a tetramer $[\text{}^t\text{BuSi}(\text{OReO}_4)]_4$ which is a model for the deposition of ReO_3 on oxidic surfaces.^{35c} The first

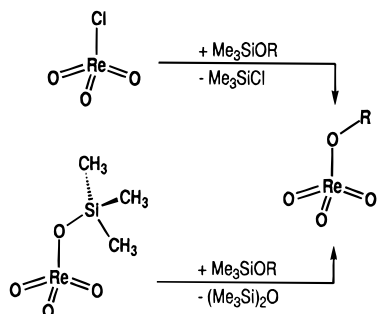
attempts to prepare the corresponding alkoxide derivatives revealed that the reaction of ${}^t\text{BuCl}$ and AgReO_4 failed to give ${}^t\text{BuOReO}_3$ which, however, is formed quantitatively from $({}^t\text{Bu})_2\text{O}$ and Re_2O_7 or from Re_2O_7 and ${}^t\text{BuOH}$.³⁶ In contrast to $\text{Me}_3\text{SiOReO}_3$, the alkoxide ${}^t\text{BuOReO}_3$ decomposes in the pure state above $-4\text{ }^\circ\text{C}$, although it can be kept at room temperature in solution. In this respect it resembles most of the RReO_3 complexes described in section III. Two interesting observations were made on the $\text{Me}_3\text{EOReO}_3$ complexes ($\text{E} = \text{C}, \text{Si}$). First, IR shows that the stretching $\text{Re}=\text{O}$ vibrations appear at even higher wavenumbers than the ones of ClReO_3 . Second, the unexpected reaction of eq 10 was observed.



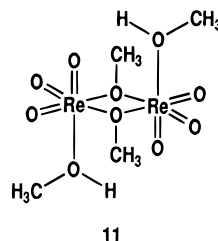
This implies that the formation of $\text{Me}_3\text{EOReO}_3$ from Re_2O_7 and $\text{Me}_3\text{EOEMe}_3$ is a solvent-dependent equilibrium since such reversibility was not observed in many other solvents.^{32a,b}

Using related methods, Edwards and Wilkinson were able to prepare ROReO_3 ($\text{R} = {}^t\text{Bu}, \text{Me}$) but not PhOReO_3 (Scheme 4).³⁷

Scheme 4

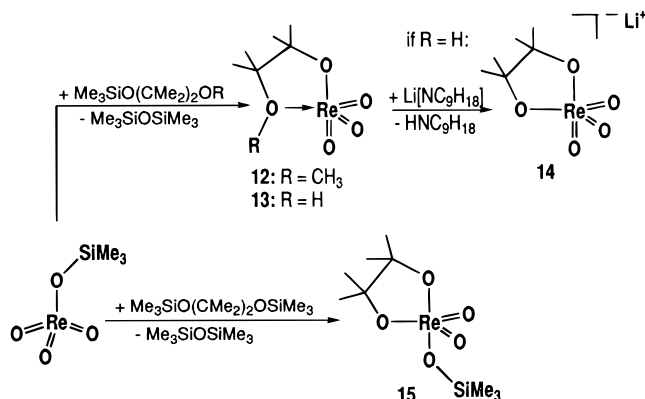


The compounds are unstable at room temperature but can be stabilized by adduct formation with TMEDA to form monomeric and room temperature stable adducts in both cases, ($\text{R} = {}^t\text{Bu}, \text{Me}$). On the basis of spectroscopic evidence their structures are assumed to be similar to the ones of the halide adducts, namely octahedral *fac*- $[\text{RO}(\text{TMEDA})\text{ReO}_3]$ ($\text{R} = \text{Me}, {}^t\text{Bu}$). The low solubility and volatility of the uncomplexed methoxide suggested a polymeric formulation $[\text{MeOReO}_3]_n$. No more related compounds were studied for a long time, although catalytic interesting and selective transformations of 5-hydroxyalkenes and acetals promoted by Re_2O_7 imply the intermediacy of these compounds.³⁸ A recent reinvestigation of this problem led to the isolation and detailed spectroscopic, and crystallographic characterization of a number of alkoxides, including the parent methoxide **11**.³³ The reaction used was the same presented in Scheme 4 for $\text{R} = \text{CH}_3$ (**11**), $\text{CMe}_2\text{CMe}_2\text{OMe}$ (**12**) and $\text{CMe}_2\text{CMe}_2\text{OH}$ (**13**). The methoxide was isolated as the room temperature stable MeOH adduct which possesses a dimeric structure with methoxide bridges as in formula **11**. This structure is closely related to the one of the hydroxide, eq 1, with a planar Re_2O_2 ring with almost equal inner angles. The complex is very



labile and the MeOH molecule is readily lost under vacuum to give the already mentioned polymer $[\text{MeOReO}_3]_n$. In the two other cases, intramolecularly stabilized alkoxides were isolated and structurally characterized as depicted in Scheme 5.

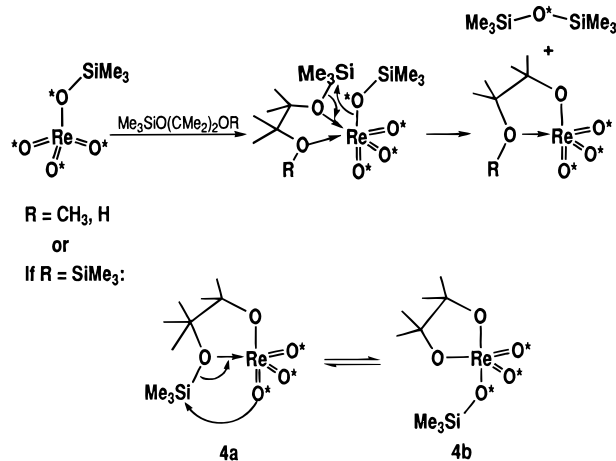
Scheme 5



In both cases, coordination of the distal OR function to the Re is observed, giving complexes that are more stable and easier to handle. Nevertheless, they are highly fluxional in solution and rigid structures are only attained below $\sim -90\text{ }^\circ\text{C}$. The anionic glycolato derivative **14** is obtained upon deprotonation of **13** with lithium 2,2,6,6-tetramethylpiperidinate.

Reaction of Re_2O_7 with the disilyl ether $\text{Me}_3\text{SiOCMe}_2\text{CMe}_2\text{OSiMe}_3$ gives **15**, a $\text{ReO}_2(\text{OR})_3$ -type derivative (cf., section III for analogues). This was structurally characterized in the solid state but it also undergoes exchange/equilibrium processes in solution (Scheme 6). The proposed mechanism of its synthesis

Scheme 6



is presented in Scheme 6.

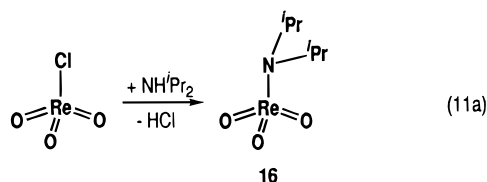
$\text{Me}_3\text{Si}^+\text{O}$ behaves as a leaving group being displaced from the Re center. The Lewis acidic "per-

phenyl" character of $\text{Me}_3\text{SiOReO}_3$ and all other alkoxo complexes was demonstrated by ^{17}O NMR spectroscopy (see Table 3) because the chemical shifts are significantly deshielded relative to the perrhenate anion ReO_4^- except for the mentioned anionic derivative **14**. The $\nu(\text{Re}=\text{O})$ frequencies in the IR spectra also confirm this assumption (Table 2).³³

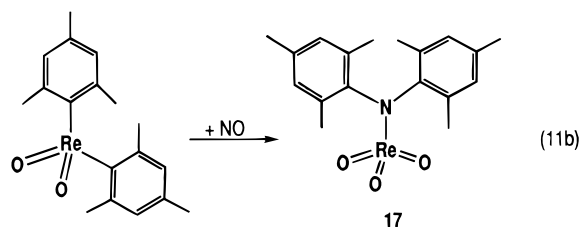
$\text{Me}_3\text{SiOReO}_3$ has been widely used as a starting material for the preparation of organometallic Re oxides. Almost invariably, reduction takes place and derivatives of Re(VI) are obtained. In this way, the complexes $\text{Re}_2\text{O}_3\text{Me}_6$,³⁹ $\text{Re}_2\text{O}_4(\text{CH}_2\text{CMe}_3)_4$,⁴⁰ and $\text{Re}_2\text{O}_4\text{Me}_4$ ⁴¹ have been prepared. The preparation of the Re(VII) dioxide *cis*- $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_3$, and some Aryl- ReO_3 (see Section IIB.5) derivatives are the few known exceptions to this behavior.⁴²

4. The Amido R_2NReO_3 , the Phosphinimato Complexes, and Their Adducts

Few compounds are known in this class. Reaction of ClReO_3 with NH^iPr_2 , in hexane, gives the highly moisture-sensitive $(^i\text{Pr}_2\text{N})\text{ReO}_3$ (**16**) as in eq 11a.³⁷



This volatile, low-melting complex slowly decomposes at room temperature ($t_{1/2} \sim 1$ day at 20°C). Again, it forms room temperature-stable 5-coordinate adducts with pyridine (py) and TMEDA: $(^i\text{Pr}_2\text{N})\text{ReO}_3\cdot\text{py}$ and $\{(^i\text{Pr}_2\text{N})\text{ReO}\}_2\cdot\text{TMEDA}$. In contrast, even adduct formation failed to stabilize Me_2NReO_3 . The sterically protected and structurally characterized $\text{mes}_2\text{-NReO}_3$ (**17**) is obtained quantitatively upon reaction of mes_2ReO_2 with NO, eq 11b.⁴³ The structure is consistent with some double-bond character of the N–Re bond.



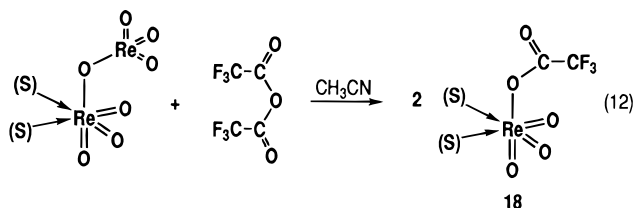
A potentially alternative approach to the synthesis of complexes of this type would be the reaction of $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ with ClReO_3 . However, the oxide functions were disrupted and a totally different result was obtained in the form of the air-stable Re(VII) 5-coordinate species bis-imido complex $\{\text{Re}[\text{N}(\text{SiMe}_3)_2](\text{NSiMe}_3)_2(\text{OSiMe}_3)_2\}$.³⁷

The phosphinimato derivatives are obtained from the reaction of Re_2O_7 with $(\text{Me}_3\text{SiN}=\text{PPh}_2)_2\text{CH}_2$, $(\text{Me}_3\text{SiN}=\text{PPh}_2)_2\text{C}_2\text{H}_4$, and $\text{Me}_3\text{SiN}=\text{PPh}_3$. $(\text{Me}_3\text{Si})_2\text{O}$ is eliminated to give the products with the formulae $(\text{O}_3\text{-ReN}=\text{PPh}_2)_2\text{CH}_2$, $\text{O}_3\text{ReN}=\text{PPh}_3$, and $(\text{O}_3\text{ReN}=\text{PPh}_2)_2\text{C}_2\text{H}_4$. The crystal structure of the latter shows that the phosphinimato ligand is inserted between two quite normal ReO_3 fragments as in **1'**. The

compounds are very stable decomposing only above $\sim 190^\circ\text{C}$.^{43b}

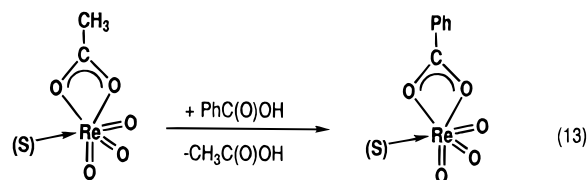
5. The Carboxylato Complexes $(\text{RCOO})\text{ReO}_3$ and Their Adducts

The first examples of this type of complexes were obtained from the reaction of carboxylic anhydrides, $(\text{RCO})_2\text{O}$, ($\text{R} = \text{Me}, \text{CF}_3, \text{CMe}_3$) with Re_2O_7 (itself the anhydride of perrhenic acid, HOREO_3), as exemplified for the $\text{R} = \text{CF}_3$ **18** in eq 12.³⁷



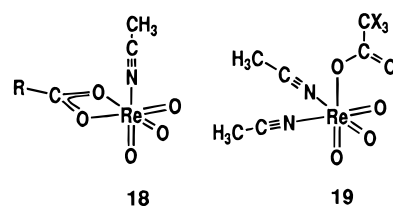
They are very strong Lewis acids and all of them have been isolated and characterized as adducts or solvates. THF remains coordinated even after recrystallization from diethyl ether. However, stronger donors like py or TMEDA displace it to give the adducts $(\text{RCOO})\text{ReO}_3\text{L}$ and $(\text{RCOO})\text{ReO}_3\text{L}_2$.

The THF adducts readily undergo carboxylate exchange providing a convenient way of preparing other derivatives, *e.g.*, the benzoate, eq 13.³⁷

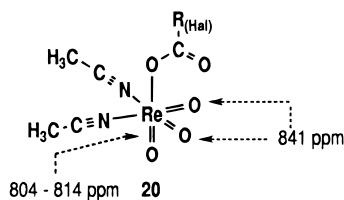


On the basis of the initially available spectroscopic data (IR and ^1H and ^{13}C NMR) the compounds were formulated as 6-coordinated, with a bidentate carboxylate, as in $(\text{RCOO})\text{ReO}_3\text{L}$ or with a monodentate carboxylate as in $(\text{RCOO})\text{ReO}_3(\text{TMEDA})$.

Due to their importance as starting materials for the preparation of RReO_3 complexes, namely MeReO_3 (see section II.B.1), a number of carboxylate derivatives was more recently prepared either in THF or, more conveniently, in MeCN.⁴⁴ Analytical data were obtained on all the crystalline complexes, which can be indefinitely kept below -20°C . This has shown that the formulation as $(\eta^2\text{-RCO}_2)\text{ReO}_3\text{L}$ or as $(\eta^1\text{-RCO}_2)\text{ReO}_3\text{L}_2$ depends on the nature of the R group, whereas hydrocarbon substituents lead to mono-adducts of formula $(\eta^2\text{-RCO}_2)\text{ReO}_3\cdot\text{MeCN}$ ($\text{R} = \text{Me}$ **19**, ^nPr , CH_2Cl), perhalocarboxylates lead to bis-adducts, $(\eta^1\text{-R}_{\text{hal}}\text{CO}_2)\text{ReO}_3\text{L}_2$ ($\text{L} = \text{MeCN}, \text{THF}$; $\text{R}_{\text{hal}} = \text{CCl}_3, \text{CF}_3, \text{C}_3\text{F}_7$). The crystal structure of the acetato and trifluoroacetato derivatives confirmed these results.

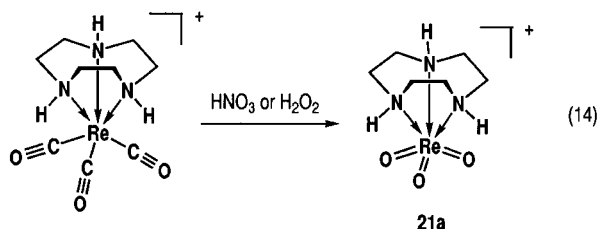


IR and ^{17}O NMR show that these structures are kept in solution. Indeed, the $\nu(\text{C}=\text{O})$ vibration typical of the monodentate carboxylato ligands ($\sim 1770\text{--}1790\text{ cm}^{-1}$) is observed in the IR of all the perhalo complexes but not in the spectra of the aliphatic and chloroacetato carboxylates where the carboxylate vibrations are observed at $\sim 1490\text{ cm}^{-1}$ (asym) and 1440 cm^{-1} (sym). ^{17}O NMR of the bidentate carboxylato complexes ($\text{R} = \text{Me}, ^n\text{Pr}, \text{CH}_2\text{Cl}$) have two signals: one corresponding to the equivalent OCO atoms (ca. $\delta(^{17}\text{O}) = 260$ ppm) and another to the equivalent oxo ligands ($\delta(^{17}\text{O}) = 790$ ppm). These data reveal a fluxional process in solution which averages the carboxylate resonances and the oxo resonances. The low line width of the ^{17}O resonances suggests that this may be due to exchange of coordinated MeCN with solvent MeCN and not to η^1/η^2 carboxylato shifts. The strongly electron-withdrawing perhalocarboxylato derivatives show four signals in the ^{17}O NMR spectrum in agreement with a rigid structure with a monodentate $\text{R}_{\text{hal}}\text{CO}_2$ ligand. The $\text{Re}=\text{O}$ bond *trans* to the $\text{R}_{\text{hal}}\text{CO}_2$ ligand appears at lower field ($\delta \sim 804\text{--}814$ ppm) relative to the other signal for the $\text{Re}=\text{O}$ bonds *trans* to the MeCN ligands which also have an invariable chemical shift in all the examples mentioned ($\delta(^{17}\text{O}) = 841$ ppm) as in **20**.⁴⁴



6. The $[\text{L}_3\text{ReO}_3]^+$ and $[\text{L}_3\text{ReO}_3]$ Complexes

The first example of this type of complex, $[(\text{tacn})\text{ReO}_3]\text{Cl}$ (**21a**) was isolated by oxidation of *fac*- $[(\text{tacn})\text{Re}(\text{CO})_3]^+$ with HNO_3 or from *fac*- $[(\text{tacn})\text{Re}(\text{NO})(\text{CO})_2]^{2+}$ with H_2O_2 , according to eq 14.^{45a}



This exhaustive oxidative decarbonylation of a *fac*- $[\text{L}_3\text{Re}(\text{CO})_3]^+$ closely parallels the similar reaction of $\text{Cp}^*\text{Re}(\text{CO})_3$ which can be completely decarbonylated to give Cp^*ReO_3 (see section II.B.6). However, this type of synthesis of $[\text{L}_3\text{ReO}_3]^+$ complexes from the corresponding $[\text{L}_3\text{Re}(\text{CO})_3]^+$ derivatives is very limited and has failed in many attempts. Indeed, the substituted analogue $[(\text{Me}_3\text{tacn})\text{Re}(\text{CO})_3]^+$ and the equivalent sulfur species, $[(\text{ttcn})\text{Re}(\text{CO})_3]^+$ cannot be oxidized with either Br_2 , Cl_2 , concentrated HNO_3 , or 30% H_2O_2 at 90°C .^{45b} A parallel is found in the oxidative chemistry of the Re(V) oxo complexes $[(\text{tacn})\text{ReCl}_2\text{O}]^+$ and its permethylated analogue, $[(\text{Me}_3\text{tacn})\text{ReCl}_2\text{O}]^+$, whereas the former is readily oxidized at room temperature by a variety of oxidants

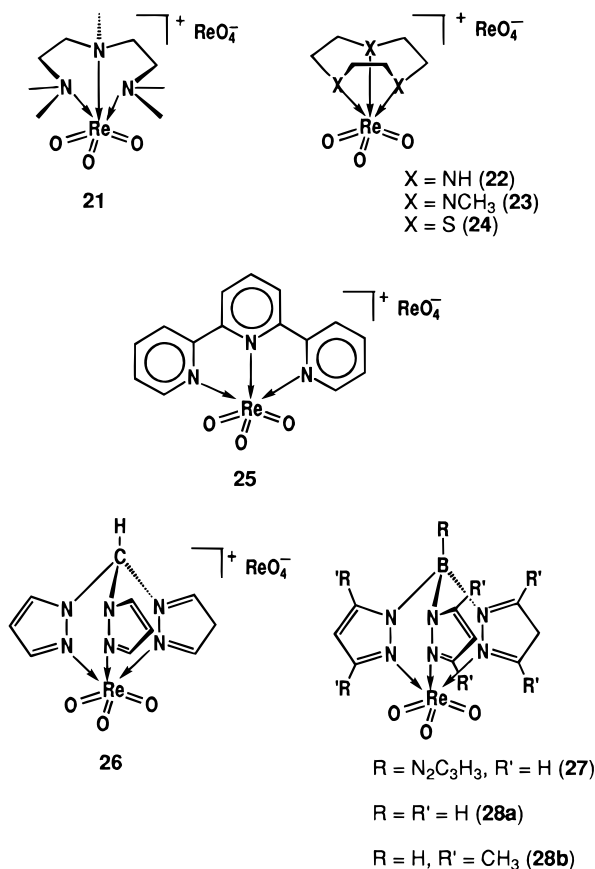
(I_2 , H_2O_2 , Me_2SO , etc.) to give $[(\text{tacn})\text{ReO}_3]^+$, the latter only suffers a similar oxidation in concentrated HNO_3 after 40 days at 80°C .^{46a} The latter type of oxidation is also capable of generating $[\{\text{HB}(\text{pz})_3\}\text{ReO}_3]$ (**28a**) from the Re(V) precursor $[\{\text{HB}(\text{pz})_3\}\text{ReCl}_2\text{O}]$.^{46b} Oxygen transfer to the analogue alkoxides, $[\{\text{HB}(\text{pz})_3\}\text{ReO}(\text{OR})_2]$ and in particular to the triflate, $[\{\text{HB}(\text{pz})_3\}\text{ReO}(\text{OR})(\text{OTf})]$, is easily accomplished with pyNO or DMSO, but not O_2 , to produce **28a** in $\sim 60\%$ yields together with aldehyde or ketones and alcohols.^{46c} The mechanism involves C–H bond cleavage in a cationic Re(VII) dioxo intermediate $[\{\text{HB}(\text{pz})_3\}\text{ReO}_2(\text{OR})]^+$ (not isolated) and is further discussed in section III together with the related chemistry of the likewise labile organometallic congeners $[\{\text{HB}(\text{pz})_3\}\text{ReO}_2(\text{R})]^+$ ($\text{R} = \text{Ph}, \text{Et}$).^{46e,f} Derivatives of type $[(\text{R}_3\text{tacn})\text{ReO}_3]^+$ ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}$) are also accessible via deprotonation of $[(\text{tacn})\text{ReO}_3]^+$ with Na_2CO_3 , in anhydrous DMF, followed by treatment with MeI or BzBr, respectively.^{45b}

The sulfur analogue $[(\text{ttcn})\text{ReO}_3]\text{BF}_4$ was isolated adding the macrocyclic ligand to a solution resulting from the treatment of ReO_4^- with HBF_4 , in MeCN solvent.^{47a} This method has also been used to prepare the analogue $[(\text{CpCo}\{\text{P}(\text{OCH}_2\text{CH}_2)_2(\text{=O})\}_3)\text{ReO}_3]$ ^{47b} and $[\{\text{HB}(\text{pz})_3\}\text{ReO}_3]$,^{46b} albeit in low yield.

Olefin extrusion from the glycolato complexes $[\{\text{HB}(\text{pz})_3\}\text{ReO}(\text{OCH}_2\text{CH}_2\text{O})]$ ^{46b,d} or $[(\text{tacn})\text{ReO}(\text{OCH}_2\text{CH}_2\text{O})]\text{Cl}$ ^{45c} also generates the corresponding $[\text{L}_3\text{ReO}_3]^+$ complexes in a reaction also paralleled by $[\text{Cp}^*\text{ReO}(\text{glycolato})]$ (see section II.B.9a). The photochemical activation of the oxalato complex $[\{\text{HB}(\text{pz})_3\}\text{ReO}(\text{C}_2\text{O}_4)]$ in the presence of DMSO produces $[\{\text{HB}(\text{pz})_3\}\text{ReO}_3]$ and Me_2S , quantitatively. A similar result is obtained upon photolysis in the presence of O_2 . In both cases the major pathway leads to the highly reactive monooxide $[\{\text{HB}(\text{pz})_3\}\text{ReO}]$ which is not isolated but is trapped by oxidizing substances (O_2 , DMSO, phenanthroquinone methane trichloride) to give either **28a** or other Re(V) products like $[\{\text{HB}(\text{pz})_3\}\text{ReOCl}_2]$.^{46d} Labeling studies have shown that in $[\{\text{HB}(\text{pz})_3\}\text{ReO}_3]$ generated photochemically under O_2 atmosphere from $[\{\text{HB}(\text{pz})_3\}\text{ReO}(\text{C}_2\text{O}_4)]$, only one O atom comes from labeled O_2 while one of the others comes from the oxalate, the third one being the initial Re–O. This rules out the simple O–O bond breaking in a putative intermediate peroxo complex $[\{\text{HB}(\text{pz})_3\}\text{ReO}(\text{O}_2)]$ to give $[\{\text{HB}(\text{pz})_3\}\text{ReO}_3]$. This result implies a large kinetic barrier to the thermodynamically favorable mononuclear cleavage of O_2 at the Re center of the simple peroxo complex. This fact is taken as another example of a general symmetry-derived restriction which has so far prevented the observation of a four-electron reduction of O_2 at a single metal site.^{46d}

However, the most general method to prepare $[\text{L}_3\text{ReO}_3]^+$ compounds has already been alluded to in eq 3. Upon the action of a suitable tridentate ligand, $\text{L}_3\text{Re}_2\text{O}_7$ is heterolytically cleaved into ReO_4^- and $[\text{L}_3\text{ReO}_3]^+$.

The examples studied include tridentate ligands such as macrocyclic N and S donors (tacn, Me_3tacn , ttcn), the acyclic triamine PMDT, and the tris-pyrazolyl ligands of complexes **26** and **28a–b**.^{14b,48,50} The much more conveniently soluble tetrapyrazolyl-



borate derivative **27** has been crystallographically characterized as a monomeric species and shown by NMR not to be able to interchange its pyrazolyl ligands.⁴⁹ The pyrazolate anion produces pzReO_3 of yet unknown structure.^{48a}

Considering the crystal structures of Me_3tacn , tacn , and ttcn , very little difference is observed between the first two but the third one shows clearly shorter (7 pm) $\text{Re}=\text{O}$ bonds. This metal-oxo bond strengthening compensates for the weak $\text{Re}-\text{S}$ bonding interactions which, with a $\text{Re}-\text{S}$ distance of 258 pm is even longer than in the low valent *fac*- $[\text{Re}(\text{ttcn})(\text{CO})_3]^+$ (246 pm).^{47a} The values of the ^{17}O NMR chemical shift also confirm this effect and $[(\text{ttcn})\text{ReO}_3]^+$ presents the oxo resonances (δ 775 ppm) clearly deshielded relative to the tacn and Me_3tacn congeners (δ 728 and 752 ppm, respectively). The stronger donor capability of the *N*-macrocycles relative to the sulfur analogue (ttcn) offers a simple rationale for these observations. These are also mirrored in the stability of the complexes. Whereas the Me_3tacn and tacn derivatives resist hydrolysis and can be recrystallized from water, all the other compounds of this type are more or less readily hydrolyzed in air or water. If this is not surprising for the stereochemically less favorable cases of the diethylenetriamine and terpyridine complexes, it is somewhat surprising in the case of the $\text{HC}(\text{pz})_3$ congener. The frequencies found for the infrared stretches of the $\text{Re}=\text{O}$ bonds increase in the order $\text{Cp}^* < \text{Me}_3\text{tacn} < \text{tacn} < \text{ttcn}$, which is to be expected since the π -acceptor capacity of these L_3 ligands also increases in the same order.^{47a}

7. Miscellaneous Inorganic LReO_3 Derivatives

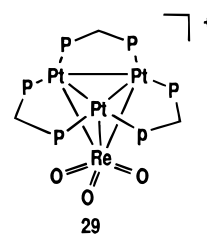
The oxidation of ReCl_5 by Cl_2O in the presence of added POCl_3 gives a compound of formula $\text{ReO}_3(\text{O}_2\text{-PCl}_2)\cdot\text{OPCl}_3$.⁵¹

Another important item in this category is the bond between a metal (part of an inorganic or organometallic fragment) and the perrhenyl cation, *e.g.*, $\text{L}_n\text{M}-\text{ReO}_3$.

Very few complexes are represented in this class, although one might foresee a large area of inorganic chemistry growing around this theme.

In 1991, Walton and co-workers isolated $(\text{Me}_2\text{PCH}_2\text{-PMe}_2)\text{Cl}_2\text{ReReO}_3$ as a minor component of the reaction of *cis*- $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ with dppm .⁵² This complex bears two Re atoms in quite different environments: a tetrahedral 4-coordinate and a pentagonal-bipyramidal, 7-coordinate. The Re are joined by an unsupported very short $\text{Re}-\text{Re}$ bond (2.4705 Å). This was the first example of the ReO_3 fragment participating in a metal-metal bond although the origin of the ReO_3 group remains unclear.

As the result of extensive oxidation of $[\text{Pt}_3\{\text{Re}(\text{CO})_3\}(\mu\text{-dppm})]^+$ with O_2 in refluxing *o*-xylene, Puddephatt *et al.* describe the synthesis of $[\text{Pt}_3(\text{ReO}_3)(\mu\text{-dppm})_3][\text{ReO}_4]$ (**29**, yield 30% after 7 h) and $[\text{Pt}_3(\text{ReO}_3)(\mu\text{-dppm})_3][\text{PF}_6]$ (yield 30% after 15 h).^{53a} The complex could almost be considered another member of the $[\text{L}_3\text{ReO}_3]^+$ family since the three Pt atoms act as donors much in the same way as the S or N heterocycles (in the picture, Ph groups have been omitted for clarity). Several ligands ($\text{L} = \text{P}(\text{OMe})_3$, CO , Cl^- , Br^- , I^-) add to the Pt atom *trans* to the Re atom.^{53b}



Oxygen atom addition to $[\text{Pt}_3\{\text{Re}(\text{CO})_3\}(\mu\text{-dppm})]^+$ by means of H_2O_2 takes place across the $\text{Pt}-\text{Re}$ bonds to give first $[\text{Pt}_3\{\text{Re}(\text{CO})_3\}(\mu_3\text{-O})_3(\mu\text{-dppm})]^+$ which is then oxidized at the Re atoms to give $[\text{Pt}_3\{\text{ReO}_3\}(\mu_3\text{-O})_3(\mu\text{-dppm})]^+$ (**29b**) which is an analogue of the $[(\text{ttcn})\text{ReO}_3]^+$ and $[(\text{tacn})\text{ReO}_3]^+$ complexes mentioned above.^{53c}

The rational synthesis of this type of complexes is still nonexistent, let alone their chemical and reactivity characterization. However, the prospect of finding a variety of stable compounds in this area is encouraged by *ab initio* SCF calculations on the putative $(\text{CO})_5\text{Re}-\text{ReO}_3$ which is predicted to be stable with a $\text{Re}-\text{Re}$ bond length intermediate between the long $\text{Re}-\text{Re}$ bond in $\text{Re}_2(\text{CO})_{10}$ (3.04 Å) and the very short one in $(\text{Me}_2\text{PCH}_2\text{PMe}_2)\text{Cl}_2\text{ReReO}_3$. The electron flow from the low-valent to the high-valent Re atom is predicted to be high in both of these complexes.⁵⁴

8. Structural and Spectroscopic Characterization

a. Structural Characterization. This section summarizes the structural information available for

Table 1. Inorganic ReO₃ Derivatives with Known X-ray Crystal Structures

compound	coordination no. of Re	ref(s)
Re ₂ O ₇ (s)	6/4	10a–c
Re ₂ O ₇ (g)	4/4	11
Re ₂ O ₇ ·(H ₂ O) ₂	6/4	13a–b
Re ₂ O ₇ ·(pyridine) ₃	6/5	15
Re ₂ O ₇ ·(CH ₃ CN) ₂	6/4	14a,44
Re ₂ O ₇ ·(THF) ₂	6/4	11
Re ₂ O ₇ ·(DME)	6/4	14b
[ReO ₃ (tacn)]Cl	6	45a
[ReO ₃ (tacn)][ReO ₄]	6	50
[ReO ₃ (ttcn)][ReO ₄]	6	47a
[ReO ₃ ((CH ₃) ₃ tacn)][ReO ₄]	6	14b
ReO ₃ (B(pz) ₄)	6	49
ReO ₃ (HB(pz) ₃)	6	48
ClReO ₃ ·(bipy)	6	56
[Cl ₃ ReO ₃]Cs ₂	6	24a
[Cl ₂ ReO ₃ ·(H ₂ O)][H ₂ phen]	6	24b
CF ₃ COOReO ₃ ·(CH ₃ CN) ₂	6	44
CH ₃ COOReO ₃ ·(CH ₃ CN)	6	44
[Pt ₃ (dppm) ₃ ReO ₃][ReO ₄]	6	53
[(Ph ₂ N) ₂ CReO ₃][ReO ₄]	4	16
(mes) ₂ NReO ₃	4	43
(CH ₃ OReO ₃ ·(CH ₃ CN)) ₂	6	33
HO(CH ₂) ₂ OReO ₃	5	33
(CH ₃)O(CH ₂) ₂ OReO ₃	5	33
(O(C(CH ₃) ₂) ₂ O)ReO ₂ (OSi(CH ₃) ₃)	5	33
[(CH ₃) ₃ SnOReO ₃] _n	6	34
(CH ₃) ₃ SiOReO ₃	4	32c
O ₃ ReOS(Ph) ₂ OSn(Ph) ₂ OH) ₂	4	35a
^t Bu ₂ Si(OReO ₃) ₂	4	35b
[^t BuSiO(ReO ₄)] ₄	4	35c

the inorganic derivatives of ReO₃ described above. The X-ray crystal structures determined so far are given in Table 1, with the appropriate literature reference.

A strictly crystallographic analysis of Re=O and Re–X bond lengths and angles is out of the scope of the present article. Leading references to discussions of these topics for oxide compounds are given in ref 55.

There are no crystallographic data on any of the XReO₃ complexes (X = F, Cl, Br, CN, SCN). However, microwave spectroscopy studies on FReO₃ and ClReO₃ allowed the determination of bond distances and angles. The Re–O distances are very similar (169.2 and 170.2 pm for the fluoride and chloride derivatives respectively) and the almost perfectly tetrahedral X–Re–O angles are 109° 31′ in both cases.^{18b} The Re–O bond length values are not very different from the ones measured in the X-ray crystal structure of the adducts ClReO₃·(bipy) (Re–O = 170.8 pm *trans* to N; 171.8 *trans* to Cl)⁵⁶ and [ReO₃·Cl₃]Cs (Re–O 170.2 pm).²⁴ These data like the one in the structure of [ReO₃Cl₂(H₂O)]Cl^{24b} confirm the earlier IR assignments of a *fac*-ReO₃ moiety. So far, only the compound [F₃ReO₃][NMe₄]₂ has been assigned a *mer* structure instead of the normal *fac*-ReO₃ geometry.¹⁹

As usual for these complexes (see section II.B.8.a for comparison), little variation is observed on the Re–O bond distances. However, they are distinctly shorter (~7pm) in the complex [(ttcn)ReO₃]⁺ which, by this reason is considered the least perturbed [ReO₃]⁺ fragment known.

The structurally characterized derivatives of type XReO₃·L_n are summarized in Table 1. A brief

Table 2. IR Data of Selected XReO₄ Compounds and Derivatives (Only ν_{as}(ReO₃) and ν_{as}[ReO₄])

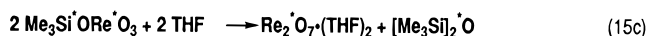
compound	ν _{as} (ReO ₄) [cm ⁻¹]	matrix	ref
Ag ⁺ [ReO ₄] ⁻	904	Nujol	56b
[NH ₄] ⁺ [ReO ₄] ⁻	907	KBr	56b
[py] ⁺ [ReO ₄] ⁻	908	KBr	56b
[bipy] ⁺ [ReO ₄] ⁻	909	KBr	56b
Zn(ReO ₄) ₂ ·(THF) ₂	909	KBr	56b
[(tacn)ReO ₃] ⁺ [ReO ₄] ⁻	912 (ReO ₄) ⁻	KBr	14b,45
	935 [(tacn)ReO ₃] ⁺		
[(CH ₃) ₃ SnOReO ₃]	911	KBr	34
Ru(η ³ -C ₅ H ₅)(PPh ₃)OReO ₃	916	Nujol	56c
Rh(PPh ₃) ₂ (CO) ₂ OReO ₃	921	Nujol	56c
(CO) ₅ ReOReO ₃	929	Nujol	56c
CF ₃ C(O)OReO ₃ ·(CH ₃ CN) ₂	937	CH ₃ CN	37,44
CH ₃ C(O)OReO ₃ ·CH ₃ CN	940	CH ₃ CN	37,44
^t (C ₄ H ₉)OReO ₃	961	CCl ₄	33,37
(CH ₃)OReO ₃	964	CCl ₄	33,37
(CH ₃) ₃ SiOReO ₃	967	CCl ₄	32a,b

comparison of some of these structures with those of organometallic derivatives is given in section II.B.8.a.

b. Spectroscopic Characterization. The structural data on the Re–O bond lengths and angles is only marginally sensitive to the electronic variations originated by coordination of a variety of neutral and anionic ligands to the ReO₃⁺ fragment. However, the understanding of such influences is important to establish accurate structure–reactivity correlations which may be useful in the design or identification of catalytically active complexes.

IR and ¹⁷O NMR are, in this respect, particularly indicative. A number of IR, Raman,^{18a} and microwave spectroscopical^{18b} studies were carried out with the halides XReO₃, (X = F, Br, Cl) namely in the gas phase.^{20b,e} In Table 2 are assembled the values of the ν(Re=O) in the IR spectra of a number of selected XReO₃ and L₃ReO₃ complexes. According to the reactivity of the compounds which has been described above and their X-ray crystal structures, the borderline between ionic perhenates and more covalent compounds of type XReO₃·L_n can be drawn between 910 and 920 cm⁻¹ for ν(Re=O). Higher wavenumbers usually indicate partially covalent or covalent Re–O interactions. A detailed discussion and assignment of the IR spectra of compounds of type XReO₃·bipy,²⁹ CX₃COOReO₃·L_n,⁴⁴ [L₃ReO₃][ReO₄],^{14b} and ROReO₃·L_n³³ may be found in each of the corresponding references.

The ¹⁷O NMR spectroscopy is also a very helpful tool in this context. A special problem which prevented extensive studies for a long time was the low natural content of ¹⁷O in nonenriched samples and the lack of an efficient method to enrich compounds of type ROReO₃, XReO₃, or their derivatives. This problem was solved only recently, but enough data for a brief discussion are already available. The reaction equations are summarized in eqs 15a–c.

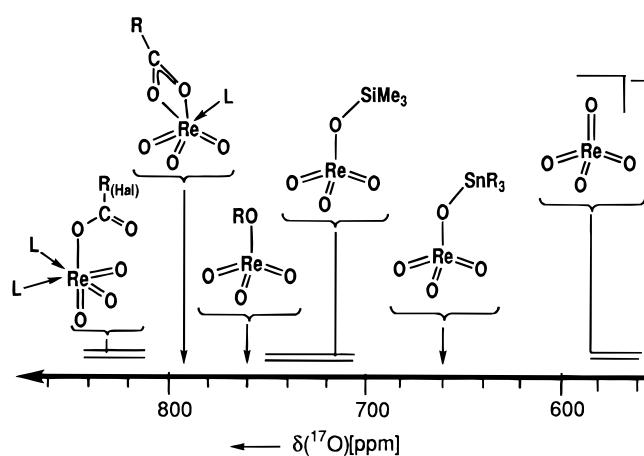


Selected ¹⁷O NMR data are given in Table 3 and in a pictorial form in Scheme 7.

Table 3. ^{17}O NMR Data of Selected Inorganic XReO_3 Compounds and Derivatives and Perrhenates

compound	$d(^{17}\text{O})$ (ppm)	solvent	$T, ^\circ\text{C}$	ref(s)
$\text{H}^+[\text{ReO}_4]^-$	559	H_2O	20	33,56b
$\text{K}^+[\text{ReO}_4]^-$	562	H_2O	20	33,56b
$[\text{NH}_4]^+[\text{ReO}_4]^-$	563	H_2O	20	33,56b
$(\text{CH}_3)_3\text{SnOReO}_3$	574	THF	20	33,56b
	660 (ReO ₃)	THF	-50	33,56b
	350 (Sn-O-Re)			
$\text{Re}_2\text{O}_7(\text{THF})_2$	740 (ReO ₃)	THF	-30	14b
	395 (Re-O-Re)			
$\text{Re}_2\text{O}_7(\text{DME})$	740 (ReO ₃)	dme	-30	14b
	365 (Re-O-Re)			
$\text{Re}_2\text{O}_7(\text{CH}_3\text{CN})_2$	747 (ReO ₃)	CH_3CN	20	14b
	320 (Re-O-Re)			
$\text{Re}_2\text{O}_7(\text{py})_3$	766 (ReO ₃)	pyridine	20	14b
	312 (Re-O-Re)			
$[\text{tacn}]\text{ReO}_3^+\text{ReO}_4^-$	728 (ReO ₃) ⁺	D_2O	20	14b,57
	563 (ReO ₄) ⁻			
$[\text{Me}_3\text{tacn}]\text{ReO}_3^+\text{ReO}_4^-$	752 (ReO ₃) ⁺	D_2O	20	14b,57
	562 (ReO ₄) ⁻			
$[\text{ttcn}]\text{ReO}_3^+\text{ReO}_4^-$	775 (ReO ₃) ⁺	D_2O	20	14b,57
	564 (ReO ₄) ⁻			
$[\text{terpy}]\text{ReO}_3^+\text{ReO}_4^-$	783 (ReO ₃) ⁺	<i>d</i> ^b -DMSO	20	14b,57
	570 (ReO ₄) ⁻			
$[\text{tacn-H}]\text{ReO}_3$	703	D_2O	20	44
$(\text{CH}_3)_3\text{SiOReO}_3$	712 (ReO ₃)	CH_2Cl_2	20	33
	215 (Si-O-Re)			
	724 (ReO ₃)	toluene	20	
	194 (Si-O-Re)			
	731 (ReO ₃)	THF	20	
	197 (Si-O-Re)			
	742 (ReO ₃)	pyridine	20	
	132 (Si-O-Re)			
$\text{CH}_3\text{C}(\text{O})\text{OReO}_3\cdot\text{L}$	790 (ReO ₃)	CH_3CN	20	44
	262 (CO)			
$\text{C}_3\text{H}_7\text{C}(\text{O})\text{OReO}_3\cdot\text{L}$	788 (ReO ₃)	CH_3CN	20	44
	252 (CO)			
$\text{CH}_2\text{ClC}(\text{O})\text{OReO}_3\cdot\text{L}$	793 (ReO ₃)	CH_3CN	20	44
	245 (C(O)-O-Re)			
$\text{CCl}_3\text{C}(\text{O})\text{OReO}_3\cdot\text{L}_2$	841 (ReO ₂)	CH_3CN	20	44
	804 (ReO)			
	252 (C(O)-O-Re)			
$\text{C}_3\text{F}_7\text{C}(\text{O})\text{OReO}_3\cdot\text{L}_2$	841 (ReO ₂)	CH_3CN	20	44
	811 (ReO)			
	270 (C(O)-O-Re)			
$\text{CF}_3(\text{O})\text{OReO}_3\cdot\text{L}_2$	841 (ReO ₂)	CH_3CN	20	44
	813 (ReO)			
	262 (C(O)-O-Re)			

^a See refs 6b and 9. ^b Data taken from ref 2b. ^c Octahedrally coordinated complexes.

Scheme 7

Again, a clear distinction between perrhenate-type ionic compounds and more covalent compounds can be made. Perrhenates are much more electron rich and therefore high field shifted. This seemingly obvious fact was often ignored in older examina-

tions.⁵⁷ As in the case of the IR and Raman data, only a comparatively high amount of data allowed correct assignments. The bridging Re-O-R oxygens give ^{17}O NMR signals usually located around 250 ppm.^{33,44} The ^{17}O NMR shift of $[\text{L}_3\text{ReO}_3]^+$ derivatives is dominated by the donor properties of the tridentate ligand. Its donor capability can overcompensate the positive charge of the cations in comparison to some neutral, 6-coordinated Re(VII) oxides which lack a strong donor ligand (see Table 3 and refs 14b and 57). Since the tetrahedral species XReO_3 are strongly acidic, the ^{17}O shifts are solvent dependent. In some cases solvent adducts can be isolated. The ^{17}O shifts in these adducts are, as expected, less high field shifted than in the highly electron-deficient tetrahedral XReO_3 compounds. A similar effect is observed for the organic derivatives RReO_3 .

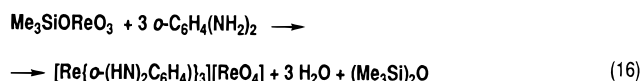
9. Reactions of Re_2O_7 and XReO_3 Compounds

Being a key starting material for the syntheses of XReO_3 and RReO_3 and also of the imido and mixed oxo-imido compounds, all but a few chemical trans-

formations of Re_2O_7 are described throughout the text in the corresponding sections. The remaining miscellaneous reactions reported below actually represent particular cases of the two most important reaction types of Re(VII) oxide compounds, namely oxygen transfer and condensation.

The deoxygenation of Re_2O_7 with PEt_3 in the presence of py gives $[\text{Re}(\text{O})_2\text{py}_4]\text{ReO}_4$ with the two oxo ligands in *trans* coordination sites.^{15a,b} By using only excess PMe_3 , the analogous compound $[\text{Re}(\text{O})_2(\text{PMe}_3)_4]\text{ReO}_4$ was obtained. Both X-ray crystal structures were determined. In the latter compound, metathesis of the perrhenate by BPh_4^- , allowed the assignment of the *trans* ReO_2 band in the IR spectrum at 778 cm^{-1} .⁵⁸ The formation of ReO_4^- originates from the already mentioned disproportionation of Re_2O_7 into $[\text{ReO}_3]^+$ and $[\text{ReO}_4]^-$.

The reaction of $\text{Me}_3\text{SiOReO}_3$ (or Re_2O_7) with *o*-phenylenediamine produces the weakly paramagnetic $[\text{Re}\{\text{o}-(\text{HN})_2\text{C}_6\text{H}_4\}]_3[\text{ReO}_4]$ in almost quantitative yield according to eq 16.⁵⁹



B. Organic RReO_3 Compounds and Derivatives

This section deals with the synthesis, characterization, and chemistry of the organic derivatives of ReO_3^+ , *i.e.*, the organometallic compounds. These compounds are presented in subsections according to the nature of the hydrocarbyl chain.

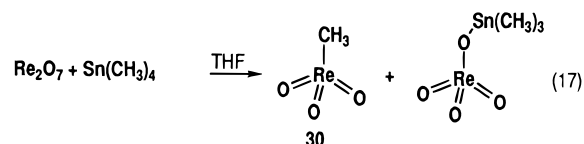
Indeed, the $\text{Re}(\text{VII})\text{O}_3$ fragment can be considered as a fairly general substituent of hydrocarbons with $\text{C}(\text{sp}_3)\text{-Re}$, $\text{C}(\text{sp}_2)\text{-Re}$ and $\text{C}(\text{sp})\text{-Re}$ bonds which present a variety of structural and chemical characteristics. The large majority of these complexes is not functionalized. So far, the only examples of functionalized hydrocarbons coordinated to the ReO_3 fragment are the pseudoallylic complex [(ethoxycarbonyl)methyl] ReO_3 , together with $\text{Me}_3\text{SiCH}_2\text{ReO}_3$, $2,6\text{-Me}_2\text{-4-X-C}_6\text{H}_2\text{ReO}_3$ ($\text{X} = \text{Me}_3\text{SiO}$, OH) and the intramolecular donor adducts of type $(\text{L}(\text{CH}_2)_3)\text{ReO}_3$ ($\text{L} = \text{NR}_2$, OR), $2,6\text{-(L)}_2\text{C}_6\text{H}_2\text{R-ReO}_3$, and $2\text{-LC}_6\text{H}_4\text{-ReO}_3$.

One of the fundamental aspects of the progress reported below concerns the development of appropriate pathways for the syntheses of the target RReO_3 compounds. These aspects are mainly discussed along with the presentation of the alkyl complexes since it was during their study that they were discovered. Particular aspects pertaining to the synthesis of Cp^*ReO_3 are given in the section devoted to the cyclopentadienyl derivatives.

1. The Alkyl RReO_3 Derivatives

The simplest member of this family, CH_3ReO_3 (**30**, often abbreviated as MTO from *methylrhenium trioxide*), was also the first to be discovered. It was serendipitously prepared in a milligram scale by slow, inadvertent, air oxidation of Me_4ReO , by Beattie and Jones in 1979.⁶⁰ The importance and uniqueness of the compound was immediately recognized but no further studies were undertaken until 1988 when Herrmann, Kuchler, *et al.* described its preparation

according to eq 17 which was suggested by a known recipe for the preparation of catalysts active in the metathesis of functionalized olefins.⁶¹



The reaction is very reliable and gives an almost quantitative yield of MeReO_3 which, however, is only 50% relative to the initial rhenium.^{62a} MTO is an unusually thermally stable compound decomposing above $300\text{ }^\circ\text{C}$.^{62b} It is highly volatile and soluble in virtually any solvent from pentane to water. The crystal structure of MTO was not possible to solve by X-ray single-crystal methods due to consistent multiple twinning of the colorless crystals. However, its volatility allowed a gas-phase electron diffraction structural determination,^{63a} which was later followed by a low temperature (5 K) neutron powder diffraction structural study of CD_3ReO_3 .^{63b} Both data sets are consistent.

The molecule is pseudotetrahedral with a short Re-C bond ($206.3(2)\text{ pm}$) lying between the typical Re-C single bond (215 pm) and Re-C double bond (195 pm) distances.^{63a,64} The ^1H NMR spectrum is solvent dependent due to the strong interactions between the solvent and the Lewis acidic metal center. These interactions are apparent both in the chemical shift variations in the ^1H NMR and ^{17}O resonances.⁵⁷ The solvent dependence of the rather low-field resonances in the ^{17}O NMR spectra of MTO correlate with Gutmann donor numbers: stronger donors shift the resonances to lower fields. As an example, the ^{17}O resonance of MTO appears at $\delta(^{17}\text{O}) = 870\text{ ppm}$ in *c*⁸-THF and at $\delta(^{17}\text{O}) = 823\text{ ppm}$ in benzene.

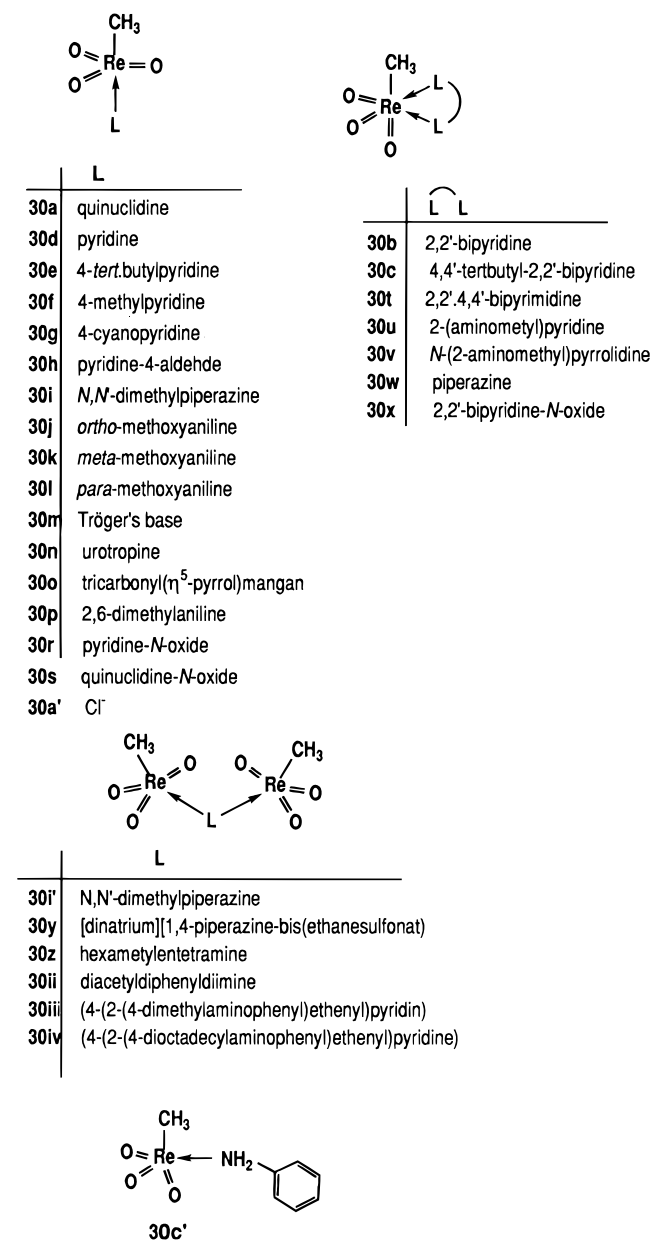
MTO easily forms adducts with Cl^- , Br^- , and a number of nitrogen ligands, *e.g.*, aniline, quinuclidine, bipyrimidine, and others⁶⁵ (see section II.B.9). Chart 2 lists a number of such adducts.⁶⁵

These yellow adducts are sensitive to hydrolysis in wet solvents and are much less thermally stable than MTO itself. Indeed, $\text{CH}_3\text{ReO}_3\cdot\text{py}$ decomposes at room temperature and $\text{CH}_3\text{ReO}_3\cdot(4,4'\text{-tBubipy})$ in boiling THF after minutes. This fact suggests a weakening of the Re-C bond in the adducts also reflected in the increase of the Re-C bond length from $206.3(2)\text{ pm}$ in CH_3ReO_3 to $209.5(5)\text{ pm}$ in *trans*- $\text{CH}_3\text{ReO}_3\cdot\text{aniline}$ ^{66a} and $208.5(6)\text{ pm}$ in $\text{CH}_3\text{ReO}_3\cdot(4\text{-tBupy})$.^{66b}

MTO is photosensitive and is split into CH_3 and ReO_3 radicals by UV/vis irradiation as described in section II.B.8.e.⁶⁷ It is rapidly hydrolyzed in basic solutions to ReO_4^- and CH_4 ,⁶⁸ but acid hydrolysis forms a highly interesting conducting material known as "poly-MTO" which is described in section II.B.10.b.⁶⁹ Most importantly still, MTO is an efficient catalyst precursor for a wealth of processes, described in section II.B.10.a.

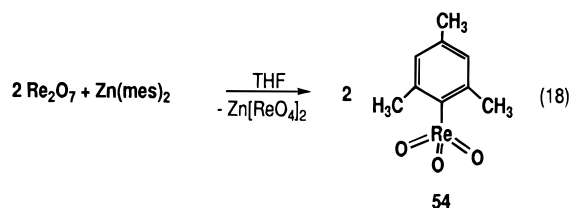
The evident versatility of the chemistry of MTO prompted the preparation of other hydrocarbyl derivatives of formula RReO_3 . It was expected that variation of the hydrocarbyl ligand R with regard to stereochemical bulk and electronic donor capability

Chart 2



would lead to derivatives with tailor-made reaction behavior. The development of appropriate synthetic routes was decisive to achieving this goal.

Carbanionic substitution on $XReO_3$ derivatives, *e.g.*, $ClReO_3$, Re_2O_7 , $Me_3SiOReO_3$, with lithium magnesium, and aluminum alkyls was ruled out because it consistently led to reduction. Zinc dialkyls offered an alternative although conflicting results had been reported. In fact, the merit of zinc diaryls as non-reductive arylation reagents for Re_2O_7 had been shown in the synthesis of $mesReO_3$ from Re_2O_7 and $Zn(mes)_2$ in eq 18.⁷⁰

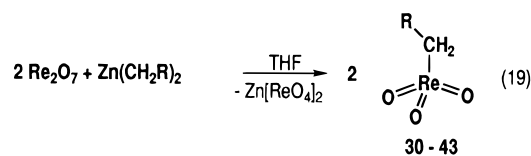


On the other hand, reaction of Re_2O_7 with $ZnMe_2$, resulted in the isolation of the known reduced Re(VI)

oxide dimers, $Me_4Re_2O_4$ and $Me_6Re_2O_3$ previously isolated in alkylations of Re_2O_7 with aluminum alkyls.³⁹⁻⁴²

However, an examination of this reaction, from $-78^\circ C$ to room temperature showed that MTO was initially formed but it was reduced by excess $ZnMe_2$ to $Me_4Re_2O_4$ (at $\sim -30^\circ C$) which was further alkylated to $Me_6Re_2O_3$ (at rt). Therefore, nonreductive alkylation of Re_2O_7 with $ZnMe_2$ is possible using low temperature techniques. Simultaneously, it was also established that the outcome of the synthesis of $mesReO_3$ strongly depends on the stoichiometry used: high yields of $mesReO_3$ are obtained according to eq 18 but a 1:1 molar ratio of $Zn(mes)_2$: Re_2O_7 leads mainly to the known Re(VI) compound $(mes)_2ReO_2$.^{71,72}

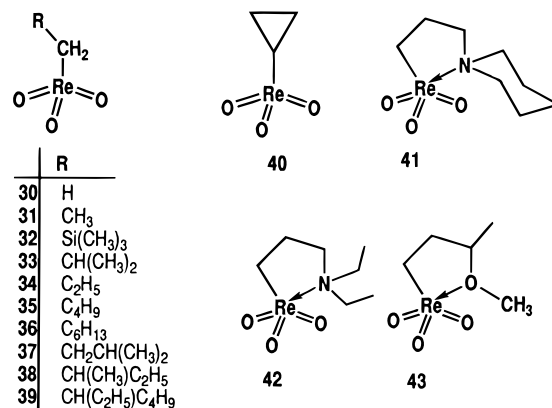
These observations originated the standardization of the so called "zinc route" which allowed the synthesis of a large number of alkyl ReO_3 derivatives according to eq 19. The compounds prepared are given in Chart 3.^{71,73}



This list is quite broad and one can consider ReO_3 as a general substituent of aliphatic hydrocarbon chains and rings including the ones bearing β -hydrogen atoms. $EtReO_3$ is a very volatile compound melting at $\sim 0^\circ C$. In contrast to MTO, it rapidly decomposes at room temperature in the pure liquid state but is almost indefinitely stable in solution at room temperature decomposing only very slowly in toluene at $80^\circ C$! This stability dependence on the concentration turns out to be a general property of $RReO_3$ compounds with the conspicuous exception of MTO. This fact coupled with the lowering of the melting point upon increasing chain length, makes it increasingly difficult to isolate $RReO_3$ complexes with longer or branched chains.⁷³

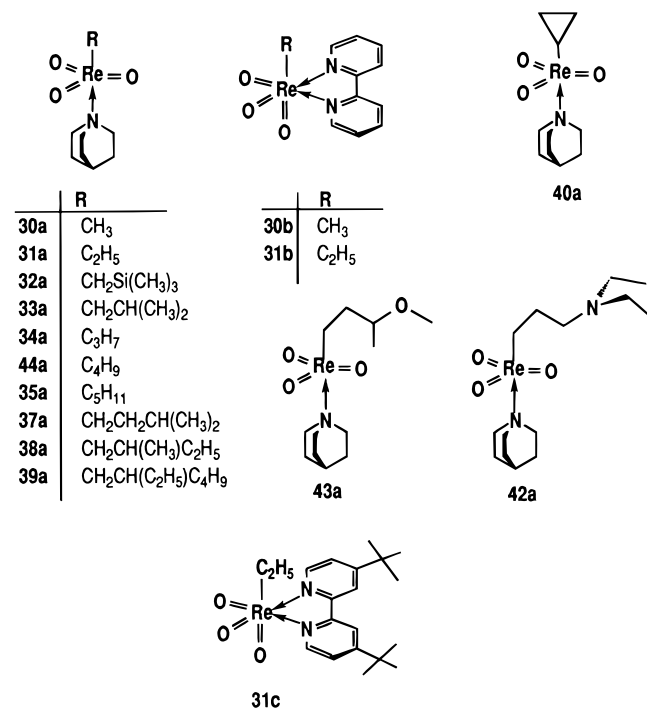
Adduct formation with quinuclidine provides the most useful means of recovering these complexes from the reaction mixtures since such adducts are easily extractable into and crystallizable from *n*-hexane or *n*-pentane. Therefore, many of these alkyl complexes have only been fully characterized as their

Chart 3



adducts $RReO_3 \cdot L$ or $RReO_3 \cdot L_2$ (usually quinuclidine or bipy). Chart 4 summarizes these adducts.

Chart 4



The so-called N and O intramolecularly coordinated $RReO_3$ derivatives, also in Chart 3, represent a closely related family of adducts.^{74a,b,75} However, due to their steric constraints, these intramolecular adducts have the donor coordinated *cis* to the Re–C bond instead of *trans*, as in the almost invariably observed TBP structure with the three equatorial Re=O bonds. The only existing exception to the latter geometry is reported for the *cis* modification of $CH_3ReO_3 \cdot$ aniline.

It must be noted that it was not possible to date to synthesize derivatives with neopentyl (^tBuCH₂), and other alkyl chains branched at the C_α position, *e.g.*, ⁱPr or ^tBu. In these cases, reaction of ZnR₂ (R = ⁱPr, ^tBu, ^tBuCH₂) with XReO₃ (X = Me₃SiO, Cl, ReO₄) gives black decomposition products upon mixing at ~–78 °C whereas ⁱPrZnCl is totally unreactive toward Re₂O₇, even at room temperature. In contrast, the cyclopropyl derivative can be prepared in good yields and, so far, represents the only case of a secondary alkyl chain bound to ReO₃. Branching at the β or further carbon atoms in the chain does not create any special instability. These findings certainly result from electron-transfer processes being favored over ligand substitution (alkylation) during the synthesis and not from the intrinsic instability of the corresponding $RReO_3$ compounds. In fact, there are many other high oxidation state transition metal neopentyl derivatives, including the isoelectronic (^tBuCH₂)ReO₂(CH^tBu) (see section III.B),^{76a} and the positive ion of (^tBuCH₂)ReO₃ has been detected by mass spectrometry.^{76b} Equally fast decomposition occurs in the similar reactions with Zn(allyl)₂ and Zn(benzyl)₂ but the corresponding $RReO_3$ derivatives were obtained by a different route.

Beside these limitations, the major drawback of this “zinc route” is the waste of the rhenium metal

as the highest possible yield of the $RReO_3$ is only 50% of the total amount of the rhenium initially used (eq 18). In order to solve this problem, rhenium starting materials other than Re₂O₇ were chosen; these allow for higher conversions of rhenium into the desired $RReO_3$ compounds.

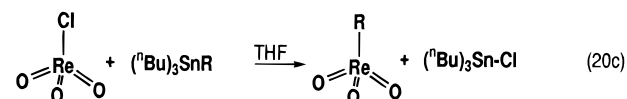
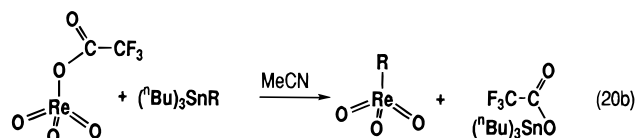
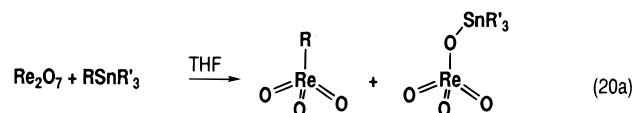
Generally speaking, they are based on the replacement of Re₂O₇ by the more reactive derivatives R_fCO₂ReO₃ and ClReO₃ which react readily at room temperature with SnMe₄ and can be quantitatively generated *in situ* from Re₂O₇ (see section II.A).^{77a} The separation of the final products is improved in the cases where the final byproduct R_fCO₂SnMe₃ is much less volatile than MTO, like in the perfluoroglutaric case. The isolated yield of MTO is ~85% relative to the rhenium used. However, the best laboratory procedure consists in the reaction of (CF₃CO)₂O with Re₂O₇, in MeCN, followed by treatment with MeSnBu₃. The yield of MTO thus obtained is practically quantitative by GC and around 95% of isolated product. After two sublimations ~80–90% yield is obtained.^{44,77} In the same vein, ClReO₃ also reacts with SnMe₄ to give MTO in virtually quantitative yield²⁹ and with SnEt₄ to give EtReO₃, in THF at rt. Although steric constraints hamper the reaction between these XReO₃ complexes and Sn(PhCH₂)₄ or SnPh₄ the use of more reactive RSnBu₃ derivatives helps in circumventing this problem. For example, (PhCH₂)₂SnBu₃ reacts with Re₂O₇ at –45 °C. A general order of reactivity in alkyl transfer reactions from Sn is given in Scheme 8.⁷⁸

Scheme 8

CF₃ = Butyl < Propyl < Ethyl < Methyl < Vinyl < Phenyl < Alkyl < Benzyl

Benzyl = Allyl = Indenyl = CH₂-CN = CH₂-COOR

These findings opened a rather general way of preparing $RReO_3$ complexes, the so called “tin route”, eqs 20a–c, which was later adapted to the preparation of inorganic derivatives of type XReO₃, from XSnBu₃, as already mentioned in section II.A.



The main advantages of this route are the lower reducing ability of the organotin compounds when compared with the Zn congeners, the ease of preparation of a wide variety of RSnBu₃ compounds bearing all sorts of chemical functions and stereochemical characteristics at R, and the ease of monitoring *in situ* reactions in the cases of very temperature sensitive complexes.

This latter characteristic was particularly relevant for the characterization of many compounds presented in the next subsections which deal with the $RReO_3$ derivatives of unsaturated hydrocarbyls.

$ClReO_3$ can also be prepared *in situ* from the reaction of perrhenates with R_3SiCl in acetonitrile. Addition of $SnMe_4$ to these solutions at room temperature leads to the formation of MTO within 20 h in nearly quantitative yield.^{77b}

2. The Methyl(vinyl)ReO₃ Complex

The only known vinyl derivative is the title complex $H_2C=C(Me)ReO_3$ (**44**) formed in the reaction of Re_2O_7 with $[H_2CC(Me)]_2Zn$ at $-50^\circ C$. The compound is very temperature sensitive and was isolated in the form of its quinuclidine adduct $H_2C=C(Me)ReO_3 \cdot$ (quinuc) (**44a**) which is stable at room temperature for short periods.⁷⁹ The instability of **44** explains the lack of success of its attempted preparations by the "tin route" insofar as the temperature needed to start the reaction, lies above the thermal stability range of the compound. The same holds for unsuccessful synthesis of the parent vinyl derivative $H_2C=CHReO_3$ from $Sn(vinyl)_4$ or $Bu_3Sn(vinyl)$ and Re_2O_7 . Compound **44** is clearly less stable than the σ -aryl derivatives which also have $C(sp^2)-Re$ bonds and has a similar stability to its isomeric allyl congener.

3. Allyl, Benzyl, and Pseudoallylic Compounds

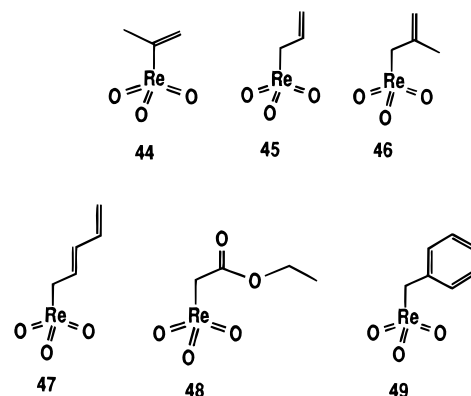
These compounds can only be prepared by the "tin route". $(C_3H_5)ReO_3$ (**45**) and the methallyl analogue **46** are easily prepared by treatment of Re_2O_7 with $Sn(C_3H_5)_4$, $Bu_3Sn(C_3H_5)$, or $Bu_3Sn(C_3H_4Me)$ at $-45^\circ C$.⁷⁹ The yellow-orange compounds start to quickly decompose above $\sim +5^\circ C$, in solution, and no significant stability difference is observed between the allyl and the methallyl complexes. Addition of quinuclidine, at $-40^\circ C$, gives the expected orange adducts which are stable enough to allow isolation from *n*-pentane, as crystalline compounds.

In situ NMR studies (^{13}C and 1H) in d^8 -THF at $-45^\circ C$ show that the allyl and methallyl ligands are coordinated in a η^1 fashion with the spectra remaining invariant between -80° and $+50^\circ C$. This coordination is also observed in the corresponding imido derivative $(\eta^3-C_3H_5)Re(NR_3)_3$ ⁸⁰ and has been predicted by theoretical calculations to be preferred to the η^3 coordination $(\eta^3-C_3H_5)ReO_3$.⁸¹

η^1 coordination is also found for the pentadienyl derivative **47** which can be isolated in pure form but decomposes above $-30^\circ C$. The pseudoallylic complex [(ethoxycarbonyl)methyl]trioxorhenium(VII), (**48**) was prepared in the same way.

$Bu_3Sn(CH_2Ph)$ reacts with Re_2O_7 between -50 and $-45^\circ C$ to give $(PhCH_2)ReO_3$ (**49**). Since decomposition is simultaneous, the *in situ* NMR spectra are not possible to assign and isolation failed even on addition of quinuclidine or bipyridine. After evaporation of the reaction mixture at $-80^\circ C$, the CI mass spectrum of the residue revealed the parent ion peak at $m/z = 326$. This is, so far, the only piece of evidence in the characterization of this compound.

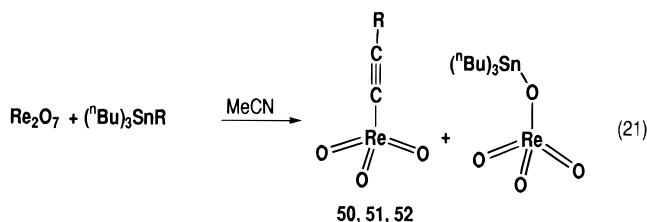
From the point of view of mechanism and catalysis, this group of compounds is rather interesting, since allyl and benzyl intermediates are supposed to be



involved in catalytic reactions as olefin ammoxidation (SOHIO process).^{82,83} Some molybdenum-allyloxo and -allylamido complexes have been used to model this process^{83b,c} but the only other reported organometallic allyloxo derivative of a transition metal is the η^3 bound $W(O)(\eta^3-C_3H_5)Cl(PMe_3)_2$.⁸⁴

4. The Alkynyl RReO₃ Derivatives

Reaction of Re_2O_7 with $Zn(C\equiv CPh)_2$ gave a mixture which mass spectrometry showed to contain the desired $PhC\equiv CReO_3$ which could not be isolated.⁷¹ However, use of the "tin route" allowed the characterization, by *in situ* NMR, of both $PhC\equiv CReO_3$ (**50**) and the parent acetylene derivative, $HC\equiv CReO_3$ (**51**) according to eq 21.⁸⁵

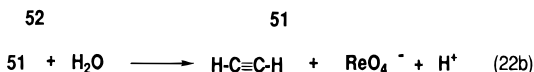
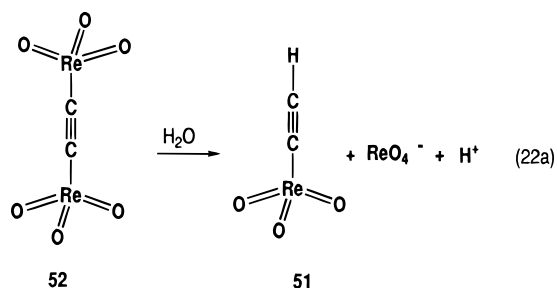


Surprisingly, **51** is somewhat more stable than **50** but both proved impossible to isolate even with workup at $-50^\circ C$, in spite of the quantitative yields revealed by the NMR spectroscopy. However, addition of bipy gives the adducts $RC\equiv CReO_3 \cdot bipy$ ($R = H, Ph$) which are stable at room temperature and can even be briefly handled in air. The adduct $HC\equiv CReO_3 \cdot bipy$ remains intact after sublimation in the mass spectrometer and the parent ion peak can be detected by CI-MS. It is the only $RReO_3 \cdot L$ or $RReO_3 \cdot L_2$ compound, so far, to exhibit this property, a fact that speaks for the very high electrophilicity of the metal center in the parent $HC\equiv CReO_3$ complex. Indeed, the 1H NMR signal of the acetylenic proton of **51** in d^8 -THF solution is strongly deshielded, $\delta(^1H)$ 4.59 ppm, when compared to the value of $\delta(^1H)$ 1.80 ppm measured for C_2H_2 , $\delta(^1H)$ 3.40 ppm for $PhC\equiv CH$ or $\delta(^1H)$ 2.31 ppm for $HC\equiv CSnBu_3$. The ^{13}C NMR spectra also attest the high electron-attracting ability of ReO_3 since the deshielding of the ^{13}C carbon attached to ReO_3 is of ~ 40 ppm relative to its value in the parent hydrocarbon.

The formation of the extremely labile $O_3ReC\equiv CReO_3$ complex **52**, from $(Bu_3Sn)_2C_2$ and Re_2O_7 in THF, can be followed by the appearance of a peak at $\delta(^{13}C)$ 143.7 ppm, clearly deshielded relative to both

the corresponding signal of the tin starting material ($\delta(^{13}\text{C})$ 25 ppm) and that of acetylene ($\delta(^{13}\text{C})$ 65 ppm).

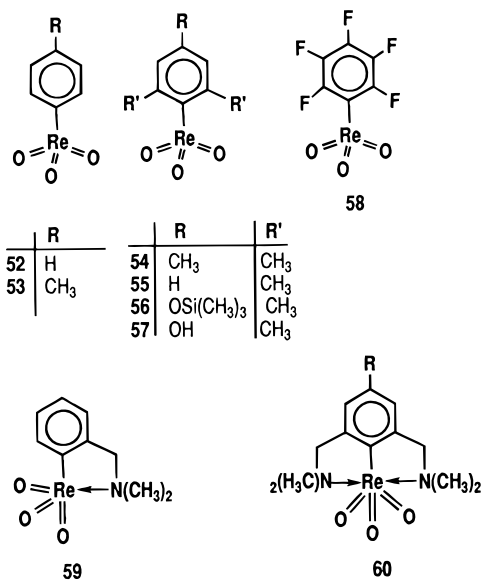
Besides their thermal instability, the alkinyl ReO_3 derivatives are extremely sensitive to hydrolysis, whereby the corresponding acetylene and perrhenate are formed. The stepwise hydrolysis of **52** can be followed by NMR and proceeds via **51**, as in eqs 22a,b.



5. The Aryl Derivatives

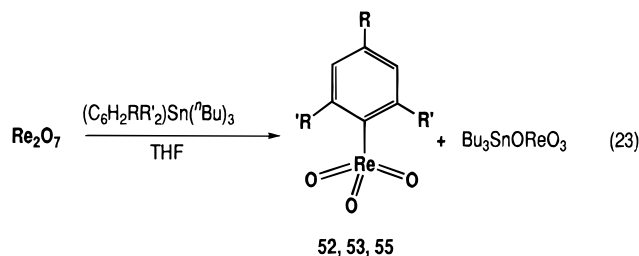
The mesityl derivative mesReO_3 (**54**), prepared in 1988, was the third example known of a RReO_3 complex, after MTO and Cp^*ReO_3 .⁷⁰ The steric protection offered by the two *o*- CH_3 groups was initially taken as a rationale for the stability of **54** but after the appropriate reaction conditions were established for the "zinc route" (eq 19) a large range of aryl ReO_3 complexes were isolated and characterized as summarized in Chart 5.^{70,72}

Chart 5



The synthesis of **52**, **53**, and **55** (quantitative by ^1H NMR and GC analysis) is also possible by the "tin route", eq 23, but this method is less convenient for the purification of the ArReO_3 products.⁴⁴

The colorless parent compound **52** does not survive long storage but can be briefly handled at room temperature. It is also more stable in solution, *e.g.*, pentane, where it can be easily stored at room temperature in the absence of light. It is a stronger Lewis acid than the alkyl analogues, forming adducts not only with quinuclidine but even with THF. The very acidic $\text{C}_6\text{F}_5\text{ReO}_3$ can only be isolated as the quinuclidine adduct. On the contrary, the ring-



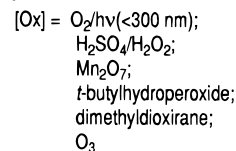
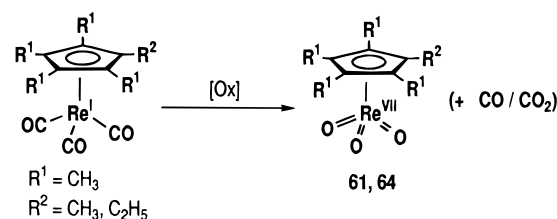
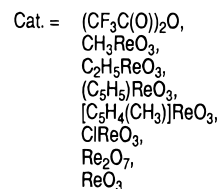
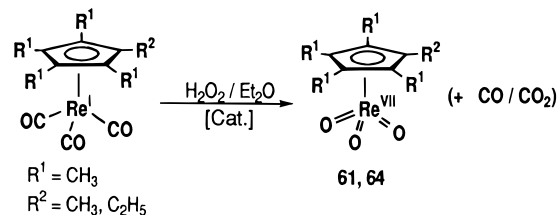
substituted derivatives **54**–**56** do not form adducts with quinuclidine possibly due to steric repulsion originated between the *o*- CH_3 substituents and equatorial $\text{Re}=\text{O}$ bonds.

The ^1H NMR spectra of the ArReO_3 complexes are solvent dependent insofar as the chemical shifts of the aromatic (but not those of the Me substituents) protons are shifted to lower fields ($\Delta\delta(^1\text{H}) \approx 0.6$ – 0.9 ppm) in polar solvents (THF, CHCl_3 , and CH_2Cl_2) relative to C_6H_6 . The chemical shifts of $\text{PhReO}_3 \cdot \text{THF}$ in C_6D_6 correspond to the ones obtained upon addition of THF to a solution of PhReO_3 in C_6D_6 and ^{17}O NMR confirms that an equilibrium exists between complexed and uncomplexed PhReO_3 in these solutions.⁷² ^{13}C NMR studies on ArReO_3 complexes classify the ReO_3 fragment as an electron attractor comparable to the phosphonium $[\text{PPh}_3]^+$ and sulfonium $[\text{SMe}_2]^+$ ions, *i.e.*, stronger than NO_2 whereas *ab initio* calculations predicted it to be similar to that of Cl .^{72,86}

6. The Cyclopentadienyl Derivatives

The serendipitous discovery of complex Cp^*ReO_3 (**61**) by two independent groups in 1984 was a major breakthrough which prompted the recent expansion of high oxidation state organometallic chemistry of

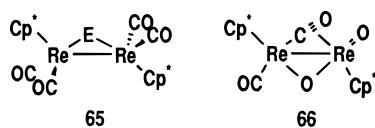
Scheme 9



Re and its neighboring metals.⁸⁷ In fact, this complex was the first good model of organometallic oxide chemistry and it is curious and worth noting that the preparation of the parent cyclopentadienyl complex, CpReO₃ (**62**) had already been attempted by E. O. Fischer and A. Riedel as long ago as 1963.⁸⁸

Cp*ReO₃ was first prepared by oxidative decarbonylation of Cp*Re(CO)₃ (**63**) by adventitious oxygen⁸⁹ but its preparation was later improved in a number of ways by using a series of oxidizing agents (Scheme 9a): H₂O₂,^{87c,90a} Mn₂O₇,^{63a} ^tBuOOH,^{90b} Me₂CO₂ (dimethyldioxirane),^{90c} and O₃.^{90d} So far, the method with the highest yield (90% below rt) is the oxidation of **63** with H₂O₂ catalyzed by MTO and other Re oxide complexes (Scheme 9b).^{90e,13e}

The detailed mechanism of its formation is not known. In the photolytic reaction intermediates like **65** (E = O) and **66** were characterized,⁹¹ whereas in the case of the H₂O₂ oxidation a peroxycarbonato intermediate (CO₄ ligand) has been suggested.^{90a}

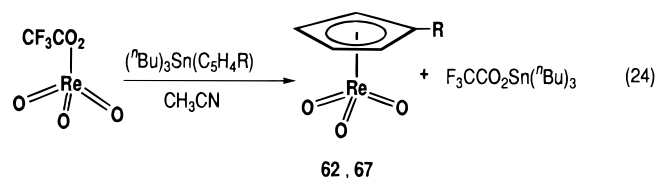


The same oxidative decarbonylation is used to prepare (η^5 -C₅Me₄Et)ReO₃ (**64**)^{92a} but fails for CpReO₃ which was prepared much later. The crystal structure of **61** has presented a number of difficult crystallographic problems resulting from crystal packing, which have remained controversial in view of the now seemingly wrong structure of the nonexistent technetium analogue "Cp*Tc₂O₃".^{92b,c} However, the crystallographic data recently obtained for **61**^{92b} agree with the one reported much earlier for **64**.^{92a} The most remarkable feature are the rather long Re–C bonds to the symmetrically bound Cp* ring when compared to other low-valent Re(I) complexes, CpReL_n. This effect results from the pronounced *trans* influence of the π -donating terminal O ligands. The O atoms in **61** are electron richer than in MeReO₃ as judged from a wealth of spectroscopic and structural data comparing these type of compounds, including ¹⁷O NMR and IR data and electron diffraction on MTO.^{63a}

The preparation of the parent CpReO₃ (**62**) posed a number of difficulties for a long time. The oxidative decarbonylation approach, from CpRe(CO)₃, was tested under various conditions with O₂/*h* ν , H₂O₂, Mn₂O₇, and Me₂CO₂ always with negative results. Modifying the originally unsuccessful approach of Fischer and Riedel (who reacted NaCp with Cl-ReO₃),⁸⁸ Re₂O₇ and XReO₃ (X = Cl, Me₃SiO) were reacted with a wide variety of Cp-transfer reagents (*e.g.*, MgCp₂, CdCp₂, HgCp₂, CpTi(O-ⁱPr)₃, SnCp₄, Bu₃-SnCp) also under several conditions always with negative results: either no reaction or total decomposition.⁹³

It was the "zinc route" reaction of Cp'₂Zn with Re₂O₇ in THF from –80 to 0 °C that produced Cp'ReO₃ (Cp' = Cp (**62**), MeCp (**67**)), both purified by sublimation.⁹⁴ The difficult experimental procedure which includes the preparation of Cp'₂Zn, was later replaced by the nearly quantitative reaction of ClReO₃ or CF₃COOREO₃ with Bu₃SnCp in CH₃CN or

THF at –40 °C.⁹⁵ Yellow Cp'ReO₃ precipitates and can be obtained pure after decanting and washing, as in eq 24. Scale up to 10 grams and probably more is possible.



Temperature control of this reaction is the crucial factor since, below –60 °C, no reaction takes place and, at room temperature, total decomposition is observed instantaneously. The pure compound is thermally stable up to 134 °C in the solid state and the thermal stability of the Cp'ReO₃ family increases in the order C₅H₅ < C₅H₄Me < C₅Me₄Et < C₅Me₅ as predicted on theoretical grounds.⁹⁶ Compound **62** is stable in a number of solvents but decomposes easily in strong donor solvents (*e.g.*, DMSO, pyridine) at room temperature with liberation of C₅H₆ (NMR). This reactivity toward donor ligands is also evident in the rapid decomposition of **62** upon reaction with Lewis base ligands, *e.g.*, quinuclidine or bipyridyl and contrasts with the inertness of **61** toward these reagents.

The pentahapticity of the Cp ring between –80 and +100 °C is confirmed by X-ray crystal structure as well as solid-state and solution NMR. Again, the Re–C bonds to Cp ring are longer than those of the structurally similar CpRe(CO)₃. As expected from the easy solvent coordination, the chemical shift of the C₅H₅ ring protons is strongly solvent dependent a high-field shift being caused by donor solvents. This effect is also observed for MeReO₃ but not for Cp*ReO₃. This reveals a more flexible and reactive nature, also reflected in the fact that **62** is active in olefin metathesis and aldehyde olefination like MTO but not **61**.⁹⁷

It is worth noting that, so far, Cp*ReO₃ and CpReO₃ have remained synthetically unrelated members of the same family as neither the zinc nor the tin route have been able to produce the former and oxidative decarbonylation of CpRe(CO)₃ does not produce CpReO₃. This point can be made as an illustration of the existing need to explore, extend, and understand the synthetic pathways available to high oxidation organometallic derivatives.

7. The Indenyl Derivative

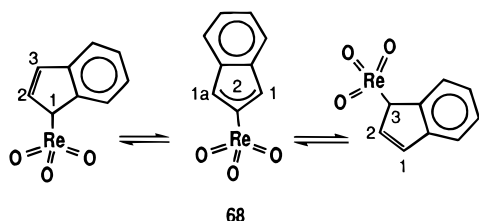
The indenyl represents an interesting case since its behavior may be either borderline or fluctuating between three hapticities: η^1 , η^3 , and η^5 . Examples of all three types are known throughout organometallic chemistry and, therefore, the coordination of the putative IndReO₃, at the outset, was an open question. Very clean reactions occur upon mixing IndSnBu₃ with Re₂O₇ in THF at –60 °C followed by warming to –30 °C. The compound can be extracted into *n*-pentane and crystallized from this solvent, at –80 °C, as a bright orange-yellow solid.⁹⁸ This solid is extremely sensitive both to temperature and

moisture and decomposes above $-30\text{ }^{\circ}\text{C}$. Hydrolysis gives indene and HOReO_3 .

In contrast to the allyl derivative and all other organic RReO_3 compounds which are considerably kinetically stabilized by adduct formation with quinuclidine or bipy, but in parallel with the Cp' derivatives **62** and **67**, IndReO_3 (**68**) decomposes instantaneously upon addition of such bases at $-70\text{ }^{\circ}\text{C}$.

In situ NMR (^1H and ^{13}C) shows that below $-35\text{ }^{\circ}\text{C}$, the indenyl in **68** is η^1 -coordinated. Above $-30\text{ }^{\circ}\text{C}$ broadening of the signals reveals a dynamic process which can only be followed up to $0\text{ }^{\circ}\text{C}$. At $+40\text{ }^{\circ}\text{C}$ total decomposition is attained and indene is the only identifiable species by ^1H NMR. This fluxional behaviour is explained by a 1 to 3 shift of the η^1 -indenyl as represented in Scheme 10.

Scheme 10



It is not yet known whether this η^1 -coordination is due to the presence of a donor solvent (d^8 -THF) in the solutions used for the *in situ* NMR studies. Indeed, the hapticity change from η^5 to η^1 could be forced by donors as it seems to be the case in CpReO_3 . Pushing this argument further, $(\text{Me}_7\text{C}_9)\text{ReO}_3$ might exhibit a higher hapticity, namely η^5 . However, the present authors have so far been unable to prepare it either by oxidative decarbonylation of $(\text{Me}_7\text{C}_9)\text{Re}(\text{CO})_3$ or by the "tin route".

8. Structural and Spectroscopic Characterization

a. Structural Studies. The organorhenium(VII) oxides and their adducts which have been structurally characterized by means of X-ray, neutron or electron diffraction studies are listed in Table 4.

The structures of RReO_3 compounds all show a slightly distorted tetrahedral geometry without "agostic" interactions between C-H and oxygen atoms, and data for some selected complexes is presented in Table 5. The Re-C bond distances in the σ -coordinated derivatives vary between 200 pm (in PhReO_3 , monoclinic modification) and 208 pm in mesReO_3 and are comparatively short considering the usual range of Re-C single bonds (202–230 pm regardless of the type of carbon hybridization) and Re-C double bonds (187–198 pm).^{56,63,99,70} These short distances seem to result from the strong electron-withdrawing effect of the ReO_3 fragment and the small steric constraint of the Re-C bond in the tetrahedral geometry. In η^5 - $\text{Cp}'\text{ReO}_3$ complexes (Table 6) the distance between Re and the centroid of the π -coordinated ring varies between 206 and 208 pm, *i.e.*, longer than in the low-valent η^5 - $\text{Cp}'\text{Re}(\text{CO})_3$ analogues due to the "trans influence" of the oxo ligands.^{87b}

The mean value of the Re-O bond distances in trioxo complexes of the type LReO_3 is 170(2) pm. Among all examined η^1 - RReO_3 oxides this mean

Table 4. ReO_3 and $\text{ReO}_3\cdot\text{L}_n$ Complexes of Known Structure

compound	coordination no. of Re	ref(s)
$(\text{CH}_3\text{ReO}_3)_n$ (polymeric)	6	63b
CH_3ReO_3 (gas phase/neutron diff.)	4	6a
$\text{CH}_3\text{ReO}_3\cdot\text{aniline}$	5	65a,66a
$\text{CH}_3\text{ReO}_3\cdot\text{quinuclidine}$	5	99a
$\text{CH}_3\text{ReO}_3\cdot\text{Tröger's base}$	5	66c
$\text{CH}_3\text{ReO}_3\cdot\text{tert-butylpyridine}$	5	66b
$\text{CH}_3\text{ReO}_3\cdot\text{bipyrimidine}$	6	66b
$(\text{CH}_3\text{ReO}_3)_2\cdot[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\cdot 2,6]$	5	142
$\text{CH}_3\text{ReO}_3\cdot\text{toluidine}$	5	99a
$\text{C}_2\text{H}_5\text{ReO}_3\cdot\text{quinuclidine}$	5	71,99a
$(\text{CH}_3)_3\text{SiCH}_2\text{ReO}_3\cdot\text{quinuclidine}$	5	71,99a
$(\text{CH}_3)_2\text{HCCH}_2\text{ReO}_3\cdot\text{quinuclidine}$	5	73
<i>c</i> - $\text{C}_3\text{H}_5\text{ReO}_3\cdot\text{quinuclidine}$	5	73
$\text{C}_6\text{H}_2(\text{CH}_3)_3\text{ReO}_3$	4	70,72
$\text{C}_6\text{H}_2(\text{CH}_3)_2[\text{OSi}(\text{CH}_3)_3]\text{ReO}_3$	4	72
$\text{C}_6\text{H}_5\text{ReO}_3\cdot\text{THF}$	5	72
$\text{C}_6\text{H}_3(\text{CH}_2\text{N}(\text{CH}_3)_2)_2\text{ReO}_3$	6	142
CpReO_3	4	95
$\text{Cp}(\text{CH}_3)\text{ReO}_3$	4	94
Cp^*ReO_3	4	92b,92c
$\text{Cp}(\text{CH}_3)_4(\text{C}_2\text{H}_5)\text{ReO}_3$	4	92a
$(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2\text{ReO}_3$	5	74a
$(\text{CH}_2)_3\text{N}(\text{C}_5\text{H}_{10})\text{ReO}_3$	5	74b
$[(\text{CH}_2)_2\text{C}(\text{CH}_3)\text{HOCH}_3]\text{ReO}_3)_2$	6	66d
$\text{C}_2\text{H}_5\text{ReO}_3$ (gas phase)	4	66e

Table 5. Bond Distances^a (in pm) and Angles (in deg) in Selected σ -Organyl-rhenium(VII) oxides $\text{R}-\text{ReO}_3$ [$\text{R} = \text{C}_6\text{H}_5$ (52**), $\text{C}_6\text{H}_2(\text{CH}_3)_3$ (**54**), $\text{C}_6\text{H}_2(\text{CH}_3)_2[\text{OSi}(\text{CH}_3)_3]$ (**56**), CH_3 (**30**)]**

52^b		54	56	30		
a	a'	b				
201	206	200	208	204	204	Re-C α
169	169	169	168	170	168	Re=O
108	108	108	107	107	107	C α ReO
111	111	111	112	111	113	OReO

^a The given bond distances and angles are the arithmetical average of the literature data (rounded on pm and deg).
^b PhReO_3 crystallizes under different conditions in a monocline (a and a') or orthorhombic (b) modification [19a].

Table 6. Bond Angles^a (in deg) and Bond Distances^a (in pm) in Selected η^5 - $\text{Cp}'\text{ReO}_3$ Complexes [$\text{Cp}' = \text{C}_5\text{H}_5$ (62**), $\text{C}_5\text{H}_4(\text{CH}_3)$ (**67**), $\text{C}_5(\text{CH}_3)_4(\text{C}_2\text{H}_5)$ (**64**)]**

62	67	64	
206	207	208	Re-Cp
170	172	170	Re=O
114	113	-	CpReO
104	105	106	OReO

^a The given bond distances and angles are the arithmetical average of the literature data (rounded on pm and deg).

value is 169(1) pm, and among the η^5 - $\text{Cp}'\text{ReO}_3$ oxides 171(1) pm showing that the Re-O bond distances are nearly not influenced by the ligand. The mean O-Re-O angle in the η^1 - RReO_3 complexes is $112(1)^\circ$, in the η^5 - $\text{Cp}'\text{ReO}_3$ complexes $105(1)^\circ$ and in all of complexes of type LReO_3 examined, $109(3)^\circ$.^{99c} The influence of the steric demand of the R or L ligands is clear: in the $\text{Pt}_3(\text{dppm})_3-\text{ReO}_3$ -cluster (**29**), this angle is 107° ,⁵³ in $(\eta^5\text{-C}_5\text{H}_5)\text{ReO}_3$ 104° ,⁹⁵ and in CH_3ReO_3 , 113° .⁶³

Tables 7 and 8 list the bond distances and bond angles of selected *trans*- $\text{RReO}_3\cdot\text{L}$ and *cis*- $\text{RReO}_3\cdot\text{L}$ complexes, respectively.

Table 7. Bond Distances^a (in pm) and Bond Angles^a (in deg) of Selected TBP 5-Coordinated Compounds of Type R–ReO₃·L [R = CH₃, L = aniline (30c'); R = CH₃, L = pyridine, (30d); R = CH₃, L = Cl⁻ (30a'); R = C₂H₅, L = quinuclidine (31a); R = (CH₃)₂CHCH₂, L = quinuclidine (33a); R = CH₂Si(CH₃)₃, L = quinuclidine (32a); R = cyclopropyl, L = quinuclidine (40a); R = C₆H₅, L = THF (44a)]

30c'	30d	30a'	31a	33a	32a	40a	44a	30m	
210	210	213	211	210	209	207	207	208	Re–C
170	170	169	170	169	169	170	167	168	Re=O
247	246	263	241	241	243	239	242	259	Re–X ^b
97	98	93	96	95	97	96	98	99	CR=O
118	118	120	119	119	118	119	119	119	OR=O
83	–	87	83	85	83	84	82	82	XReO ^b
180	177	179	180	179	178	179	176	177	CR=O ^b

^a The given bond distances and angles are the arithmetical average of the literature data (rounded on pm and deg). ^b X = Donor atom of the Lewis base ligand (N or O).

Table 8. Pentagonal Coordinated Lewis Base Adducts of Organorhenium(VII) Oxides (The oxo ligands are in facial position. R = C₃H₆N(C₅H₁₀) (41); R = C₃H₅N(C₂H₅)₂ (42).]

30c' ^a	41	42	
212	212	214	Re–C
171	171	172	Re=O
233	239	238	Re–N
75	75	–	CR=O

^a CH₃ReO₃(aniline) (30c'); there exists also a modification with all oxo ligands in the equatorial plane, see Table 7.

Comparing Tables 5 and 7 reveals that the Re=O bond distance remains virtually unchanged after coordination of L, *trans* relative to R, whereas Re–C bond distances increase by ~5 pm, the anionic complex [CH₃ReO₃Cl]⁻ (30a') possessing the longest Re–C distance.^{65c,66a,71,73} The Re–L bonds are abnormally long showing a relatively weak coordination. The oxo ligands lie out of the equatorial plane and the C–Re–O angle is 97(1)° instead of 90°.

In comparison, the *cis*-RReO₃L complexes in Table 8 have even longer Re–C bonds, ~212 pm, shorter Re–L bonds and only marginally longer Re=O bonds than their *trans* congeners. Interestingly, the C–Re–N angle is 75° in both the intramolecular chelate and the aniline complex 30c'.⁷⁴

From all these data it can be concluded that the electron and X-ray diffraction measurement of Re–O bond lengths are rather insensitive to the type of geometry and substituents present in RReO₃ compounds and their adducts. Therefore, they are of little use for the direct characterization of the ReO₃ fragment in terms of structure–reactivity correlations which are best seen by spectroscopic methods, namely ¹⁷O NMR and IR spectroscopy, as discussed below.^{63a}

b. Spectroscopic Studies. ¹⁷O NMR is particularly useful in probing the ligand effects that the R substituents bring on to the ReO₃ fragment as judged from the selected data given in Table 9 and the Scheme 11.⁵⁷ A distinction between the σ - and π -bonded RReO₃ complexes is immediately apparent which reflects the higher electron density on the ReO₃ fragment in the latter complexes.

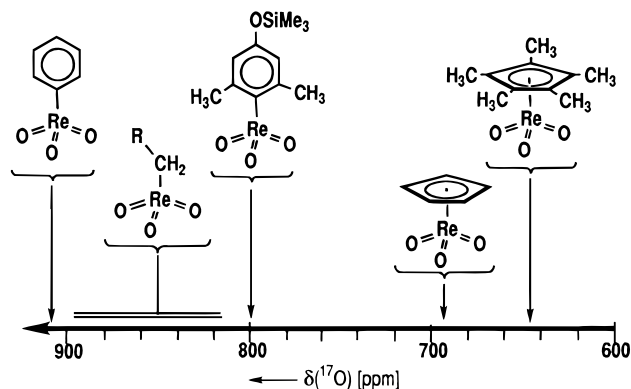
The strong solvent dependence of the ¹⁷O NMR data of organorhenium oxides is mirrored in the data of Table 10. These data can be explained by the

Table 9. Chemical Shifts $\delta^{17}\text{O}$ (in ppm) of Complexes of Type R–ReO₃^a

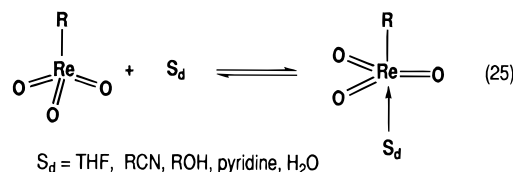
complex	$\delta^{17}\text{O}$	solvent
PhReO ₃	912	THF
CH ₂ =CHCH ₂ ReO ₃ ^b	894	THF
C ₂ H ₅ ReO ₃	844	CDCl ₃
CH ₃ ReO ₃	829	CDCl ₃
MesReO ₃	811	CDCl ₃
(CH ₃) ₃ SiCH ₂ ReO ₃	808	<i>n</i> -pentane
C ₅ H ₅ ReO ₃	691	CDCl ₃
[C ₅ H ₄ (CH ₃)]ReO ₃	674	CDCl ₃
[C ₅ (CH ₃) ₅]ReO ₃	647	CDCl ₃
[C ₅ (CH ₃) ₄ (C ₂ H ₅)]ReO ₃	646	CDCl ₃

^a Abbreviations: Ph, phenyl; Mes, 2,4,6-trimethylphenyl; Xy, 2,6-dimethyl-4-(trimethylsiloxy)phenyl. ^b Spectrum recorded at –55 °C (compound is temperature sensitive).

Scheme 11



equilibrium shown in eq 25. Strong donor solvents, *e.g.*, THF lead to low field shifts in the ¹⁷O NMR



spectra due to the 5-coordination of the product compounds. In noncoordinating solvents, *e.g.*, toluene, the tetrahedral geometry of the RReO₃ complexes remains unchanged.^{57,74b}

Less steric crowding and less electronic density at the Re(VII) center also favor stronger adducts. The chemical shifts in the ¹⁷O NMR spectra of electron-deficient complexes with sterically undemanding ligands in donor solvents are comparable to the shifts of Lewis base complexes, as given in Table 11. Unable to form such Lewis base and solvent adducts, Cp*ReO₃ does not show a significant solvent dependence which, however, is present in CpReO₃.⁵⁷

A solvent dependence of the chemical shift is also observed in the ¹H NMR spectra of MeReO₃ and CpReO₃. A good correlation is obtained between the ¹H chemical shifts of Me and Cp and the Gutmann's donor numbers of the respective solvent.^{57,74b}

The values of the ¹⁷O chemical shifts of the Lewis base adducts R–ReO₃·L_{*n*} (Table 11) and Scheme 12, have a more complex dependence on the nature of both R and L as well as on the geometry of the complex.⁵⁷

Labeling studies have shown that both RReO₃ and their adducts R–ReO₃·L_{*n*} undergo oxygen exchange

Table 10. Solvent Dependence of the Chemical Shift $\delta(^{17}\text{O})$ (in ppm) of R-ReO₃ Complexes^a

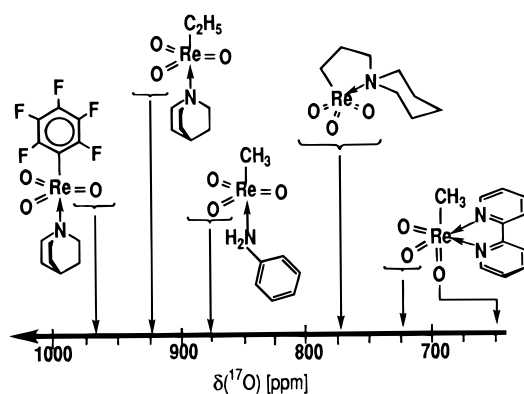
solvent	Me-ReO ₃	Ph-ReO ₃	mes-ReO ₃	Me ₃ SiOXy-ReO ₃	Cp ⁺ -ReO ₃
THF	870	912	836	821	653
CH ₃ OH	861				
<i>n</i> -pentane	835	872		813	
acetone	833				
CHCl ₃	829	849	811		647
CH ₃ CN	824				
toluene	823				
benzene	823	856	809	805	655
Δ^b	47	63	27	21	8

^a Abbreviations of R see Table 9. ^b Δ : Total shift difference of the compound in different solvents.

Table 11. Chemical Shifts $\delta(^{17}\text{O})$ (in ppm) and Half-Width $\nu_{1/2}$ (in Hz) of Donor Substituted Trioxorhenium(VII) Complexes R-ReO₃·L_{*n*}^a (*n* = 1, 2)^{57,74b}

compound	$\delta(^{17}\text{O})$	$\Delta\nu_{1/2}$	solvent
PhReO ₃ (quinuc)	978		C ₆ D ₆
PhReO ₃ (quinuc)	947		THF
C ₂ H ₅ ReO ₃ (quinuc)	925	170	THF
CH ₃ ReO ₃ (quinuc)	920	170	THF
CH ₃ ReO ₃ (^t Bupy)	881	180	CDCl ₃
(CH ₃ ReO ₃) ₂ (urotropine)	879	254	CDCl ₃
(CH ₃ ReO ₃) ₂ (dpi)	861	110	CDCl ₃
CH ₃ ReO ₃ (H ₂ NC ₆ H ₅)	849		C ₆ D ₆
CH ₃ ReO ₃ (bpm)	838	300	CDCl ₃
CH ₃ ReO ₃ (H ₂ NC ₆ H ₅)	837	81	CDCl ₃
CH ₃ ReO ₃ (<i>o</i> -moa)	826		CH ₂ Cl ₂
CH ₃ ReO ₃ (<i>m</i> -moa)	826		CH ₂ Cl ₂
CH ₃ ReO ₃ (<i>p</i> -moa)	829		CH ₂ Cl ₂
CH ₃ ReO ₃ (^t Bubipy) ^b	728	1340	CDCl ₃
	720 ^c	260 ^c	CDCl ₃
	644 ^c	670 ^c	
C ₂ H ₅ ReO ₃ (^t Bubipy) ^b	719 ^c	300 ^c	CDCl ₃
	627 ^c	660 ^c	

^a Abbreviations of ligands R and L: Ph, pentafluorophenyl; Ph, phenyl; quinuc, quinuclidine; ^tBupy, 4-*tert*-butylpyridine; dpi, *N,N*-dimethylpiperazine; bpm, 2,2'-bipyrimidine; moa, methoxyaniline; ^tBubipy, 4,4'-*tert*-butyl-2,2'-bipyridine. ^b Complexes are octahedrally coordinated in the solid state. ^c Measured at -20 °C.

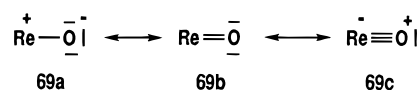
Scheme 12

in solution. Ligand exchange in the R-ReO₃·L_{*n*} adducts is also readily observed even for the bidentate adducts, like MeReO₃·bipy and the intramolecular base adducts.^{74b} This is in agreement with the weak (rather long) Re-L bonds inferred from X-ray data (Table 7).

The electron-attracting ability of the ReO₃ fragment can be quantified by means of a known correlation between the ¹³C chemical shift of the *p*-C of an aryl derivative (PhX) relative to the chemical shift of the benzene ring carbon.⁸⁶ Following this crite-

rium, quantitatively expressed by the quantity $Sp = \delta(p\text{-C}(\text{C}_6\text{H}_5\text{X}) - \delta(\text{C}_6\text{H}_6))$, strong donors like NH₂ have $Sp = -10.0$ whereas strong acceptors like NO₂ have $Sp = +6.1$. Accordingly, ReO₃ is classified as a very strong acceptor since its Sp value of +7.0 is similar to the one of the phosphonium [PPh₃]⁺ and sulfonium [SMe₂]⁺ ions which have $Sp = 7.4$.

IR spectroscopy is also a very useful tool for establishing the electronic properties of the ReO₃ fragment in R-ReO₃ and R-ReO₃·L_{*n*} complexes. As rationalized on the basis of the valence-bond resonance structures **69a**–**c** representative of the Re–O bond the hybrid **69c**, prevailing in electron-poor systems, makes them show their $\nu(\text{ReO})$ vibrations at higher frequencies than electron-rich systems.



Scheme 13 displays the observed range of values for $\nu(\text{ReO})$ in the RReO₃ and R-ReO₃·L_{*n*}. The assignment of the vibration modes of the ReO₃ fragment in these complexes has been reported.¹⁰⁰

Even more obvious than stretching vibration frequencies, force constants $F(\text{ReO})$ reflect the electronic influence of the organic ligands R on the Re–O bond order.^{63a,100} Table 12 gives the ReO stretching force constants of selected organorhenium(VII) oxides. As can be seen, π -bonded hydrocarbon ligands as well as Lewis bases L lower the Re–O bond order as a result of their electron-donating abilities. The order of increasing Re–O bond order is, according to these data, Cp⁺ReO₃ < MeReO₃·bipy < PhReO₃ < EtReO₃ < MeReO₃.¹⁰¹

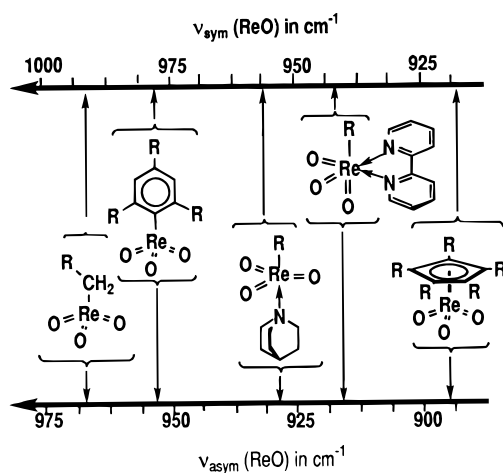
Scheme 13

Table 12. ReO Force Constants of Some Organotrioxorhenium(VII) Complexes^{56b,100}

compound	$F(\text{ReO})$ (mdyn/Å)	$f(\text{ReO}, \text{ReO})$
CH ₃ ReO ₃	8.309	0.355
C ₂ H ₅ ReO ₃	8.252	0.397
<i>n</i> -C ₃ H ₇ ReO ₃	8.252	0.397
(C ₆ H ₅)ReO ₃	8.08	
[η ⁵ -C ₅ (CH ₃) ₅]ReO ₃	6.99	
(C ₂ H ₅) ₂ NC ₃ H ₆ ReO ₃	7.736	0.362
CH ₃ ReO ₃ (bipy)	7.291	0.355
C ₂ H ₅ ReO ₃ (bipy)	7.467	0.362
HC≡CReO ₃ (bipy)	7.293	0.388

Table 13. Computed Dissociation Energies (D_e , kJ/mol) for Selected L–ReO₃ Complexes^{96b,54}

R	D_e^a
CH ₃	237
C ₅ H ₅	102
F	267
Cl	179
CF ₃	177
Re(CO) ₅	271

^a Optimized fragments (planar ReO₃, $d(\text{ReO}) = 169.9$ pm). For others see references.

The dipole moments of R–ReO₃ reflect the strong electron-withdrawing character of the ReO₃ fragment (exp, $\mu(\text{CH}_3\text{ReO}_3) = 2.6 \pm 0.1$ D in benzene; $\mu([\eta^5\text{-C}_5\text{(CH}_3)_5\text{]ReO}_3) = 6.2 \pm 0.1$ D; calcd, $\mu(\text{C}_6\text{H}_5\text{ReO}_3) = 4.45$ D, $\mu([\eta^5\text{-C}_5\text{H}_5\text{)ReO}_3) = 5.58$ D).^{63a,96c}

The photoelectron spectra of MeReO₃, mesReO₃, and Cp*ReO₃ have been measured and assigned with the aid of theoretical calculations.^{63a,89a} The strong acceptor effect of ReO₃ is seen on the first ionization energy of mesReO₃ which exceeds that of mesitylene by 0.6 eV.

c. Theoretical Studies. The usual valence-bond description of MTO as depicted throughout the text, assigns the metal a total count of 14 electrons. However, extended Hückel Molecular Orbital (EHMO) calculations and fragment orbital analysis reveal that nine two-center/two-electron interactions are operative between the metal and the carbon and oxygen ligands, therefore, raising the total electron count to 18. A 2²/₃ bond order may be formally assigned to each Re=O bond.^{81a} The calculations also show that the instability of compounds with sterically hindered ligands R, *e.g.*, R = C(CH₃)₃, stems from the higher energy of the higher alkyl σ -hybrid orbitals. The presence of a π -acceptor group such as CH₂CN or CH₂NO₂ should overcompensate this effect but such compounds have not yet been prepared. Earlier on, Hartree–Fock calculations (HF) had predicted the stability of a large number of RReO₃ derivatives given the isolobality of pyramidal ReO₃ and CH₃ fragments.^{96a} On the basis of the same calculations the photoelectron spectrum of Cp*ReO₃ was assigned and the Cp*–Re bond lengthening observed on going from Cp*ReO₃ to Cp*Re(CO)₃ was explained. By means of *ab initio* two-configuration self-consistent field (TC-SCF) and configuration interaction (CI) calculations, bond dissociation energies and dipole moments for some existing R–ReO₃ and X–ReO₃ compounds were computed. Some results are shown in Table 13.^{96b} From these values it may be concluded that the hypothetical complex CF₃ReO₃ should be a stable

molecule which, in spite of many efforts to synthesize it, has not yet been isolated.^{96b} These calculations also agreed with the HF results in assigning a covalent character to the Cp–ReO₃ as well as all other bonds in Table 13 with the exception of FReO₃ which is clearly more ionic. The dipole moments are oriented in the R→ReO₃ direction except for FReO₃ and CF₃ReO₃ which have the inverse orientation. Furthermore, these calculations have shown that the ReO₃ fragment, considered as a single atom, has the same electronegativity as chlorine.^{96b} Experimental ¹³C NMR data on (σ -Aryl)ReO₃ compounds, confirms that the ReO₃ fragment behaves as a very strong electron acceptor, probably even stronger than SO₃H.^{63a,72}

Similar TC-SCF and CI calculations were performed on both the known O₃Re–ReCl₂(dmpm)₂¹⁰² and the hypothetical bimetallic species O₃Re–Re(CO)₅.⁵⁴ In the former case, which has a very short Re–Re bond, extensive charge transfer occurs from the formal Re(II) center to the formal Re^{VI}O₃ acceptor such that the electronic structure of the final complex is best described in terms of a Re^{VO}O₃[–] and a [Re^{III}–Cl₂(dmpm)₂]⁺ binuclear species. Much less pronounced charge transfer is expected for the putative O₃Re–Re(CO)₅, where a homolytic dissociation energy value of 271 kJ mol^{–1} was computed. This value surpasses the ones shown in Table 13 and confirms earlier predictions on the good stability for this yet unknown compound.^{96a}

A recently published density functional study using LCGTO-DF calculations on three RReO₃ complexes (R = Me, Ph, Cp) has reached a good agreement with their He I photoelectron spectra and shown, once again, that ReO₃ is a strong ($\pi + \sigma$) acceptor hydrocarbon substituent.^{96c} The positive charge density on the ReO₃ fragment decreases in the order CH₃–ReO₃ (0.37 au) > (C₆H₅)ReO₃ (0.27 au) \approx ($\eta^5\text{-C}_5\text{H}_5$)–ReO₃ (0.28 au). An examination of the Mulliken charges on the oxygen atoms correlates well with the ¹⁷O NMR chemical shift for these compounds.^{96c}

An *ab initio* study on the structure and properties of the hypothetical dimer, trimer and tetramer of MTO has been carried out to help explaining some of the features of polymeric MTO as described in section II.B.10.b.^{69c}

d. Electrochemical Studies. So far, the electrochemical studies carried out on LReO₃ compounds comprise the cyclic voltammetry of a small number of selected complexes.^{63a} Although the reduction waves observed are in all cases irreversible, therefore strictly invalidating a comparison of ligand effects, the general results depicted in Table 14 fit in with the expected trend deduced from the other spectroscopic data available, namely NMR and IR. Thus, the L₃ReO₃ type complexes, L₃ = HB(pz)₃, Cp*, are reduced at clearly more negative potentials than the alkyl congeners, MeReO₃ or CH₂SiMe₃ReO₃. The only aryl derivative measured, mesReO₃, is even easier to reduce. The adducts like MeReO₃(bipy) show increased stability against reduction resulting from their higher electronic richness and structural analogy to the L₃ReO₃ complexes.^{63a,103} Interestingly, alkyl substitution on the Cp ring produces a marked variation in the observed reduction potential of

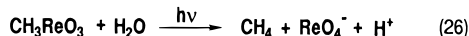
Table 14. Electrochemical Data on LReO_3 and L_3ReO_3 Complexes^{63a,95}

compound	E_{pc} in THF ^a V vs Ag/ AgCl/3 M KCl	E_{pc} in MeCN ^a V vs Ag/ AgCl/3 M KCl
Cp^*ReO_3	-1.72	-1.45
$(\text{C}_5\text{Me}_4\text{Et})\text{ReO}_3$		-1.60
$(\text{C}_5\text{H}_4\text{Me})\text{ReO}_3$		-0.90
$(\text{C}_5\text{H}_5)\text{ReO}_3$		-0.92
$(\text{HB}(\text{pz})_3)\text{ReO}_3$	-1.55	
$\text{MeReO}_3 \cdot (\text{bipy})$	-0.98	
$\text{Me}_3\text{SiCH}_2\text{ReO}_3$	-0.84	
MeReO_3	-0.84	
mesReO_3	-0.69	
	(quasi-reversible)	
$\text{Re}_2\text{O}_7 \cdot (\text{THF})_2$	-0.50	
$\text{Re}_2\text{O}_7 \cdot (\text{MeCN})_2$		-0.97
$(\text{CF}_3\text{COO})\text{ReO}_3 \cdot (\text{MeCN})_2$		-0.70
$(\text{CCl}_3\text{COO})\text{ReO}_3 \cdot (\text{MeCN})_2$		-0.96
$(\text{CH}_3\text{COO})\text{ReO}_3 \cdot (\text{MeCN})_2$		-1.29

^a All waves are irreversible except otherwise stated.

Cp^*ReO_3 compounds which is also noticeable in the corresponding, parallel, variation of ^{17}O NMR chemical shifts and $\text{Re}=\text{O}$ stretching frequencies.

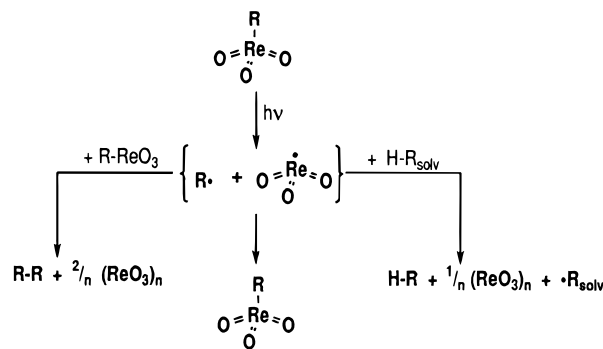
e. Photochemical Studies. The light sensitivity of many organic RReO_3 complexes is evident and sometimes presents problems to their purification since in daylight most of the compounds decompose slowly. In a first examination, the photochemical decomposition of MeReO_3 was studied and the ready homolytic cleavage of the $\text{H}_3\text{C}-\text{Re}$ bond in water was demonstrated:⁶⁷



In a more detailed study it was later shown that CH_4 is first formed in a cage reaction by H^\bullet abstraction from the H_2O solvent in a radical mechanism and EPR spectroscopy shows that radical pairs $\text{R}^\bullet/\text{R}^\bullet\text{ReO}_3$ are generated in a primary step. $\text{C}_2\text{H}_5\text{ReO}_3$, mesReO_3 , CpReO_3 , and CpMeReO_3 undergo similar photolysis which, however, is very inefficient for Cp^*ReO_3 . In water free MeCN solvent, insoluble ReO_3 is formed in all cases.¹⁰⁴ Light in the range of $\lambda = 200-400$ nm is most efficient for homolysis and the most light-stable derivatives (lowest quantum yield) are the cyclopentadienyl complexes, the most sensitive ones being the σ -alkyl derivatives. Ligand to metal charge-transfer excitation leads to this photoredox decomposition. The overall efficiency is determined by the reactivity of the radicals R^\bullet . The regeneration of RReO_3 is favored with increasing stability of R^\bullet which explains the lower photoreactivity of the cyclopentadienyl compounds which recombine with ReO_3 radicals and do not abstract H^\bullet from the solvent. Therefore, the photochemical decomposition of RReO_3 compounds, summarized in the Scheme 14, is very similar to their thermal decomposition.

Photoredox decomposition of an adduct formed in solution between MeReO_3 and $[\text{Fe}(\text{CN})_6]^{4-}$ has also been reported recently.¹⁰⁵

The photochemical behavior of inorganic trioxorhenium(VII) compounds has not been examined to date.

Scheme 14

f. Thermogravimetric and Thermochemical Studies. Thermal stability of organorhenium oxides varies in a large temperature range. While CH_3ReO_3 (**30**) decomposes only above 300°C ,^{69,62b,106,107} and $[\eta^5\text{-C}_5\text{Me}_5]\text{ReO}_3$ (**62**)^{95,107} is stable up to $\sim 210^\circ\text{C}$, (indenyl) ReO_3 (**68**)⁹⁸ is not stable above -30°C and (benzyl) ReO_3 (**49**)⁷⁹ decomposes even below -40°C . As it is known from gas-phase analyses and TG/MS experiments, the hydrocarbon ligands react with the oxo ligands mainly under formation of CO_2 and H_2O , if a temperature triggered intramolecular redox reaction can take place.¹⁰⁷ The higher the hydrocarbon content of the organorhenium(VII) oxide, the lower the oxygen content of the resulting residue. Higher decomposition temperatures also lower the oxygen content of the residue. Thus, decomposition of **30** at $\sim 350^\circ\text{C}$ leads to ReO_2 layers, decomposition at 450°C results in ReO layers and decomposition of **62** leads to a residue which contains $\sim 98\%$ Re at 500°C .¹⁰⁷ Similar results were obtained in plasma-enhanced chemical vapor deposition studies (PECVD) at lower temperatures: **30** produces relatively pure, X-ray amorphous, rhenium films of $<1.5\%$ carbon contamination upon treatment in a H_2/Ar plasma at $300-450^\circ\text{C}$. Microcrystalline rhenium results in a H_2/Ar plasma at 190°C with large H_2 excess. These films are free of carbon (SIMS) and contain only small traces of oxygen and hydrogen.¹⁰⁷ If **30** is tempered at 130°C in a sealed tube, a red colored, amorphous, polymeric compound is formed which closely resembles polymeric MTO in its characteristics (see below, section II.B.10.b and Figure 1) and is interpreted as its water-free form. In contrast to hydrated polymeric MTO (**99**) it is much more hygroscopic and less stable.^{107b,108}

Most of the thermally unstable organorhenium(VII) oxides are much more stable in (diluted) organic solutions (especially in non-coordinating solvents, e.g., benzene). In solution, thermal decomposition follows mainly radical pathways. The decomposition rate depends both on the concentration and the temperature.⁷⁹

The thermal behavior of several Lewis base adducts of organotrioxo rhenium(VII) compounds and also of inorganic organorhenium(VII) oxides has been examined.^{29,95} The covalent complexes of Re_2O_7 are very similar in terms of their thermogravimetric behavior. Upon heating under TG/MS conditions they first lose solvent molecules in two or three steps. After removal of the ligands, Re_2O_7 sublimes partially together with decomposition products. The ionic

complexes of general type $[L_3ReO_3][ReO_4]$ decompose in a multistep process with liberation of mainly H_2O , CO_2 , and oxidized ligand fragments.

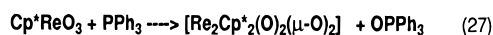
In the case of halogenato and pseudohalogenato compounds of type $X-ReO_3 \cdot L$, usually three decomposition steps occur. During the first two steps, mainly ligand or oxidized ligand fragments are eliminated and free $X-ReO_3$ compounds sublime out. In the third step, only CO_2 and H_2O have been detected, indicating a redox reaction between the remaining Re oxides and ligand fragments.

$RReO_3$ complexes are too volatile or unstable to be examined by TG/MS. For example, **30** and **2** sublime quantitatively without any residue under TG/MS conditions. Their bipyridine adducts show two decomposition steps, one caused by the removal of the ligand and subsequent sublimation of the free $R-ReO_3$ compound, the other caused by CO_2 and water elimination of the remaining residues.²⁹

Comparison of the TG curves of Cp^*ReO_3 derivatives shows increasing decomposition onsets with improving donor capability of the π -ligand. During a first step removal of the π -ligand and, to a certain extent, sublimation of the ligand is observed. In a second step mainly extrusion of H_2O and CO_2 takes place.⁹⁵

In all cases the removal of the ligand takes place between 100 and 200 °C, the redox reaction of the nonvolatile decomposition residues around or above 300 °C.^{29,79,85,95,98}

The first thermochemical estimation of the bond dissociation energy (BDE) of the $Re=O$ bond in Cp^*ReO_3 gave a value of 116.8 ± 1.2 kcal/mol. This estimate was based on the oxygen transfer reaction of eq 27 (cf., section II.B.9.b). The fact that it is lower than many other BDEs simply means that the average BDE of molecules with several $M=O$ bonds is different from the BDE for the removal of the first of these O ligands.¹⁰⁹



9. Reactions of Organic $RReO_3$ Compounds

As has been abundantly exemplified in the preceding sections, the Lewis acidity of $XReO_3$ compounds results in general adduct formation to give *fac*-octahedral complexes with the general formulations $[XL_2ReO_3]$ or trigonal-bipyramidal complexes of $XL-ReO_3$ formulation. The most important exception to this behavior is the Cp^*ReO_3 complex which is electronically saturated and does not form such adducts. In the case of $ClReO_3$ adducts with stronger Lewis acids (*e.g.*, $SbCl_5$) have been reported (see formula **4c**).

X substitution in the case of inorganic $XReO_3$ complexes ($X = ReO_4$, halide, $OSiMe_3$) is a trivial reaction used to prepare a number of other derivatives, namely the organic $RReO_3$ compounds and, therefore, will not be mentioned here.

Apart from these reactions, the chemistry of organic and inorganic $XReO_3$ complexes is dominated by few other types of reactions, namely: condensation reactions with diols and reductive reactions whereby oxygen transfer is the most important.

The reactivity leading to catalytic processes, *e.g.*, oxidation, will be discussed in section II.B.10.a.

a. Reactions of Cp^*ReO_3 . As the rapid growth of the chemistry of Cp^*ReO_3 (**61**) was accompanied by several reviews,⁸⁷ only its guidelines will be presented now. Nevertheless, these reactions were the first to expose the chemistry of organometallic oxides in a consistent way and are widely used as reference for comparison with the reactivity of other metal oxide complexes, namely MTO.

As we have pointed out previously, **61** is a structurally rigid 18-electron complex that does not add strong electron donors, *e.g.*, quinuclidine. Therefore, its chemistry is dominated by reductive processes leading mainly to $Re(V)$ species as summarized in Scheme 15.

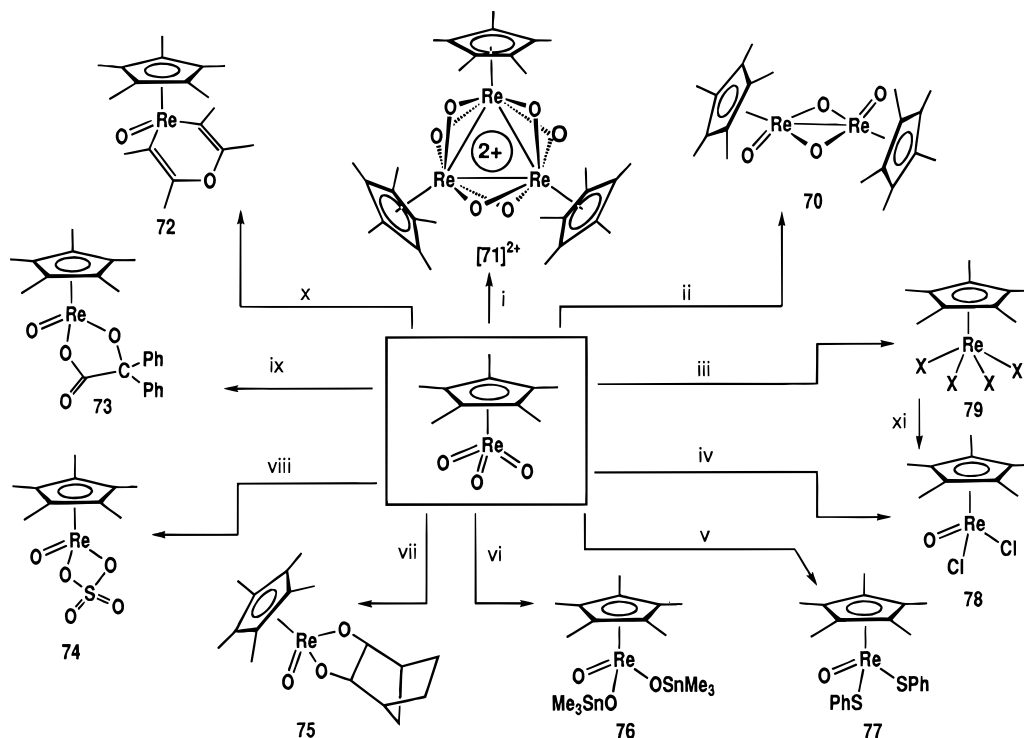
In these reactions the Cp^* ligand is rarely lost as in the formation of the diamagnetic mixed-valence cluster $[Re_3Cp^*_3(\mu-O)_6][ReO_4]_2$ (**71**) isolated from the reaction of **61** with PPh_3 and O_2 .^{110a} When performed in strict absence of O_2 , the same reaction gives the $Re(V)$ dimer $[Re_2Cp^*_2O_2(\mu-O)_2]$ (**70**)^{110b} which is quantitatively converted to (**71**) by oxidation with $AgBF_4$.^{110c} Compound **70** has an extensive chemistry that has been reviewed⁸⁷ (see also refs 115 and 122).

In the presence of acetylenes and PPh_3 , **61** reacts to give $OPPh_3$ and either the $Re(III)$ complexes $Cp^*ReO(RC \equiv CR)$ ($R = Ph, Me, Et$) or **70** for very bulky alkynes. Prolonged reactions lead to " $Cp^*ReO_2(RC \equiv CR)_2$ " (**72**) which, in fact, has the metallacyclic 1,4-rhenapyrane structure.¹¹¹ The putative intermediate of this reaction, $Cp^*ReO_2(RC \equiv CR)$, was never isolated or detected apparently following the theoretical prediction of the instability of $Cp^*Re(O)_2(RC \equiv CR)$ complexes.¹¹² In fact, the $Re(III)$ complexes $Cp^*Re(O)(RC \equiv CR)$ also available from **61**, by different routes, are stable entities which accept oxygen atoms from a variety of reagents, *e.g.*, C_5H_5NO , to re-form **61** and liberate the alkyne.¹¹³ Obviously, the reactivity and stability of the $[Cp^*ReO_2]$ fragment is different from the one of the analogue fragment $[MeReO_2]$ which adds alkynes to give the complexes $MeReO_2(\eta^2-C_2 \equiv R_2)$.¹¹⁴

Reaction with oxophilic low-valent metal complexes also abstracts oxygen to form **70** and/or its derivatives like Cp^*ReOX_2 or Cp^*ReOR_2 ($R = Me, Ph, Bz, Np$; $R_2 = Me_2C(CH_2)_2$). The rich and synthetically useful chemistry as well as the structural features of these oxohalides and oxoalkyls which display a pronounced asymmetry of the Cp^* ring coordination, has also been partly reviewed.^{87b,c} Other derivatives of Cp^*ReOX_2 are the thiolates,¹¹⁵ glycolates,¹¹⁶ thioglycolates,¹¹⁶ and a variety of chalcogenates.¹¹⁷

$CpTiCl_3$, as well as a mixture of PPh_3/Me_3SiCl , perform the exhaustive reductive chlorination of **61** to Cp^*ReCl_4 (**79**) another useful starting material for a variety of Cp^*Re derivatives.^{87,115}

Cycloadditions of **61** to diphenylketene and SO_2 to give **73** and **74**, respectively, were observed,¹¹⁸ but as a result of its electronic richness, **61** does not undergo the synthetically important cycloaddition to unstrained $C=C$ double bonds to give glycolato complexes in contrast to $RtCo_3$ ¹¹⁹ and OsO_4 .¹²⁰ However, it was recently shown that strained olefins, *e.g.*, norbornene, norbornadiene, and, to a lesser

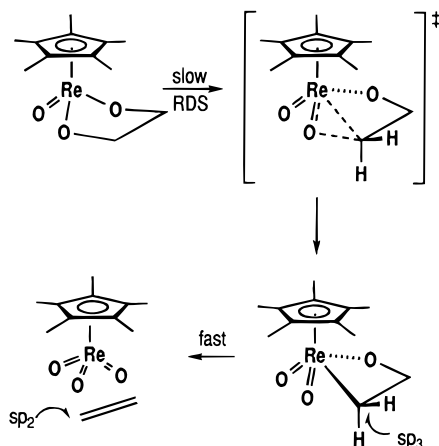
Scheme 15^a

^a (i) PPh₃/O₂; (ii) PPh₃; (iii) PPh₃/Me₃SiX; (iv) GeX₂ or [Cp₂ZrCl]₂; (v) PhSH; (vi) Me₃SnSnMe₃; (vii) norbornene; (viii) SO₂; (ix) Ph₂C=C=O; (x) PPh₃/MeC≡CMe; (xi) H₂O/py.

extent *trans*-cyclooctene, do undergo such cycloadditions forming glycolates like **75** (several isomers).¹²¹ For the first and last of these olefins, equilibria are obtained at temperatures between 90 and 125 °C whereas the second one reacts completely under these conditions. Independent syntheses of this type of glycolates and some thioglycolates, are available by straightforward substitution on **78**¹¹⁶ or **70** with glycols under basic conditions.¹²²

The kinetic and thermodynamic data gathered from the extrusion of alkenes from several glycolates is inconsistent with a [3 + 2] concerted addition for the reverse reaction, *i.e.*, the interaction of alkenes with Cp*ReO₃. Instead, the data support a stepwise mechanism with a metallaoxetane intermediate as proposed in Scheme 16.¹²³

Scheme 16

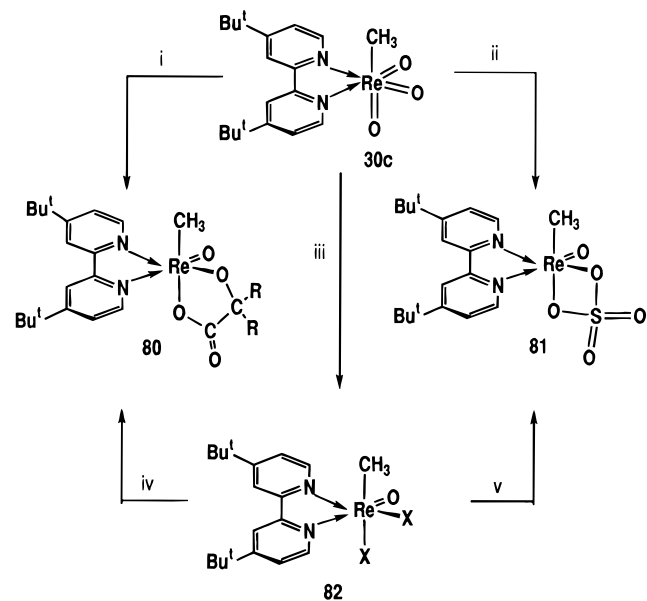


While MTO readily condenses with a number of diols and thiols to form glycolates and thiolates,

respectively, Cp*ReO₃ requires refluxing in toluene to react with HSPH. The rhenium(V) dithiolate Cp*ReO(SPh)₂ (**77**) is obtained probably by following reductive elimination of (PhS)₂ which is also isolated from the reaction mixture.¹¹⁵ The aminothiolo derivative [Cp*Re(1,2-S(NH)C₆H₄)₂] complex is readily formed from **61** and the amino thiol, although the dithiolate 1,2-(HS)₂C₆H₃-4-CH₃ does not react. Reduction also takes place on the formation of the bisstannoxy complex Cp*ReO(OSnMe₃)₂ (**76**).¹²⁴ The chemistry of most of these Re(V) complexes remains to be thoroughly explored.

b. Reactions of Octahedral [L₃ReO₃] Type Complexes. As expected from their structural and electronic similarities, the chemistry of these compounds resembles that of Cp*ReO₃, but some reactivity differences are apparent. The complexes [{HB(pz)₃}ReO₃] and [{B(pz)₄}ReO₃] (**27**) react with PPh₃ in the presence of excess Me₃SiX (X = Cl, Br) to give the dichlorides [L₃ReOX₂],^{49,125} whereas the more sterically crowded [{HB(3,5-Me₂C₃N₂H)₃}ReO₃] (**28b**) leads to inseparable mixtures of [{HB(3,5-Me₂-C₃N₂H)₃}ReO(OH)Cl] and [{HB(3,5-Me₂-C₃N₂H)₃}ReOCl₂] even under reflux.^{48b} In contrast with the similar reaction of Cp*ReO₃ which gives **79** under the same conditions, the remaining oxo ligand of [{HB(pz)₃}ReOX₂] cannot be removed by reaction with Me₃SiCl even in refluxing toluene. The reverse oxidation of [{HB(pz)₃}ReOX₂] (X = Cl, OR, Ph, Et, Bu) to **28a** has been mentioned in section II.A.6 and is further discussed in section III.^{46c}

In the presence of only PPh₃, **27** is reduced to the highly reactive green dimer [{B(pz)₄}ReO(*μ*-O)].^{49b} This analogue of **70** is readily reoxidized to **27** by DMSO and reacts with XH to give a variety of [{B(pz)₄}ReOX₂] derivatives (X = Cl, RS, RO, catechol,

Scheme 17^a

^a (i) $\text{Ph}_2\text{C}=\text{C}=\text{O}$; (ii) SO_2 ; (iii) $\text{PPh}_3/\text{Me}_3\text{SiCl}$; (iv) $\text{R}_2\text{C}(\text{OH})\text{CO}_2\text{H}$; (v) AgSO_4 .

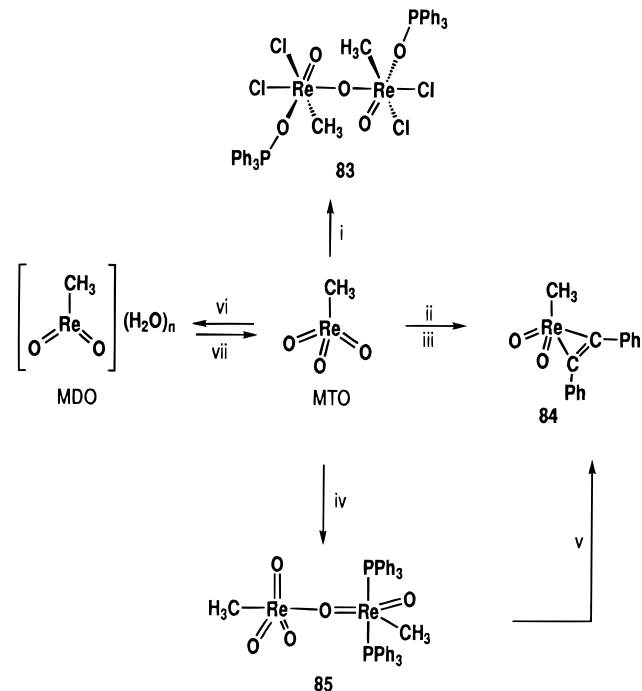
$\text{OCH}_2\text{CH}_2\text{O}$).^{49b,c} The corresponding cationic dimer $[(\text{tacn})\text{ReO}(\mu\text{-O})_2]^{2+}$ has also been made in a similar reduction from $[(\text{tacn})\text{ReO}_3]^+$ and PPh_3 .⁴⁵

The bipyridine adduct of MTO, $\text{MeReO}_3(\text{bipy})$ may also be regarded as another example of the L_3ReO_3 -type complexes like Cp^*ReO_3 , $[(\text{tacn})\text{ReO}_3]^+$ or $\{\text{HB}(\text{pz})_3\}\text{ReO}_3$. This analogy has been explored with the analogue $\text{MeReO}_3(\text{tBubipy})$ (**30c**) where the ^tBu substituents provide both enhanced stability and a useful NMR handle.^{66b}

Cycloadditions of both $\text{Ph}_2\text{C}=\text{C}=\text{O}$ and SO_2 , but not ethylene, occur readily to give the corresponding glycolato **80** and sulfato **81** complexes depicted in Scheme 17. In both cases the cycloaddition is regioselective only one isomer being formed (NMR evidence). This was confirmed by X-ray crystallography to be the one sketched as **80** in Scheme 17.

The corresponding cycloaddition of $\text{Ph}_2\text{C}=\text{C}=\text{O}$ to the monoadduct $\text{MeReO}_3(\text{tBupy})$ only proceeds cleanly upon addition of a second equivalent of ^tBupy in a close parallel to the reaction of OsO_4 with ethylene in the presence of pyridine.¹²⁰

The cycloreversion of **80** or of the parent glycolato $\text{MeRe}(\text{tBubipy})\text{O}(\text{OCH}_2\text{CH}_2\text{O})$ is not observed upon warming. However, SO_2 is readily eliminated from **81**. The partial reductive chlorination of $\text{MeReO}_3(\text{bipy})$ or **30c** with $\text{PPh}_3/\text{Me}_3\text{SiX}$ gives $\text{MeRe}(\text{L}_2)(\text{O})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$)^{65a} (**82**, $\text{L} = \text{bipy}$; ^tBubipy). This reaction is also regioselective, giving the product with the same coordination geometry as **80** or **81** as confirmed by an X-ray structure determination. Reaction of **30c** with α -hydroxy carboxylic acids under basic conditions, with glycolate or AgSO_4 leads to the chelates like **80** or **81**. The geometry is always the same and similar to the one obtained in the corresponding cycloadditions. Since **82** exists as a mixture of the two enantiomers, its reaction with enantiomerically pure (*S*)-(+)-mandelic acid originated two diastereomers which could be separated by crystallization as confirmed by NMR and the crystal structure of the *R,S* diastereomer.

Scheme 18^a

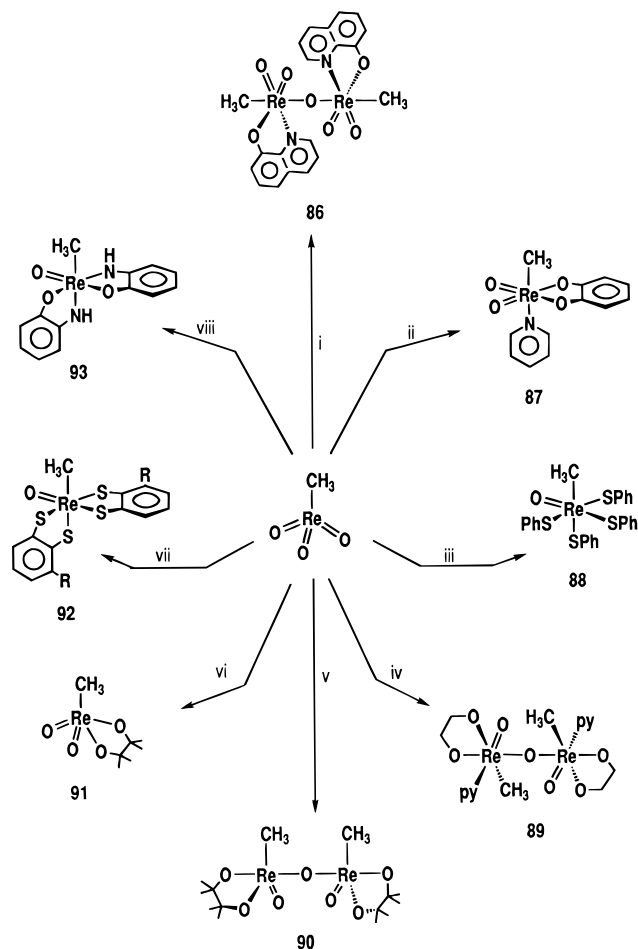
^a (i) $\text{PPh}_3/\text{Me}_3\text{SiCl}$; (ii) PPh_3 (polymer bound) + $\text{PhC}\equiv\text{CPh}$; (iii) $\text{H}_3\text{PO}_2 + \text{PhC}\equiv\text{CPh}$ in MeCN ; (iv) PPh_3 in Et_2O (also PCy_3); (v) $\text{PhC}\equiv\text{CPh}$; (vi) H_3PO_2 in H_2O ; (vii) DMSO , pyNO , VO_2^+ , MnO_4^- .

A number of other $\text{Re}(\text{V})$ derivatives were prepared from $\text{MeReOX}_2(\text{tBubipy})$ (**30c**), namely $\text{MeReOR}_2(\text{tBubipy})$, which can be considered as members of the large family of ReOX_3L_2 complexes, e.g., $\text{ReOCl}_2(\text{OR})\text{PPh}_3)_2$.²

c. Reactions of MeReO_3 (MTO). The mixture of $\text{PPh}_3/\text{Me}_3\text{SiCl}$ has been mentioned above as capable of performing total deoxygenation of Cp^*ReO_3 to Cp^*ReCl_4 and partial deoxygenation of $\{\text{HB}(\text{pz})_3\}\text{ReO}_3$ to $\{\text{HB}(\text{pz})_3\}\text{ReOX}_2$. In the case of MTO, the $\text{Re}(\text{VI})$ dimer **83** is formed (Scheme 18). It has a linear $\text{Re}-\text{O}-\text{Re}$ bridge.¹¹⁴

One of the earliest observations on the chemistry of MTO was the clean formal monodeoxygenation reaction that takes place when MTO is treated with $(\mu, \eta^5:\eta^5\text{-fulvalene})[(\eta^5\text{-CpZr}(\mu\text{-Cl})_2)_2]$ or, much more conveniently, with polymer-bound PPh_3 in the presence of a large variety of symmetric and asymmetric alkynes.^{126a} In the complexes $\text{MeReO}_2(\eta^2\text{-C}_2\text{RR}')$ the alkynes are strongly bound and do not rotate in the NMR time scale and no signs of further rearrangement to produce rhenapyranes, e.g., **72**, are detectable. The crystal structure of the tolane derivative **84** agrees with a description of the alkyne coordination as a metallacyclopropene. The typical distance for a $\text{C}=\text{C}$ double bond and ¹³C NMR supports its behavior as a two-electron donor, therefore making the complex an extreme case of a R_3ReO_2 complex. Further deoxygenation takes place in the presence of excess polymer bound PPh_3 , to give $\text{Re}(\text{VI})$ dimers with $\text{Re}-\text{Re}$ bonds^{126a} and not with $\text{Re}-\text{O}-\text{Re}$ bonds as initially interpreted.¹¹⁴

The very labile product of the reaction of MTO with PPh_3 (or PCy_3) (Scheme 18), was crystallographically identified as the dimer **85** which was recognized to be the previously described adduct " $\text{MeReO}_3(\text{PPh}_3)$ " by means of low-temperature ³¹P NMR.^{126b} This

Scheme 19^a

^a (i) 8-Hydroxyquinoline; (ii) catechol + py; (iii) 4PhSH; (iv) 1,2-ethylene glycol in MeOH + py; (v) pinacol in MeOH; (vi) pinacol in CH_2Cl_2 ; (vii) 1,2-benzenedithiol or 3,4-toluenedithiol; (viii) *o*-aminophenol.

complex proves the previously assumed simple oxygen abstraction from MTO by the phosphine but it also reveals that the complex $\text{MeReO}_2(\text{PPh}_3)_2$, although isoelectronic with the well-known $\text{IReO}_2(\text{PPh}_3)_2$,^{126c} is extremely labile and electron rich, being capable of donating electrons to another MTO molecule.

Compound **85** reacts with alkynes to give the expected $\text{MeReO}_2(\eta^2\text{-C}_2\text{RR}')$ derivatives. The Re(V) of "MeReO₂" is reoxidized by 9,10-phenanthroquinone to give a blue diolato complex stabilized by added pyridine, with a structure entirely analogous to the one determined for the catecholato complex **87** in Scheme 19.^{127c}

In acidic aqueous solution the formation of hydrated "MeReO₂", also termed MDO from *methylrhenium dioxide*, is accomplished by reaction of MTO with hypophosphorous acid ($\text{H}_2\text{P}(\text{O})\text{OH}$) which is oxidized to phosphorous acid, $\text{HPO}(\text{OH})_2$.^{126d} Under these conditions MDO is reoxidized to MTO by a variety of oxygen atom donors, like R_2SO , pyNO , VO^{2+} or MnO_4^- via a $[\text{MDO}\cdot\text{XO}]$ adduct (Scheme 18). MDO is also capable of reducing ClO_4^- and other oxanions and polymerizes to a blue-black precipitate.^{126d}

Another early detected type of reactions of MTO were the condensations with alcohols, amines, and

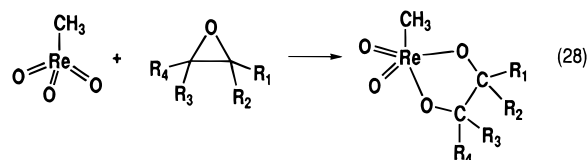
thiols. The first example was the reaction of MTO with 8-hydroxyquinoline, reaction i in Scheme 19, which led to an intermolecular condensation, whereby the structurally characterized dimer **86** was formed.^{127a} Double condensation occurs on reaction of MTO with PhSH, benzene-1,2-dithiol, toluene-3,4-dithiol and 2-aminophenol giving the mononuclear, monooxo products **88**, **92** ($\text{R} = \text{H}, \text{Me}$), and **93**, respectively.^{127a} Monocondensation is observed upon reaction of catechol or 2-aminothiophenol with MTO to give the deep blue products **87** and $\text{MeReO}_2(1\text{-S}, 2\text{-(NH)C}_6\text{H}_4)$ respectively.^{127c} Compound **88** is thermally labile and readily eliminates $(\text{PhS})_2$ upon warming leading to a dimeric Re(V) sulfur-bridged species.^{127c} A corresponding but much faster $(\text{PhS})_2$ elimination was proposed above for the reaction of Cp^*ReO_3 with PhSH.

Both complexes are stabilized by donor ligands like pyridine or halide ions to give octahedral adducts, e.g., $[\text{MeReO}_2(1,2\text{-O}_2\text{C}_6\text{H}_2\text{R}_2)\text{L}]^{0,-}$ ($\text{L} = \text{py}, \text{Cl}, \text{Br}, \text{I}$; $\text{R} = \text{H}, \text{Me}$). The two oxo groups occupy *cis* positions and the iodide is substitutionally labile.^{127b,c} The crystal structure of **87** confirms this coordination. Reaction of **87** with anhydrous HCl leads to $[\text{MeReO}_2(1,2\text{-O}_2\text{C}_6\text{H}_2\text{R}_2)\text{Cl}][\text{C}_5\text{H}_5\text{NH}]$.^{127b}

In spite of the pronounced reactivity of the $-\text{NH}_2$ groups in these kinds of condensations, a brief report on the monocondensation of MTO with *o*-phenylenediamine, to give $[\text{MeReO}_2\{o\text{-(HN)}_2\text{C}_6\text{H}_4\}]$ has appeared.⁵⁹

The similar condensation with aliphatic diols is much slower and is solvent dependent. When performed in MeOH in the presence of pyridine reduction takes place and Re(VI) dimers with linear Re–O–Re bridges are obtained, like **89**. In dichloromethane, pinacol reacts with MTO forming the yellow, sublimable pinacolato complex **91**.^{127d} All three glycolato complexes **89–91** were structurally characterized. Both the Re(VI) and Re(VII) pinacolato derivatives can be easily alkylated with ZnMe_2 or MeMgBr to the known $(\text{Me}_3\text{ReO})_2(\mu\text{-O})$.

Glycolato complexes are also accessible in high yields via the reaction of MTO with epoxides, eq 28.¹²⁸ Sterically hindered epoxides, e.g., *trans*-stilbene oxide do not react, suggesting that the coordination of the epoxide oxygen atom is the first step of the reaction. The glycolato complexes $\text{MeReO}_2(\text{OCR}_2\text{CR}_2\text{O})$ react with PPh_3 to form MTO, OPPh_3 and liberate the olefin $\text{CR}_2=\text{CR}_2$. This olefin extrusion is only very slow in the absence of phosphine.



10. Applications

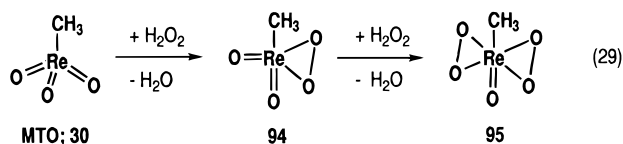
a. Catalytic Applications. 1. *Oxidation Catalysis.* Only a few years ago the importance of rhenium compounds in oxidation catalysis was not considered worth mentioning.¹²⁹ This picture changed drastically during the recent five years as organorhenium oxides, especially MTO, have proven to be

Table 15. Selected Bond Distances and Bond Angles of $\text{CH}_3\text{Re}(\text{O}_2)_2\text{O}$ (95**), $\text{CH}_3\text{Re}(\text{O}_2)_2\text{O}\cdot\text{H}_2\text{O}$ (**95a**), $\text{CH}_3\text{Re}(\text{O}_2)_2\text{O}\cdot\text{O}=\text{P}(\text{N}(\text{CH}_3)_2)_3$ (**95b**), and $(\mu\text{-O})_2\text{Re}_2(\text{O}_2)_4\cdot(\text{H}_2\text{O})_2$ (**96**)**

	95	95a	95b	96
bond distances				
Re—O	185(5) 188(5)	191.8(3) 190.4(3)	190.5(5) 192.1(5) 191.7(4) 191.5(5)	191.2(9) 187(1) 187(1)
Re=O	167(1)	166.8(6)	167.6(5)	167.4(9)
Re—C	201(4)	213.2(6)	213.2(7)	
Re—O _{br}				186(1) 190(1)
Re—O _L		225.3(4)	217.5(4)	221.7(9)
bond angles				
Re—O—Re				150.6(5)
C—Re=O	99(4)	95.6(3)	93.6(3)	
O=Re—O				97.2(5) 97.6(4)

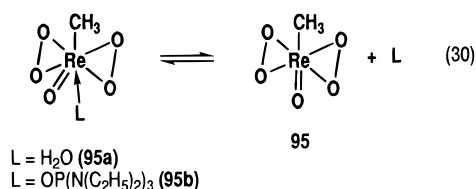
excellent oxidation catalysts. In the last few years, dozens of papers have appeared on the catalytic applications of MTO and related derivatives.^{130–141}

The catalytic activity of MTO in the oxidation of olefins was noticed soon after its discovery.¹³⁰ However, the breakthrough in the understanding of the role of organorhenium oxides in oxidation catalysis was the isolation and characterization of the reaction product of MTO with H_2O_2 . According to eq 29 a bis-peroxo complex of stoichiometry $(\text{CH}_3)\text{Re}(\text{O}_2)_2\text{O}$ (**95**) is formed.



In the solid state it is isolated as an adduct with a donor ligand L (L = H_2O , **95a**; L = $\text{O}=\text{P}(\text{N}(\text{CH}_3)_2)_3$, **95b**),^{75,131} which is lost in the gas phase. The structures of **95** (electron diffraction),⁶⁴ **95a**, and **95b** (X-ray diffraction) were determined and the selected bond angles and distances are given in Table 15. The ligand-free complex **95** has a trigonal-bipyramidal structure, with significant shorter Re—O and Re—C bond distances than in **95a,b**. This is very likely due to the enhanced Lewis acidity of the free complex **95**. If each peroxo group is considered a coordinative unit, the molecular structure of complexes **95a,b** can be also described as trigonal bipyramidal. The adduct **95a** melts at 56 °C and can be sublimed at room temperature in oil pump vacuum, whereas **95b** melts at 65 °C and decomposes at ~75 °C. Both are explosive.

¹⁷O NMR experiments showed that **95a,b** exchange their ligand L rapidly in solution^{13e,56b} and are in equilibrium with the uncoordinated form **95** (eq 30).



The terminal oxygen of **95a** is observed at $\delta(^{17}\text{O}) = 762$ ppm, the peroxo groups at $\delta(^{17}\text{O})$ 422 and 362 ppm, respectively. In **95b** the terminal oxygen is observed at $\delta(^{17}\text{O})$ 774 ppm. Only the terminal oxygen atom is involved in an exchange.^{13e,75,131}

Experiments with the isolated complex **95a** have shown, that it is an active species in oxidation catalysis, *e.g.*, in the oxidation of olefins.^{75,131} *In situ* experiments indicated that the reaction of MTO with 1 equiv of H_2O_2 leads to a monoperoxo complex **94** according to eq 29. Unfortunately, this complex has never been isolated and the known spectroscopic data, recorded *in situ*, remain rather poor for such a widely used compound. Spectroscopic data of **95a**, **95b**, and **94** are compared in Table 16.

Complex **94** is also catalytically active in certain oxidation processes as discussed below. The decomposition of **94** and **95** in solution was also examined.¹³³ In the presence of hydrogen peroxide they decompose to methanol and perrhenate ion with a rate that is dependent on $[\text{H}_2\text{O}_2]$ and $[\text{H}_3\text{O}^+]$.¹³³ The complex peroxide and pH dependences are explained by two possible pathways: attack of either hydroxide on **94** or HO_2^- on MTO. The bis-peroxo complex **95** decomposes much more slowly to yield O_2 and MTO.¹³³ Mechanistic studies in the gas phase showed that high-valent rhenium compounds, *e.g.*, derivative **95** and high-valent chromium compounds are oxygen-transfer reagents while iron derivatives usually catalyze the decomposition of H_2O_2 .^{132d} The activation parameters for the coordination of H_2O_2 to MTO have also been determined. They indicate a mechanism involving nucleophilic attack. The protons lost in converting H_2O_2 to a coordinated O_2^{2-} ligand are transferred to one oxide oxygen which remains at the metal as an aqua ligand. The rate of this reaction is not pH dependent.^{132c} The photochemical and photophysical behavior of **95** has also been closely examined.^{132e}

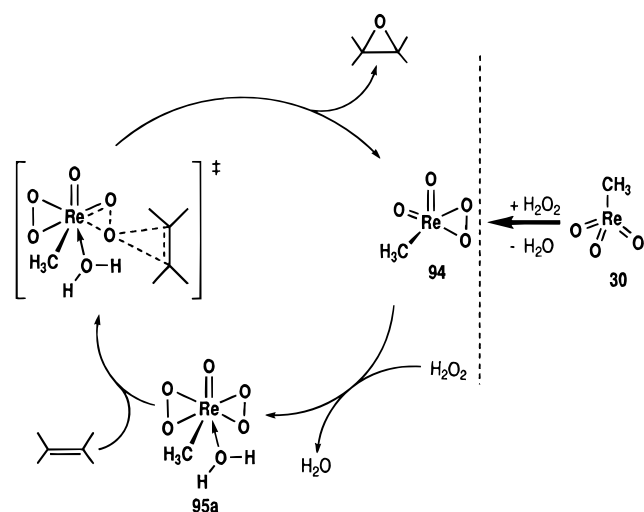
The amazing versatility of MTO as an oxidation catalyst precursor is seen on the fact that **94** and **95** perform on the catalytic oxidation of alkenes,^{74a,130,134} alkynes,¹³⁵ aromatic compounds,¹³⁶ sulfur compounds,¹³⁷ phosphines, arsines and stibines,¹³⁸ amines and other organonitrogen compounds,¹³⁹ halide ions,¹⁴⁰ and oxygen insertion into C—H bonds.¹⁴¹

One of the best examined catalytic processes, working with MTO as catalyst precursor, is olefin oxidation. H_2O_2 is normally used at <5 wt %, MTO typically in concentrations of 0.2–0.4 mol %. Turnover numbers up to 2000 mol (mol of catalyst)⁻¹ and turnover frequencies of ~1200 mol (mol catalyst)⁻¹ h⁻¹ can be reached. The catalytic system MTO/ H_2O_2 is already active below room temperature, *e.g.*, at -30 °C. The solvent, in which the highest product yields are obtained is *tert*-butyl alcohol. The reactions between **95** and alkenes are about 1 order of magnitude faster in the semiaqueous solvent than in methanol. The rate constants for the reaction of **95** with aliphatic alkenes correlate closely with the number of alkyl groups on the olefinic carbons. The reactions become markedly slower when electron-attracting groups, such as hydroxy, carbonyl, halo, and cyano are present. It has been suggested that a concerted mechanism in which the electron-rich

Table 16. Selected Spectroscopic Data on the Peroxo Compounds $\text{CH}_3\text{Re}(\text{O}_2)\text{O}_2$ (94**), $\text{CH}_3\text{Re}(\text{O}_2)_2\text{O}\cdot\text{H}_2\text{O}$ (**95a**), $\text{CH}_3\text{Re}(\text{O}_2)_2\text{O}\cdot\text{O}=\text{P}(\text{N}(\text{CH}_3)_2)_3$ (**95b**), and $(\mu\text{-O})\text{O}_2\text{Re}_2(\text{O}_2)_4\cdot(\text{H}_2\text{O})_2$ (**96**)**^{56,75,131,133}

	94	95a	95b	96
¹ H NMR (CH ₃) (THF)	2.4 ppm	2.71 ppm	2.54 ppm	
¹³ C NMR (CH ₃) (THF)		30.5 ppm	30.6 ppm	
¹⁷ O NMR (Re=O) (Et ₂ O)	778 ppm	760 ppm	774 ppm	816 ppm
IR (Re=O)		1020 cm ⁻¹ vst (THF)	992 cm ⁻¹ vst (CH ₂ Cl ₂)	1108 cm ⁻¹ vst (CH ₂ Cl ₂)
UV/vis	$\lambda_{\text{max}} = 305$ $\epsilon_{\lambda} = 600 \text{ L}/(\text{mol cm})$ (THF)	$\lambda_{\text{max}} = 364 \text{ nm}$ $\epsilon_{\lambda} = 700 \text{ L}/(\text{mol cm})$ (THF)		$\lambda_{\text{max}} = 350 \text{ nm}$ $\epsilon_{\lambda} = 1315 \text{ L}/(\text{mol cm})$ (THF)

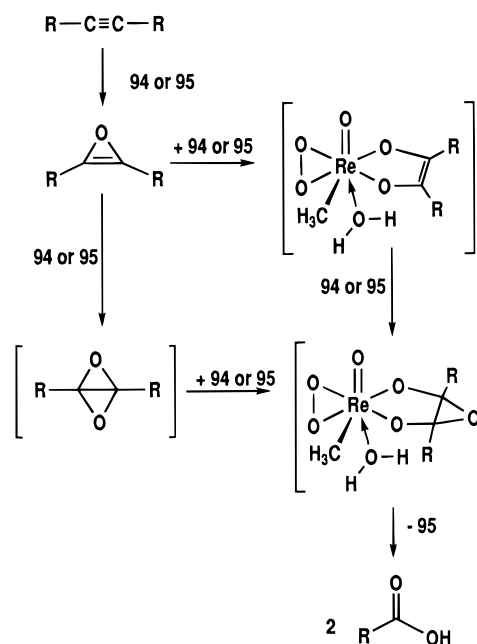
double bond of the alkene attacks a peroxidic oxygen of **95** takes place, according to Scheme 20.

Scheme 20

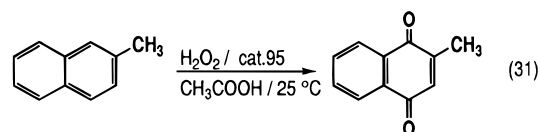
It has been deduced from experimental data that the system might show a spiro arrangement.^{74a,130,134a,e} The selectivity toward epoxides can be enhanced by addition of Lewis bases such as quinuclidine, pyridine, or 2,2'-bipyridine to the system.^{66c,d,74a} Diol formation is then suppressed. It has also been shown that the selectivity toward epoxides is dependent on the pK_b values of the Lewis bases used. The lower the pK_b values are, the higher the selectivity is.^{65,66} Excess of Lewis base usually leads to quicker reaction and better yields.^{66c} Another possibility of enhancing the selectivity toward epoxides is the use of the urea- H_2O_2 adduct. It allows the performance of the oxidation in water-free solutions, therefore, avoiding formation of diols and other side reactions. In the case of the oxidation of chiral allyl alcohols high diastereoselectivities have been reached.^{134c,f} Alkyl- and alkenylrhenium oxides of type RReO_3 form similar active species, but they are not so stable as **95**.^{13e,74a} The $\text{Cp}'\text{ReO}_3$ compounds are inactive in olefin epoxidation catalysis.^{74a,130,142}

In the oxidation of alkynes with hydrogen peroxide in the presence of MTO an oxirane intermediate has been postulated to be formed between the rhenium peroxo complex and the alkyne (Scheme 21).

Internal alkynes yield carboxylic acids and α -diketones. Rearrangement products were observed only for aliphatic alkynes. Terminal alkynes give carboxylic acids, derivatives thereof, and α -keto acids as the major products. The yields of these products vary with the solvent used.¹³⁵

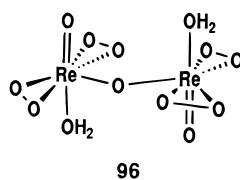
Scheme 21

The mechanistic aspects of the oxidation of aromatics have not been examined in great detail up to now. It seems to be clear, however, that complex **95** plays an important role as catalyst.¹³⁶ Especially noteworthy is the high regioselectivity, most notably in the industrial interesting synthesis of vitamin K3 (see eq 31).



Since water is an inhibitor, concentrated (85%) H_2O_2 is preferred. Alternatively, commercially available 35% H_2O_2 in acetic anhydride can be employed; a considerable regioselectivity is obtained with this system. The conversion improves for electron-rich arenes and values of nearly 100% and selectivities of more than 85% have been reached.^{136a} Hydroxy-substituted arenes can be oxidized by 85% aqueous hydrogen peroxide in acetic acid to afford the corresponding p -quinonones in isolated yields up to 80%.^{136d} Anisol, too, was found to undergo selective oxidation with the system $\text{MTO}/\text{H}_2\text{O}_2$ to yield o - and p -methoxyphenols. There is no need to use a solvent. It is assumed, that the active species in this system might be a highly electrophilic species.^{136b} It has also been shown that some other RReO_3 complexes and even

inorganic rhenium oxides, *e.g.*, Re_2O_7 and ReO_3 are surprisingly active in the oxidation of aromatic compounds.^{13e} The catalytically active species in the former case, **96**, has been isolated.



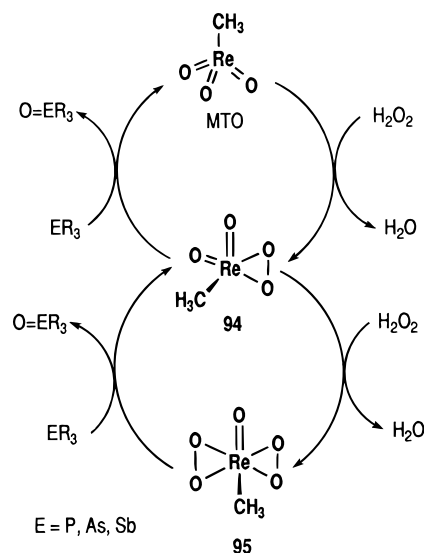
Spectroscopic and structural data are summarized in Tables 15 and 16. The hydrolysis product of **96** is perrhenic acid, which does not react with H_2O_2 . This explains why the $\text{Re}_2\text{O}_7/\text{H}_2\text{O}_2$ system must be used under anhydrous conditions to avoid early deactivation by hydrolysis. However, water is continuously formed when H_2O_2 acts as an oxidant. Thus, the ready hydrolysis of **96** is the intrinsic weakness of this species in oxidation by H_2O_2 .

Organic sulfides can be oxidized to the corresponding sulfoxides by hydrogen peroxide in the presence of MTO. Both complexes **94** and **95** seem to be active in this reaction, but kinetic results indicate that **94** might be more active than **95**. The kinetic results also point to a mechanism that involves the nucleophilic attack of the sulfur atom on a coordinated peroxide oxygen since electron-donating substituents have accelerating effects.^{137a} The first reports on the scope and selectivity of the reaction^{137b} were reexamined more recently. Using ethanol as solvent, the system $\text{MTO}/\text{H}_2\text{O}_2$ can be used to oxidize dialkyl, diaryl, and alkyl aryl sulfides to sulfoxides ($\text{R}_2\text{S}:\text{H}_2\text{O}_2 = 1:1.1$) or sulfones ($\text{R}_2\text{S}:\text{H}_2\text{O}_2 = 1:2.2$) with excellent yields and selectivity even in the presence of oxidatively sensitive functions on the side chain of the sulfides.^{137c} This mild selectivity has been also demonstrated in the oxidation of thioether Fischer carbene complexes.^{137d} Oxidation of thiophene and its derivatives has also been achieved with this system but with rate constants 2–4 orders of magnitude smaller than those reported for the “aliphatic” sulfides where the S atom is not part of an aromatic heterocyclic ring.^{137e} Oxidation studies of coordinated thiolates were carried out on the model Co(III) complex $[(\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)]^{2+}$. The thiolato complex is first oxidized to a sulfenato complex, $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)]^{2+}$, which is then more slowly oxidized to the sulfinato complex, $[(\text{en})_2\text{Co}(\text{S}(\text{O})_2\text{CH}_2\text{CH}_2\text{NH}_2)]^{2+}$. The second step is ~ 1500 times slower than the first. From these kinetic examinations **94** seems to be the catalytically active species which is attacked by the nucleophilic coordinated S atom.^{137f}

Tertiary phosphines, triphenylarsines, and triphenylstilbines are converted to their oxides, R_3EO ($\text{E} = \text{P}, \text{As}, \text{Sb}$) by $\text{MTO}/\text{H}_2\text{O}_2$. Kinetic studies led to the assumption that **94** and **95** have similar catalytic activities in all cases. The kinetic data support a mechanism involving nucleophilic attack of the substrate at the rhenium peroxides. The proposed catalytic cycle is given in Scheme 22.¹³⁸

The system $\text{MTO}/\text{H}_2\text{O}_2$ also catalyzes the oxidation of anilines. The major product of the oxidation of aniline is nitrosobenzene. For 4-substituted *N,N*-dimethylanilines, the *N*-oxide is the only oxidation

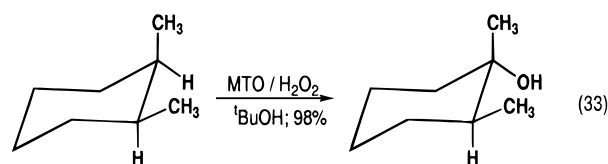
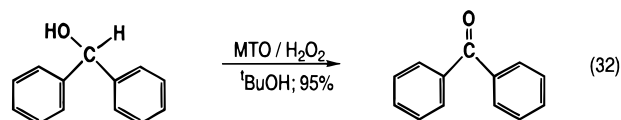
Scheme 22



product. Electron-withdrawing substituents inhibit the reaction. Both compounds **94** and **95** are involved in the oxidation process, according to kinetic results.^{139a} It is suggested that the rate-controlling step is the nucleophilic attack of the nitrogen lone pair electrons of anilines on a peroxidic oxygen of the catalyst. Electron-donating groups attached to the nitrogen atom of aniline increase the rate constant. In the case of ArNH_2 derivatives, the oxidation proceeds ~ 50 times quicker than without catalyst.^{139a} Furthermore, not only anilines but a broad variety of other aromatic and aliphatic amines are oxidized to the corresponding *N*-oxides. The reactions are facile and high yielding at room temperature or below.^{139b}

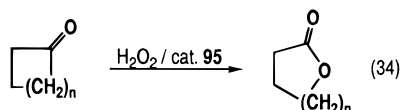
Another application of the system $\text{MTO}/\text{H}_2\text{O}_2$ is the catalytic oxidation of chloride and bromide ions in acidic aqueous solutions. The chloride oxidation steps are 3–4 orders of magnitude slower than the corresponding bromine oxidation steps. Both compounds **94** and **95** have been shown to be active catalysts in this processes. In both cases the catalyzed reactions were about 10^5 times faster than the uncatalyzed reactions under similar conditions. In a first step HOX is formed, then HOX reacts with X^- to X_2 . When H_2O_2 is used in excess, the reaction yields O_2 .^{140a,b}

$\text{MTO}/\text{H}_2\text{O}_2$ also catalyzes the insertion of oxygen into a variety of activated and unactivated C–H bonds with yields varying from good to excellent. Alcohols or ketones are formed as shown in eqs 32 and 33. Suitable substrates proved that the reaction



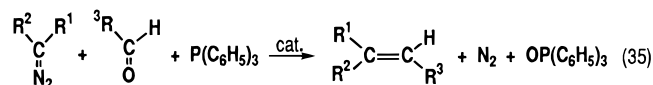
is stereospecific with retention of configuration. Alcohols, *e.g.*, ethanol and *tert*-butyl alcohol, are used as solvents, the reaction temperatures range between 40 and 60 °C and yields up to 98% have been obtained. However, the reaction times are generally longer than those used for most epoxidations, ranging between 10 and 72 h.^{134d}

It has been shown, that **95** also acts as the active species in the Baeyer–Villiger oxidation of ketones, eq 34, and in the Dakins reaction.¹⁴³



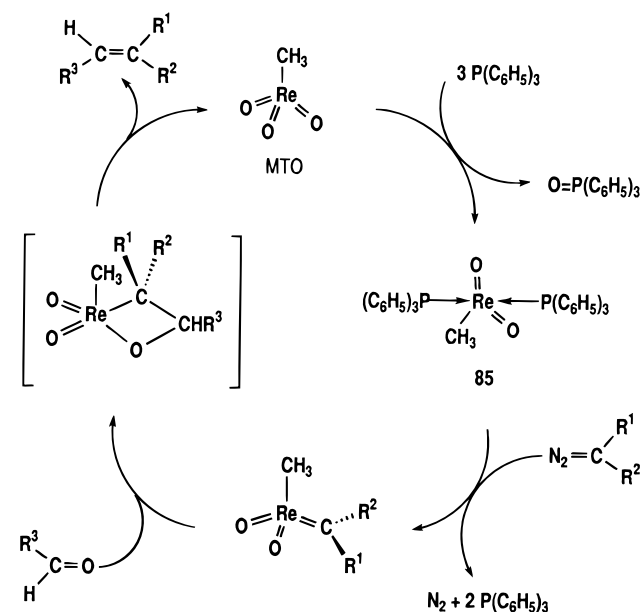
It is somewhat surprising that the MTO/H₂O₂ system presents this activity since these oxidations involve nucleophilic attack at the carbonyl group which contrasts with all the preceding examples where the substrates attacked the electrophilic Re–peroxo complexes, *e.g.*, in the olefin epoxidation. Indeed, **95** reacts stoichiometrically with cyclobutanone in the absence of H₂O₂ as in eq 34 (*n* = 1). This reversed behavior may be due to substrate binding to rhenium and the reaction was found to be strongly solvent dependent by means of the mechanistic probe for oxygen-transfer reactions, thianthrene 5-oxide.¹⁴³ Donor solvents such as acetonitrile seem to enhance the nucleophilicity of the peroxo groups. It has been suggested that the double bond of the enol form, the major tautomer, attacks a peroxo oxygen of the peroxorhenium complex **94** or **95**, respectively. This reaction affords a 2-hydroxy-1,3-dicarbonyl intermediate, which can be detected by ¹H NMR. This hydroxy intermediate is susceptible to cleavage via Baeyer–Villiger oxidation to yield carboxylic acids as final products. Low H₂O₂ concentrations are sufficient, and no H₂O₂ decomposition is observed at temperatures up to 70 °C. This is an advantage of the catalytic system MTO/H₂O₂ over the known transition-metal catalysts containing V, Mo, Mn, or Os. However, the nucleophilic character of the peroxidic atoms in **95** is not as pronounced as in Pt or Ir peroxo complexes that react with CO₂ or SO₂ to give isolable cycloaddition products.¹⁴³ In the case of **95** turnover frequencies of 18 000 mol (mol of catalyst)^{−1} h^{−1} are obtained in the case of cyclobutanone, in other cases turnover numbers up to 100 are usual.^{62b} Cycloketones can be converted into lactones even below room temperature (15 °C) by means of dilute hydrogen peroxide (10 wt %).

2. Aldehyde Olefination and Related Reactions. Aldehydes or strained cycloketones, treated with aliphatic diazoalkanes in the presence of an equimolar amount of a tertiary phosphine and MTO as catalyst, afford an olefinic coupling product in good yields already at room temperature according to eq 35.^{144a}



The *trans* selectivity is between 60 and 95%, depending on the substrate, and the yields are

Scheme 23



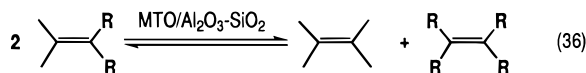
around 85%. The *trans* selectivity is higher when lower catalyst concentrations are used, but with catalyst concentrations below 5 mol % significant amounts of azines (RCH=N–N=CHR') are formed as undesired byproducts. However, the advantage of this method over Tebbe–Grubbs coupling is that it does not require the use of a stoichiometric amount of an organometallic coupling reagent. It has been shown by *in situ* NMR spectroscopy and isolation and crystallization of the reaction product of MTO with tertiary phosphines **85** (Scheme 18) that Re(V) species act as catalysts in this process. Therefore, ligand- or solvent stabilized methylidyne rhenium(V) seems to be the key compound in the olefination reaction cycle represented in Scheme 23.^{101,126a,144}

Methylidyne rhenium generated *in situ* is also able to abstract successively oxygen atoms from the notoriously sluggish oxidation agent perchlorate.^{144c} These observations explain the catalytic behavior: the Re–O bond is weaker than the Ti–O bond in the case of Tebbe–Grubbs reagents. Only the former is amenable to reductive elimination by phosphines as phosphine oxides. The deoxygenation of epoxides, sulfoxides, *N*-oxides, triphenylarsine, and triphenylstibine oxide at room temperature is also catalyzed by MTO with PPh₃ as oxygen acceptor. A possible reaction mechanism involves phosphine attack at a compound formed between MTO and the epoxide or other oxygen–donor compounds.^{144b} It is noteworthy in this context, that MTO was also found to be a good catalyst for the oxidation of tertiary phosphines by molecular oxygen at room temperature. Again, an intermediate of type **85**, containing the (ligand stabilized) “methylidyne rhenium”, seems to be involved.

Other organorhenium oxides form less active catalysts for aldehyde olefination. On the other hand, taking into account the findings that the catalyst is a Re(V) species derived from MTO, it was found that trichlorooxo rhenium(V) and derivatives are very active aldehyde olefination catalyst precursors, even more active than MTO.^{66b,145} Olefin yields of nearly 100% are reached, and the *trans* selectivity is con-

siderably higher than 90%. In contrast to the oxidation catalysis with organorhenium oxides the presence of a rhenium carbon bond seems not to be crucial for this process.

3. *Olefin Metathesis.* The system $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ is an effective heterogeneous catalyst for carrying out olefin metathesis under mild conditions, eq 36, and its activity can be further increased by the addition of tetraalkyl tin compounds, an observation that triggered the synthesis of MTO.¹⁴⁶

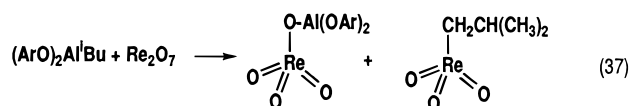


Since tin-containing cocatalysts are essential for the metathesis of functionalized olefins,¹⁴⁶ it was soon discovered that MTO and other R-ReO_3 oxides supported on acidic metal oxides form metathesis catalysts that are active without additives even for functionalized olefins.¹⁴⁷ Standard supports are $\text{Al}_2\text{O}_3\text{-SiO}_2$, or Nb_2O_5 and the activity is related to the surface acidity.¹⁴⁸ A high metathesis activity is observed when MTO is chemisorbed on the surface. No evidence for a surface carbene species was obtained, but there appears to be a correlation between the catalytic activity and the presence of an alkyl fragment on the surface.^{147,148} The surface-fixed catalyst is significantly more sensitive to water than the free MTO, being rapidly decomposed to methane, ethylene, and perrhenate in the presence of moisture. Free MTO can neither be removed from the surface with solvents nor sublimed out of the carrier at temperatures up to 150 °C. At higher temperatures decomposition accompanied by predominantly methane and ethylene evolution is observed.¹⁴⁷ The carbene species which is implied in the metathesis catalytic cycle seems not to originate from the methyl group of MTO.^{148b} It was also possible to encapsulate MTO in zeolite, maintaining its metathesis activity. IR and EXAFS data indicate that the structure of MTO remains unchanged and that it is anchored by hydrogen bridges to the zeolite oxygens.^{149a,b} There is evidence in the case of zeolite Y that the loading level of MTO corresponds to 4 molecules per supercage. The still intact molecules of MTO can either hydrogen bond to Bronsted acid sites or interact with extraframework cationic sites in the supercages of M_{56}Y , where $\text{M} = \text{H}, \text{Na}, \text{Rb}$. The favored anchoring interaction is found to be $\text{CH}_3\text{ReO}_3 \cdots \text{MOZ}$, in which the oxygen end of the bond in MTO binds preferentially to supercage cation or proton sites. The guest molecules associate through $\text{Re}=\text{O} \cdots \text{Re}$ interactions. The formation of these aggregates of MTO is induced by the high Lewis acidity and intense electric fields associated with the anchoring cation or proton sites, respectively. Adsorption of water causes the deaggregation of the guest molecules. Thermal treatment around 120 °C is found to yield methane and water together with the formation of an intrazeolite cluster species containing Re-Re bonds.^{149c}

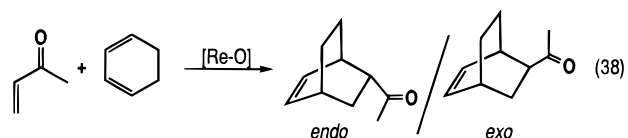
The MTO supported on $\text{Al}_2\text{O}_3\text{-SiO}_2$ catalyzes in particular the self-metathesis of allyl aldehydes, ethers, silanes, and unsaturated carboxylates and nitriles, but also the ethenolysis of olefins with internal double bonds.⁹⁷ The catalyst system is also

suitable for the metathesis of simple open-chain and cyclic olefins. Otherwise frequent side reactions such as double-bond isomerization and olefin dimerization are insignificant. Ring-opening polymerization is catalyzed by the homogeneous catalyst $\text{MTO}/\text{R}_n\text{-AlCl}_{3-n}$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n = 1, 2$). As in the case of the heterogeneous olefin metathesis the reaction can be performed at room temperature.¹⁴⁷

Bis(2,6-di-*tert*-butyl-4-methylphenoxy)isobutylaluminum reacts with Re_2O_7 to give complexes containing aluminum coordinated with perrhenate and 2,6-di-*tert*-butyl-4-methylphenoxy ligands which are new active catalysts for the metathesis of alkenes without the help of any cocatalyst (eq 37). Turnover frequencies up to 3500, strongly dependent on the substrate used, have been reached.¹⁵⁰



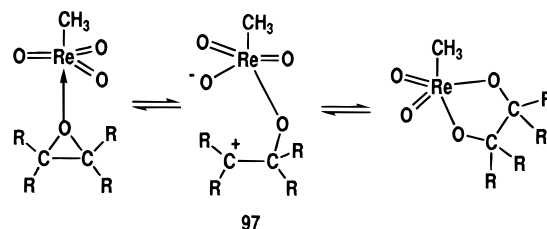
4. *Other Catalytic Reactions.* There are some other catalytic applications of organorhenium oxides, mainly of MTO, which have not yet been examined in great detail. For instance, MTO enhances the Diels–Alder reactivity of unsaturated $\text{C}=\text{C}$ compounds the standard case of which is given in eq 38.^{151a}



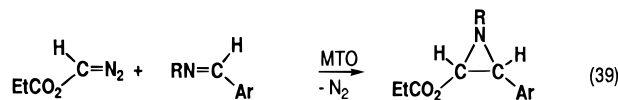
The use of MTO allows the combination of the Diels–Alder reaction with a subsequent epoxidation reaction. Besides MTO several other Re(VII) oxides catalyze the Diels–Alder reaction, due to their Lewis acidity. In the case of Re_2O_7 turnover frequencies of 4000 mol (mol of catalyst)⁻¹ h⁻¹ are reached at room temperature, using 0.05 mol % catalyst. In the specific example of eq 38 the *endo* selectivity is 98%.^{151a}

In the presence of MTO the catalytic alkoxylation of cyclohexene oxide with secondary and tertiary alcohols can be performed. This catalyst is known to cause disproportionation of epoxides, yielding olefins and diols. FT-IR spectroscopy indicated the formation of an active intermediate composed of MTO and an oxirane which evolves as depicted in Scheme 24. The carbocationic species **97** must be regarded as highly reactive with respect to nucleophilic compounds.^{151b}

Scheme 24

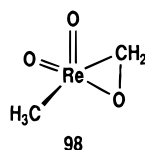


A third very recent application is the conversion of aromatic imines to aziridines by catalytic amounts of MTO with ethyl diazoacetate, as in eq 39.



R = Ph, Bu, Hex

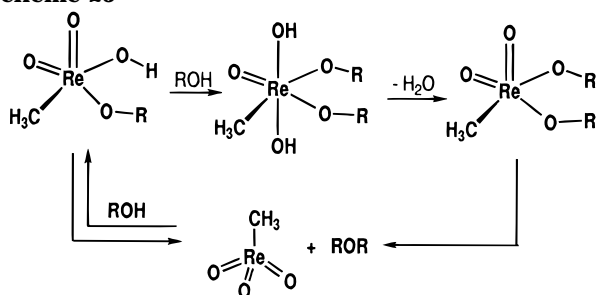
The same type of cycloadditions occurs between ethyl diazoacetate and olefins or carbonyl compounds, in the presence of catalytic amounts of MTO, to produce cyclopropanes, and epoxides, respectively. The mechanism of these transformations is unknown, but a metal-carbene intermediate seems plausible thus making MTO the first high-valent oxo complex for carbene transfer. The presence of an oxyethylidene type active species **98**, analogous to **94**, is proposed.^{151c}



Under mild conditions and in the absence of other substrates ethyl diazoacetate is converted to a 9:1 mixture of diethyl maleate and diethyl fumarate. In the presence of alcohols α -alkoxy ethyl acetates were obtained in good yield. An electron-donating group in the *para* position of phenols favors the formation of α -ethyl acetates. In the presence of an oxygen source such as an epoxide, ethyl diazoacetate and azibenzil are converted to an oxalic acid monoethyl ester and to benzil. Epoxide is converted to an olefin.^{151e}

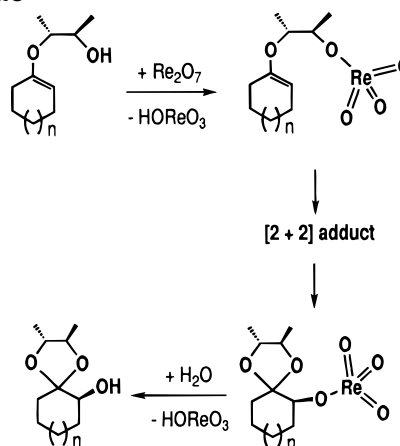
MTO has also been claimed to be the first transition metal complex to catalyze the direct, solvent independent formation of ethers from alcohols. Aromatic alcohols give better yields than aliphatic ones and reactions between different alcohols have been used to prepare asymmetric ethers. Also, catalyzed by MTO is the dehydration of alcohols to form olefins at room temperature. When primary or secondary amines, respectively, are used as the limiting reagents, direct amination of alcohols gives the expected secondary or tertiary amines in yields of ~95%. Disproportion of alcohols to carbonyl compounds and alkanes is also observed for aromatic alcohols in the presence of MTO as catalyst. Hypothetic rhenium compounds which might act as intermediates in these processes are given in Scheme 25.^{151d}

Scheme 25



Some organic reactions working with Re(VII)oxo complexes do not work with MTO or related organometallic compounds but do work with stoichiometric amounts of inorganic Re complexes. One example is the oxidation of homochiral ketals by Re₂O₇. Stereochemical complex 2-(hydroxymethyl)tetrahydrofurans can be prepared via Re₂O₇-mediated oxidation of 5-hydroxyketals. 2-Hydroxyethyl enol ethers react with Re₂O₇ to produce 2-hydroxyketals. Where homochiral starting enol ethers are employed, diastereoselectivities greater than 99:1 are obtained. The stereocontrol is rationalized by invoking a transition state that approximates the geometry of a metalla-oxethane. A possible mechanism of this reaction type is shown in Scheme 26. Homochiral ketals are

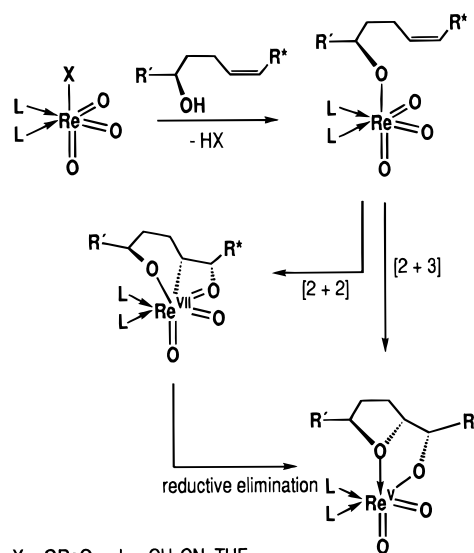
Scheme 26



themselves oxidized to provide 2-hydroxyketals with high diastereoselectivity.¹⁵²

Acyl perrhenates were used to induce tandem *syn*-oxidative cyclizations of hydroxydienes. The acyl-perrhenate reagent seems to represent a comparatively general solution to the problem of tandem *syn*-oxidative cyclizations of acid-sensitive hydroxy diene models for biomimetic synthesis routes to chain polymers. A proposed mechanism is shown in Scheme 27.¹⁵³

Scheme 27



X = OReO₃, L = CH₃CN, THF

X = RC(O)O, L = CH₃CN, THF

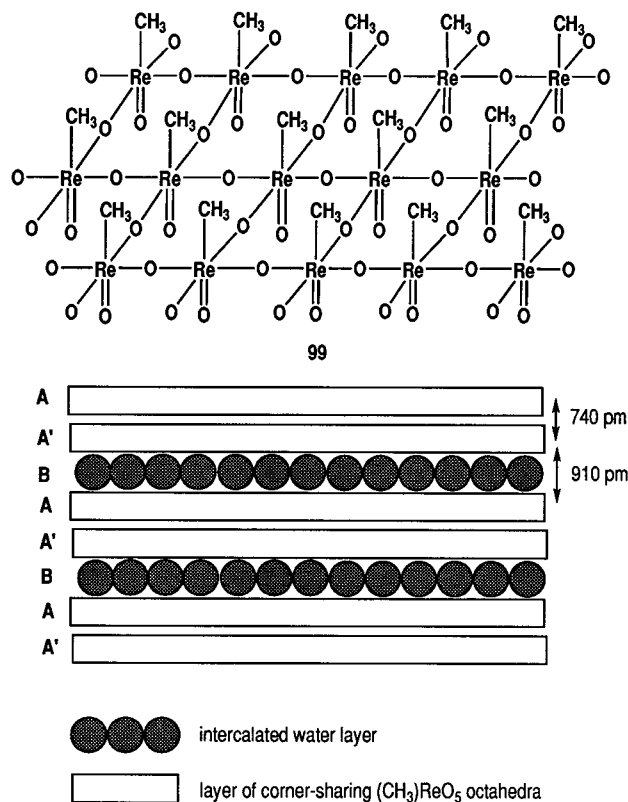
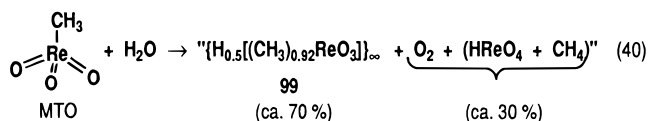


Figure 1. Stacking model for "crystalline" areas of "poly-MTO".

b. Materials Science Aspects: Polymeric MTO.

Heating MTO in aqueous solution for several hours at 70 °C leads to the formation of a golden colored, polymeric compound of empirical formula $\{H_{0.5}[(CH_3)_{0.92}ReO_3]\}_n$ (**99**) in high yield (eq 40).^{69a,106} This compound is the first example of a polymeric organometallic oxide.



The structure of the crystalline domains of **99** can be described as double layers of corner-sharing CH_3 - ReO_5 octahedra (AA') with intercalated water molecules (B) in a ...AA'BAA'... layer sequence (see Figure 1).

It adopts the three-dimensional extended ReO_3 motif in two dimensions as a $\{ReO_2\}_n$ network. 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 unpolar methyl groups which are orientated inside the double layer. These structural features explain the observed lubricity of **99**. Understoichiometry 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 **99**.^{69a,106}

For the amorphous areas of **99** a model with turbostratic and 001 defect stacking of double layers

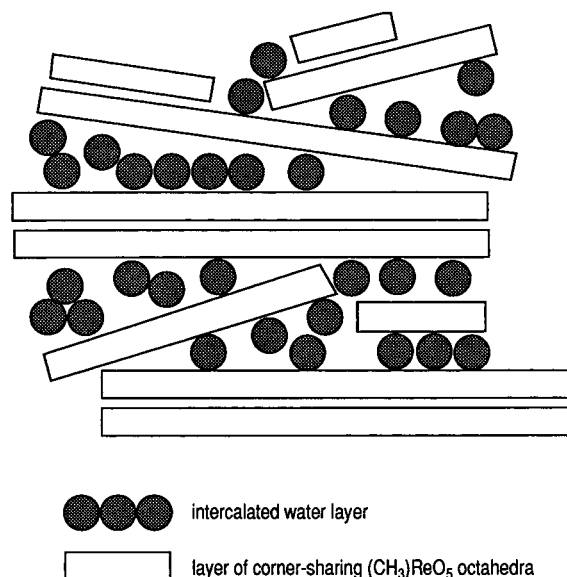


Figure 2. Turbostratic and 001 defect stacking model for "crystalline" areas of "poly-MTO".

of corner sharing $(CH_3)ReO_5$ octahedra with smaller water content has been proposed (Figure 2).^{69a,106}

As compared to the classical ReO_3 -type structure, an additional CH_3 group present in **99** cannot connect adjacent layers by acting as bridging ligand. Elimination of this CH_3 group from **99** under thermal or photochemical conditions leads to the three-dimensional ReO_3 structure only with small structural changes.^{63b,68a,106}

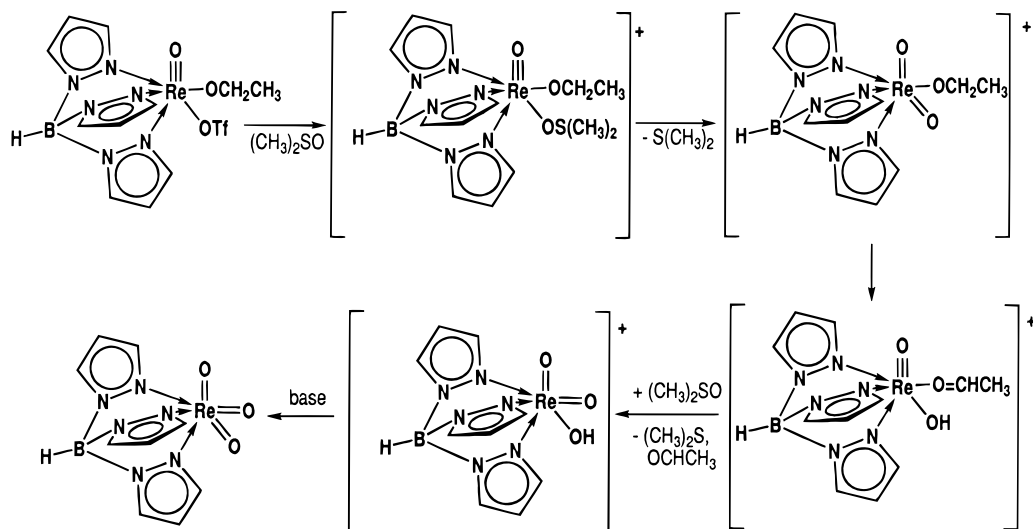
To explain the conductivity of **99** in greater detail, EHMO calculations have also been performed.^{69b} The band structure of **99** resembles that of ReO_3 , but important differences arise from its two-dimensional nature. The conductivity of **99** is attributed to occasional demethylation and to the inclusion of extra hydrogen in the lattice. Due to the polymeric nature of **99**, rhenium centers missing methyl groups are found to be oxidized rather than reduced. The included hydrogen is protonic and provides further reduction of the Re and weakens locally some of the Re-O bonds.^{69b} A theoretical study of MTO dimers, trimers, and tetramers has appeared. The tetramer already provides a good model for the interpretation of the IR and Raman spectra of poly-MTO and assigns the bridging oxygen atoms as the best candidates to bind the excess protons present in poly-MTO.^{69c}

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.^{62b,99c} Cyclopentadienylrhenium(VII) oxides are insoluble in water. All organorhenium(VII) oxides of type $RReO_3$, including MTO and **99** are sensitive to OH^- ions. In basic solutions they decompose quickly under formation of perrhenate.^{62b} The decomposition in acidic medium is very slow.¹⁵⁴

III. The L_3ReO_2 Compounds and Derivatives

A. Inorganic X_3ReO_2 Derivatives

The simplest compound in this class, ReO_2F_3 , was first prepared by fluorination of $KReO_4$ under con-

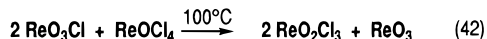
Scheme 28^a

trolled temperature (100 °C) where the contamination of ReOF_5 can be reduced to 1/10.¹⁵⁵ Fluorination of Re_2O_7 at 200 °C is, however, a better procedure.^{155c} This pale yellow compound melts at 90 °C and sublimes *in vacuo*. It is readily hydrolyzed to HF and HReO_4 . The octahedral adducts $[\text{ReO}_2\text{F}_4]\text{M}$ (M = Na, K, Rb, Cs, Ag) are obtained on dissolution of the corresponding ReO_4M salt in BrF_3 .^{158a} The same compounds are obtained by reaction of ReO_2F_3 with MF salts at 200 °C.^{158b} The fluoride analogue ligand OTeF_5 forms the complex $\text{ReO}_2(\text{OTeF}_5)_3$ in the clean reaction of eq 41.^{159a,b}



The structure of $\text{ReO}_2(\text{OTeF}_5)_3$ has been assigned by means of ^{19}F and ^{125}Te NMR and Raman data as trigonal bipyramidal with both $\text{Re}=\text{O}$ bonds on the equatorial plane.^{159b} The complex is a Lewis acid and readily adds another OTeF_5 anion to give the octahedral *cis*- $[\text{O}_2\text{Re}(\text{OTeF}_5)_4]^-$ anion, isolated and structurally characterized as its NMe_4^+ salt.^{159b}

Improved preparations of ReO_2Cl_3 were developed by double decomposition reactions as the one in eq 42.



The dark brown trichloride (mp 45 °C) is purified by sublimation. Mention is made of adducts with dioxane, DMSO, DMF, and other ligands but no details are given.¹⁶⁰ The adduct $[\text{ReO}_2\text{Cl}_4]\text{Cs}\cdot\text{CsCl}$ has an unknown structure.¹⁶¹

Reaction of Re_2O_7 with HF in ethanol gave a mixture of products where $[\text{ReO}_2(\text{OEt})\text{F}_3]^-$, $[\text{ReO}(\text{OEt})\text{F}_4]$, $[\text{ReO}_2\text{F}_4]$, and ReO_3F were identified by ^{19}F NMR.¹⁶² Another alkoxide with the general formula $\text{ReO}_2(\text{OR})_3$ was mentioned in Schemes 5 and 6.

As mentioned in section II.A.6, the oxidation of $[\{\text{HB}(\text{pz})_3\}\text{ReO}(\text{OR})_2]$ with pyNO or DMSO produces $[\{\text{HB}(\text{pz})_3\}\text{ReO}_3]$ (**28a**) together with aldehydes or ketones.^{46c} The detailed study of the mechanism of this reaction using the oxidation of $[\{\text{HB}(\text{pz})_3\}\text{ReO}(\text{OEt})(\text{OTf})]$ (Scheme 28) revealed the intermediacy of a very labile and strongly electrophilic $\text{Re}(\text{VII})$

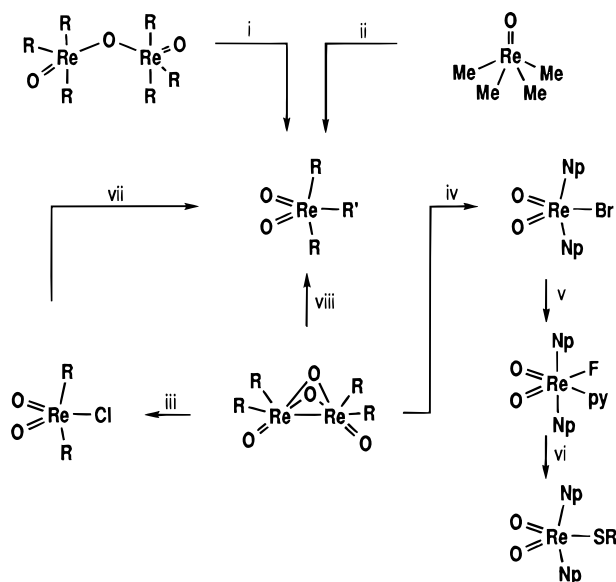
dioxo complex $[\{\text{HB}(\text{pz})_3\}\text{ReO}_2(\text{OEt})\text{OTf}]$ formed after displacement of triflate by DMSO and subsequent loss of Me_2S . This dioxo complex was not observed directly but is indicated by kinetic, labeling and NMR studies and the high electrophilic character of its oxo ligands is responsible for the proposed intramolecular hydride transfer from the alkoxide to an oxo group.

B. Organic and Mixed Derivatives

In contrast to compounds of type RReO_3 only very few examples of R_3ReO_2 compounds are known although the methyl derivative Me_3ReO_2 (**100**) was the first organorhenium(VII) oxide to be synthesized by the reaction of Me_4ReO with NO at -78 °C.¹⁶³ Compound **100** is a liquid at room temperature and can be easily distilled under vacuum. A more reliable synthesis uses the oxidation of the $\text{Re}(\text{VI})$ dimer $[\text{Me}_3\text{Re}(\text{O})]_2(\mu\text{-O})$ with Me_3NO ⁴¹ following the method used to prepare $(\text{Me}_3\text{SiCH}_2)_3\text{ReO}_2$ from $[(\text{Me}_3\text{SiCH}_2)_3\text{Re}(\text{O})]_2(\mu\text{-O})$.¹⁶⁴ The neopentyl derivative, $(\text{Me}_3\text{CCH}_2)_3\text{ReO}_2$ was prepared by reaction of $\text{Me}_3\text{SiOReO}_3$ with $\text{Al}(\text{Me}_3\text{CCH}_2)_3$.⁴² A gas-phase structure of **100** shows the two oxygen atoms lying on the equatorial plane of a trigonal bipyramidal-coordination geometry,⁶⁴ the same that is present in the crystal structure of $(\text{Me}_3\text{CCH}_2)_3\text{ReO}_2$,⁴² $(\text{Me}_3\text{CCH}_2)_2\text{PhReO}_2$,¹⁶⁷ and was also spectroscopically assigned to $(\text{Me}_3\text{SiCH}_2)_3\text{ReO}_2$.¹⁶⁴

Oxidation of the $\text{Re}(\text{VI})$ dimer $(\text{Me}_3\text{CCH}_2)_4\text{Re}_2\text{O}_4$ with X_2 (X = Cl, Br) leads to $(\text{Me}_3\text{CCH}_2)_2\text{XReO}_2$ which is suggested to have a trigonal-bipyramidal structure (with the two neopentyl groups in apical *trans* positions).¹⁶⁵ These compounds add pyridine to give the octahedral $(\text{Me}_3\text{CCH}_2)_2\text{XReO}_2(\text{py})$ with a *cis*-dioxo geometry (X-ray for X = Br). Upon reaction of $(\text{Me}_3\text{CCH}_2)_2\text{BrReO}_2$ with AgBF_4 , the pyridine-stabilized fluoride $(\text{Me}_3\text{CCH}_2)_2\text{FReO}_2(\text{py})$ is formed attesting the high Lewis acidity of the cation $[(\text{Me}_3\text{CCH}_2)_2\text{ReO}_2]^+$, isoelectronic with the known (mesityl)₂- MoO_2 .¹⁶⁶

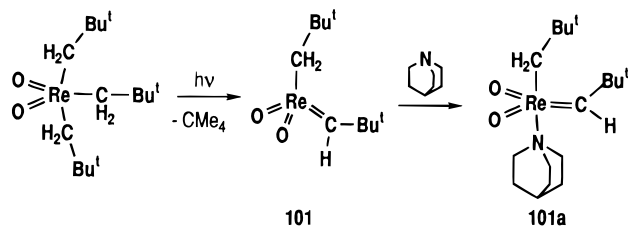
Other simple substitutions on $(\text{Me}_3\text{CCH}_2)_2\text{XReO}_2(\text{py})$ produce $(\text{Me}_3\text{CCH}_2)_2(\text{SR})\text{ReO}_2$ (R = Me, Ph) and $(\text{Me}_3\text{CCH}_2)_2(\text{OR})\text{ReO}_2$ (R = Me, ^tBu, CH_2CM_3),^{76b} whereas alkylation of $(\text{Me}_3\text{CCH}_2)_2\text{ClReO}_2(\text{py})$ with $\text{Zn}(\text{CH}_2\text{Me}_3)_2$ leads to $(\text{Me}_3\text{CCH}_2)_3\text{ReO}_2$.¹⁶⁵ Analogous alky-

Scheme 29^a

^a (i) Me₃NO or pyNO; (R = Me, CH₂SiMe₃); (ii) NO (-78 °C); (iii) Cl₂/py; (iv) Br₂ (pentane); (v) AgBF₄; (vi) Me₃SiSR; (vii) ZnR'₂ (R = R' = Me, CH₂SiMe₃; R = CH₂Me₃, R' = Me, Ph, CH₂SiMe₃); (viii) Al(CH₂Me₃)₃.

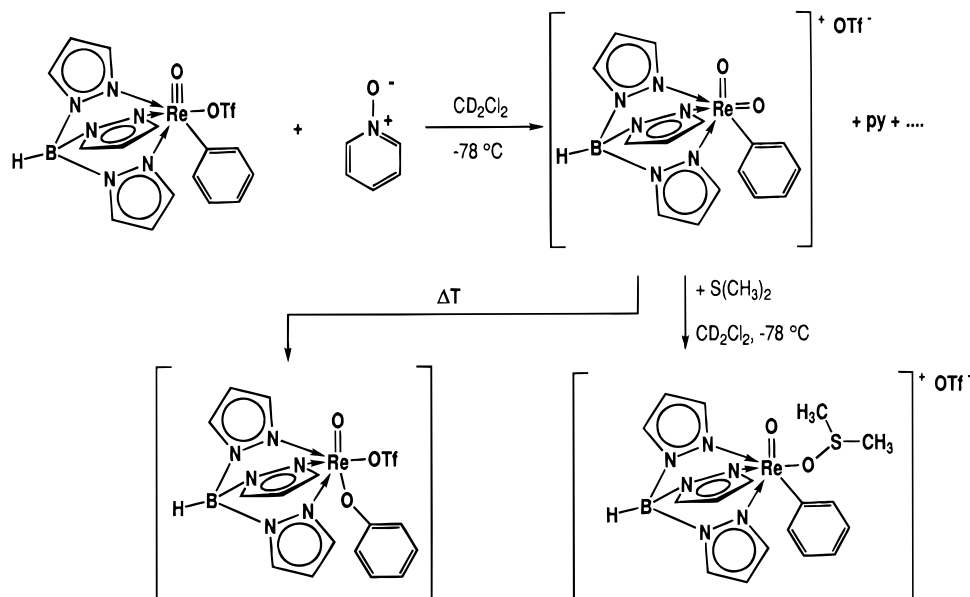
lations performed with appropriate zinc reagents lead to the mixed derivatives (CH₂CMe₃)₂RReO₂ (R = Me, CH₂SiMe₃, Ph)¹⁶⁷ (Scheme 29). Some related complexes of type MeReO₂(OR)₂ are mentioned in Scheme 19 (**86**, **87**, and **91**) and result from transformations of MTO.

Scheme 30



Reduction takes place on the attempted synthesis of the aryl analogues with formation of Ar₂ReO₂ (Ar

Scheme 31



= *o*-tol, xyl) from Me₃SiOReO₃ and the respective Grignard reagents.¹⁶⁸ The paramagnetic dioxide mes₂ReO₂ reacts rapidly and quantitatively both with NO to give the amido derivative mes₂NReO₃ (**17**) and with NO₂ to give the known mesReO₃ (**54**) (eq 11).⁴³

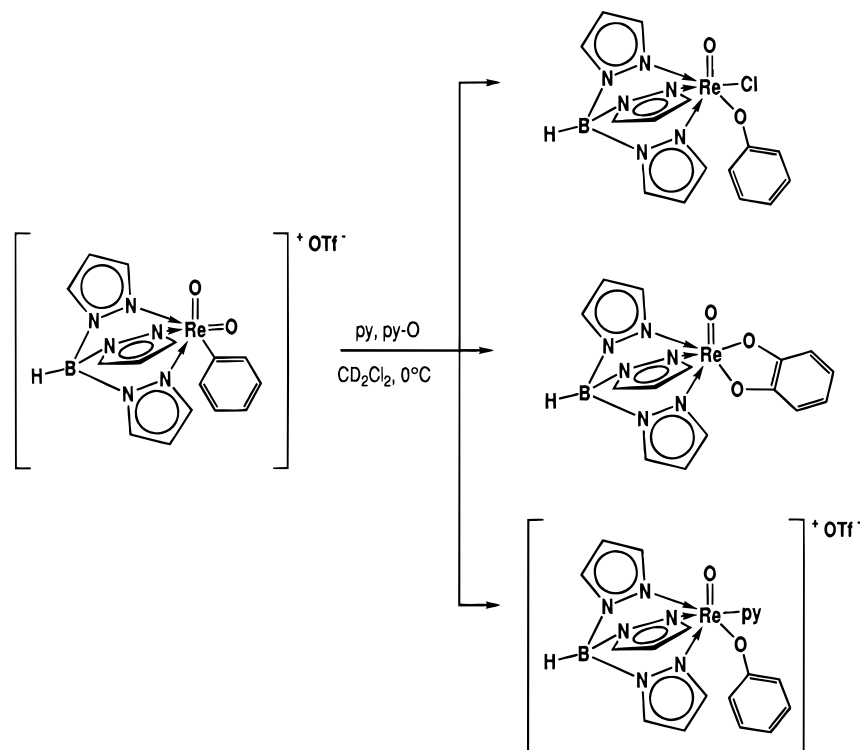
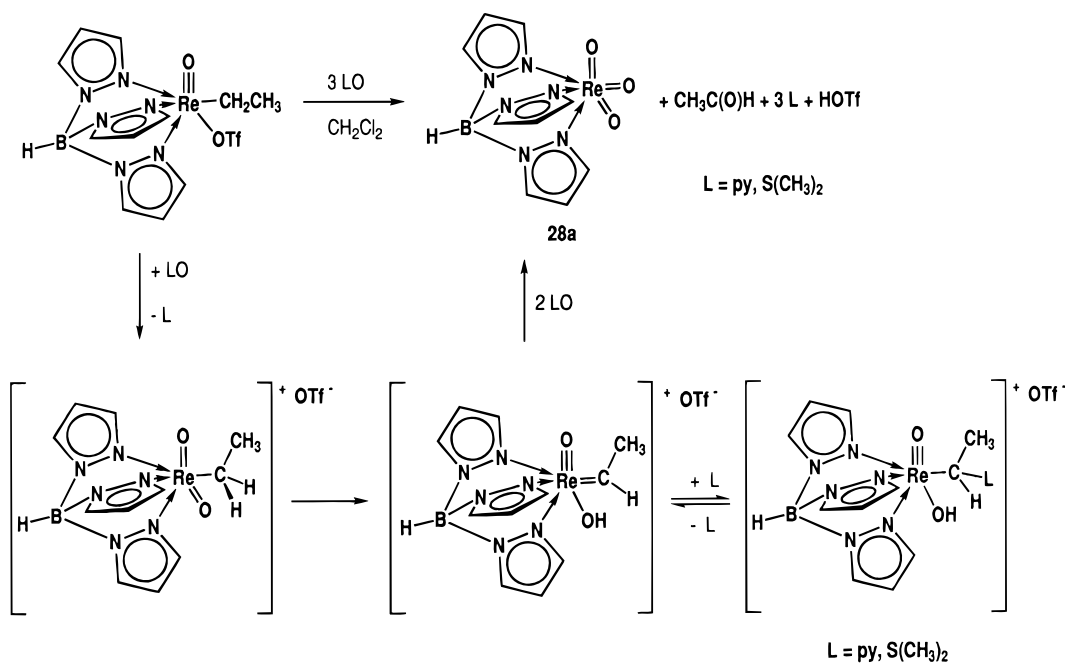
Very little is known about the chemistry and catalytic activity of all these complexes. Not surprising in view of its synthesis, deoxygenation of (Me₃-SiCH₂)₃ReO₂ occurs readily with PPh₃ to give [(Me₃-SiCH₂)₃ReO]₂(μ-O).¹⁶⁴ More interesting, however, is the result of the photolysis of (Me₃CCH₂)₃ReO₂ in pyridine. Neopentane is liberated and the alkylidene complex (Me₃CCH₂)₂ReO₂{C(H)CMe₃} (**101**) is formed.^{76a,167} It has the distorted tetrahedral structure expected for a formal analogue of RReO₃ or RRe(NR)₃ since the alkylidene ligand is isoelectronic with both =O and =NR. Several imido analogues of **100** are described in section VI. Interestingly, like all the RReO₃ compounds, but not RRe(NR)₃, **101** also adds quinclidine to give a trigonal bipyramidal adduct, **101a** where the two Re=O and the Re=C bonds lie on the equatorial plane (X-ray) (Scheme 30).^{76a,167}

Photolysis or thermolysis of (CMe₃CH₂)₂PhReO₂ in pyridine eliminates neopentylbenzene and forms the Re(V) complex (CMe₃CH₂)ReO₂(py)₃ which possesses a *trans*-ReO₂ moiety.¹⁶⁷ The py ligands are rather labile and are readily replaced by alkynes to give the complexes (CMe₃CH₂)ReO₂(R'CCR) (R = R' = Me; R = H, R' = Ph).¹⁶⁷

Extension of the oxygen-transfer chemistry described in Scheme 28 to the organometallic Re(V) complexes [{HB(pz)₃}ReOR(OTf)] produced the highly reactive Re(VII) cations [{HB(pz)₃}ReO₂R]⁺ (R = Ph, Et, Bu) as the triflate salts.^{46e,f} The phenyl derivative [{HB(pz)₃}ReO₂Ph](OTf) can be directly observed by NMR at low temperature, can be stored for days at -78 °C, and is trapped by Me₂S, according to the reactions in Scheme 31.^{46e} A very careful and extensive study of its reactions, their kinetics and activation parameters allowed the mapping of the free energy surface of [{HB(pz)₃}ReO₂Ph](OTf).

At 25 °C the half-life for the disappearance of [(HB(pz)₃)ReO₂Ph](OTf) is ~4 min and the three products

Scheme 32

Scheme 33^a

^a (i) $\text{C}_3\text{H}_5\text{MgCl}$; (ii) $\text{C}_2\text{H}_5\text{MgCl}$; $\text{LiC}\equiv\text{CPh}$; (iv) MeMgCl .

of phenyl oxidation formed (Scheme 32) all seem to derive from $[(\text{HB}(\text{pz})_3)\text{ReO}(\text{OPh})(\text{OTf})]$ as established by reaction kinetics, relative yield and independent syntheses of the same products from $[(\text{HB}(\text{pz})_3)\text{ReO}(\text{OPh})(\text{OTf})]$.^{46e}

These studies have established the first clear example of the thermal migration of a ligand (phenyl) from a metal center to an oxo ligand. This type of migration step which bears resemblances to the alkyl/aryl migrations to coordinated carbonyls, is implied in the Sharpless mechanism for osmylation of olefins but has had very little precedent.^{46e} The ethyl and

the butyl derivatives are much more reactive and, indeed, remain as putative intermediates in the essentially quantitative oxidation reaction of $[(\text{HB}(\text{pz})_3)\text{ReO}(\text{OTf})\text{R}]$ with DMSO or pyNO ($\text{R} = \text{Et}, \text{Bu}$) described in Scheme 33.^{46f}

The alkylidene-oxo-hydroxo complex is formed by α -hydrogen elimination in a process quite similar to the one reported above for the formation of **101** and, likewise, can be reversibly trapped by donor ligands ($\text{L} = \text{py}, \text{Me}_2\text{S}$) to give adducts stable enough to be analyzed by low-temperature NMR.^{46f}

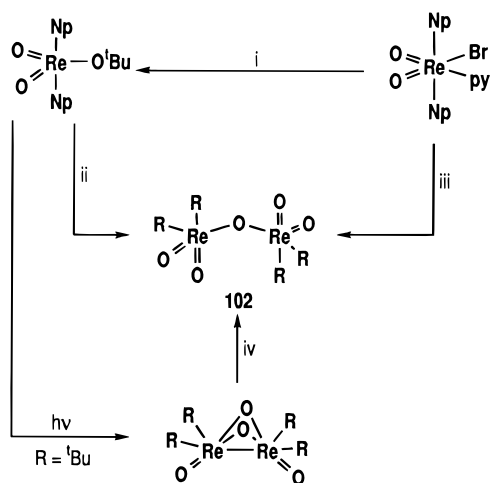
The only known applications of R_3ReO_2 compounds in catalysis refers to the activity of **100** in olefin metathesis both in homogeneous and heterogeneous phase. It is more stereoselective and less active than MTO, particularly in homogeneous reactions. The lower activity and higher selectivity may be due to the greater steric hindrance and decreased Lewis acidity of its Re center as compared to that of MTO.⁹⁷ In contrast, the alkylidene compound **101** and its imido analogues (section VI) are inactive in olefin metathesis reactions.

IV. The $\text{L}_4\text{Re}_2\text{O}_5$ Compounds and Derivatives

The title complexes correspond to a family of dimeric Re(VII) oxides that can be stoichiometrically derived from molecular (gas phase) Re_2O_7 or solvated $\text{Re}_2\text{O}_7 \cdot \text{L}_2$ upon replacement of one oxo by two alkyl ligands. No inorganic derivatives of this stoichiometry have been reported so far.

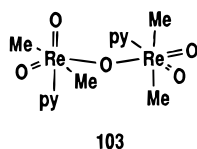
The first $\text{R}_4\text{Re}_2\text{O}_5$ compound reported and structurally characterized, $[(\text{Me}_3\text{CCH}_2)_2\text{ReO}_2]_2(\mu\text{-O})$ (**102**) was synthesized in the three different ways shown in Scheme 34.^{76b} The Re–O–Re bridge is bent, like in gaseous molecular Re_2O_7 .

Scheme 34^a



^a (i) LiOR (R = Me, ^tBu); (ii) H_2O ; (iii) AgO; (iv) pyNO, (R = Np); Me_3NO (R = Me).

The analogous permethylated complex $[(\text{Me}_2\text{-ReO}_2)]_2(\mu\text{-O})$ is available from $\text{Me}_4\text{Re}_2\text{O}_4$ upon reaction with Me_3NO (route iv) in Scheme 34), but only crystallizes in the presence of added pyridine as **103**. Unlike Re_2O_7 , but quite understandably, pyridine coordinates to both Re atoms which then become octahedral, as shown by a crystal structure. The Re–N bonds are relatively long, therefore explaining the observed lability of the py ligands.⁴¹



103

V. The L_5ReO Compounds and Derivatives

In contrast with the preceding section, no organic derivatives of the title compounds have been reported

and only two representatives of this class of compounds are known. The first is the fluoride ReOF_5 **104**. This octahedral complex was first prepared by fluorination of KReO_4 but it appeared as a contamination of the main product ReO_2F_3 .^{155a} An improved preparation was achieved by fluorination of ReO_2 as in eq 43.^{155b,c}



The structure has been assigned C_{4v} symmetry on the basis of gas-phase Raman and IR spectroscopy^{155b} and, more recently, by UV/vis and IR low-temperature matrix isolation studies.^{155c} The other complex is $\text{ReO}(\text{OTeF}_5)_5$ prepared by oxidation of $\text{ReO}(\text{OTeF}_5)_4$ with $\text{Xe}(\text{OTeF}_5)_2$. The X-ray crystal structure reveals the expected octahedral ligand arrangement with little distortion and a Re=O double bond.^{156a}

Compound **104** is readily hydrolyzed to HF and HReO_4 . The 7-coordinate adducts $[\text{ReOF}_6][\text{NO}]$ and $[\text{ReOF}_6][\text{NO}_2]$ are obtained from **104** and NOF or NO_2F respectively. IR and ^{19}F NMR agree with a C_{5v} symmetry.^{156b} Reverse loss of F^- is observed in the reactions with AsF_5 and SbF_5 where $[\text{ReOF}_4][\text{AsF}_6]$ and $[\text{Re}_2\text{O}_2\text{F}_9][\text{Sb}_2\text{F}_{11}]$ (X-ray crystal structure) are formed, respectively.¹⁵⁷

The more closely related organic derivatives are the well-known $\text{Re}^{\text{VI}} \text{R}_4\text{ReO}$ (R = Me, CH_2SiMe_3) but its oxidation to a stable Re(VII) species with a X_5ReO framework has not been reported.³⁹ Instead, further oxidation is possible with NO or O_2 resulting in $\text{Me}_3\text{-ReO}_2$ or even MeReO_3 .

The oxo-alkyne complexes of general formula $\text{XReO}(\eta^2\text{-C}_2\text{R}_2)_2$ (X = halide, alkyl) might be considered as belonging to this class provided the alkyne coordination is described as the extreme case of a dianionic cyclopropene ligand.¹⁶⁹ The structural rigidity in solution without rotation of the alkyne ligands together with the C–C distance within the alkyne ligand might give some support to this extreme description. However, a more detailed structural, chemical and spectroscopical analysis of the compounds together with EHMO calculations support the formulation of these compounds as Re(III), d^4 species.^{169c} Similar examples are found for the imido analogues in section VI.8.a.

VI. The Re(VII) Imido Compounds and Derivatives

Two important factors make a distinction between the chemistry of the isoelectronic and isostructural imido and oxo complexes: the improved electron donating capability and dramatically increased steric bulk of the =NR ligand over the =O ligand. The former factor renders the Re(VII) less prone to reduction resulting in the possibility of widening the nature of the X ligand in $\text{XRe}(\text{NR})_3$ compounds to readily oxidizable species as H^- , PR_2^- , and PR_3 . Moreover, conventional synthetic methods, such as the use of Grignard reagents in the alkylations, can be used making the synthesis of inorganic $\text{XRe}(\text{NR})_3$ and $\text{X}_3\text{Re}(\text{NR})_3$ complexes a good deal more predictable than in the case of their oxo congeners, where reduction has to be avoided. The second factor stems from the tunable size of the imido complexes which can be used to prevent oligomerization or intramo-

lecular decomposition, therefore allowing for the stabilization of otherwise elusive, highly reactive species. The trigonal-planar $[\text{Re}(\text{NAr})_3]^-$ is one such example which shows a varied and synthetically useful chemistry ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{iPr}_2$).

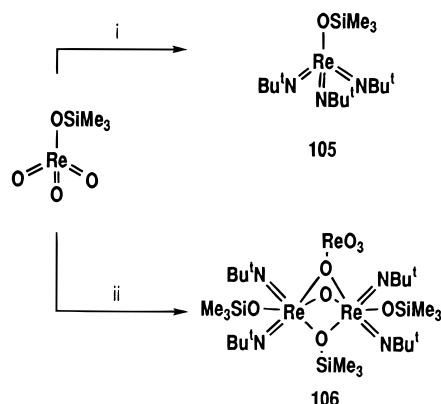
On the other hand, the high electron density of species like $\text{RRe}(\text{NR})_3$ makes them very reactive toward Lewis acids and, more specifically, toward the proton. These interactions readily lead to NR loss and constitute the general synthetic pathway to $\text{X}_3\text{-Re}(\text{NR})_2$ species.

These facts suggested a slightly different arrangement of the description of the several inorganic and organic imido complexes and their reactions as presented in this section.

A. The Inorganic $\text{XRe}(\text{NR})_3$ Derivatives

The first $\text{Re}(\text{VII})$ imido complexes were reported in 1979 by Nugent and Harlow who obtained $\text{Me}_3\text{-SiORe}(\text{N}^t\text{Bu})_3$ (**105**) together with the trinuclear, $\text{Re}_3(\text{N}^t\text{Bu})_4\text{O}_5(\text{OSiMe}_3)$, according to the reaction conditions in Scheme 35.¹⁷⁰

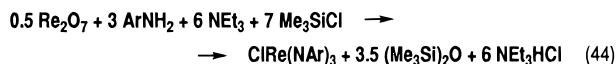
Scheme 35^a



^a (i) Excess ${}^t\text{BuNHSiMe}_3$; (ii) default ${}^t\text{BuNHSiMe}_3$.

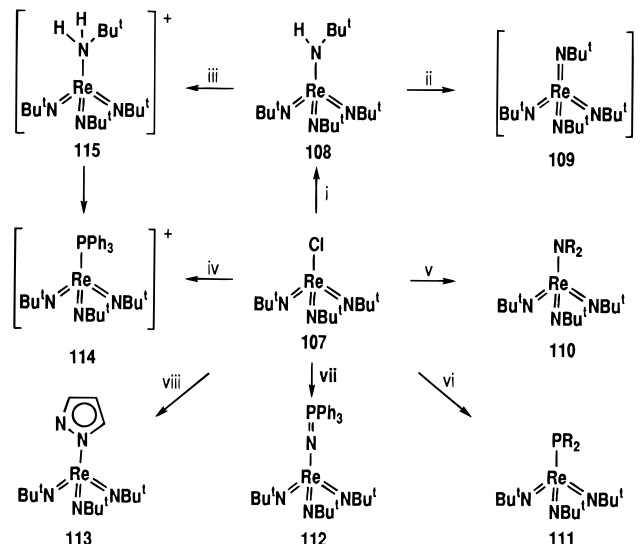
Compound **105** plays a central role in $\text{Re}(\text{VII})$ imido chemistry since it is the starting material for a large number of other complexes. Its crystal structure was determined later and suggests that all ligands are participating in π -bonding to the Re , although the O ligand only to a lesser extent.¹⁷¹ The other representatives of the $\text{R}_3\text{EORe}(\text{NR})_3$ family of complexes ($\text{E} = \text{C}, \text{Si}, \text{Sn}$) are $\text{Ph}_3\text{SiORe}(\text{NR})_3$ ($\text{R} = {}^t\text{Bu}, 2,6\text{-C}_6\text{H}_3\text{iPr}_2; 2,6\text{-C}_6\text{H}_3\text{Me}_2$) and were made from the parent trioxides and the corresponding isocyanates.^{35a} The general reaction of metal oxides ($\text{M}=\text{O}$) with isocyanates (RNCO) to give metal-imido bonds ($\text{M}=\text{NR}$)^{170c} was, in fact, used to produce the first arylimido complexes $\text{Me}_3\text{SiORe}(\text{NAr})_3$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{iPr}_2, 2,6\text{-C}_6\text{H}_3\text{Me}_2, 2,6\text{-C}_6\text{H}_3\text{Cl}_2$).¹⁷²

The only halides or pseudohalides of type $\text{XRe}(\text{NR})_3$ prepared, so far, are the chlorides $\text{ClRe}(\text{N}^t\text{Bu})_3$ (**107**) and $\text{ClRe}(\text{NAr})_3$ (**107'**) ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{iPr}_2, 2,6\text{-C}_6\text{H}_3\text{Me}_2$). The former was obtained by reaction of **105** with PhICl_2 , and the latter are readily prepared by the very simple, high-yield, one-pot reaction of eq 44:¹⁷³



Compound **107** is an orange distillable substance that crystallizes at room temperature. The crystal structure also shows some "averaging" of the three potentially four-electron donor imido ligands.¹⁷¹ This compound has been particularly useful for the preparation of a number of other organic and inorganic $\text{XRe}(\text{N}^t\text{Bu})_3$ derivatives by the simple substitution reactions summarized in Scheme 36.

Scheme 36^a



^a (i) LiNH^tBu ; (ii) LiMe ; (iii) $\text{CF}_3\text{SO}_3\text{H}$; (iv) PPh_3 ; (v) LiNR_2 ($\text{R} = \text{Me}, \text{Ph}$); (vi) LiPR_2 ($\text{R} = \text{Ph}, \text{SiMe}_3; \text{R}_2 = \text{H}, \text{mes}$); (vii) $\text{LiN}=\text{PPh}_3$; (viii) $\text{NaC}_3\text{H}_3\text{N}_2$.

Reaction with LiNH^tBu gives the amido derivative $(\text{NH}^t\text{Bu})\text{Re}(\text{N}^t\text{Bu})_3$ (**108**). Other dialkylamido and the diphenylphosphido complexes $(\text{NR}_2)\text{Re}(\text{N}^t\text{Bu})_3$ ($\text{R} = \text{Me}, \text{Ph}$) and $(\text{PR}_2)\text{Re}(\text{N}^t\text{Bu})_3$ ($\text{R} = \text{SiMe}_3, \text{Ph}; \text{R}_2 = \text{H}, \text{mes}$) are readily prepared from **107** or **105** and the corresponding LiER_2 salts ($\text{E} = \text{N}, \text{P}$).¹⁷⁴

The amido derivative **108** undergoes both deprotonation and protonation reactions at the amido ligand (reactions ii and iii in Scheme 36, respectively).¹⁷¹ Deprotonation with LiMe in ether (-40°C) produces the homoleptic tetraimido anion $[\text{Re}(\text{N}^t\text{Bu})_4]^-$ [LiTMEDA] the imido analogue of perrhenate.¹⁷¹

Deprotonation of the related $(\text{PHmes})\text{Re}(\text{N}^t\text{Bu})_3$ failed to give the corresponding phosphinidino anion $[\text{mesP}=\text{Re}(\text{N}^t\text{Bu})_3]^-$.¹⁷⁴

The phosphiniminato derivative $\text{Re}(\text{N}^t\text{Bu})_3(\text{N}=\text{PPh}_3)$ (**112**), which has the resonance formula $\text{Re}-\text{N}=\text{PPh}_3$, could be prepared from **107** and LiNPPH_3 in the same manner as the pyrazolate $\text{Re}(\text{N}^t\text{Bu})_3(\text{C}_3\text{H}_3\text{N}_2)$ (**113**) from $\text{NaC}_3\text{H}_3\text{N}_2$.¹⁷⁴

Related cyclophosphazene imido complexes were prepared from silylated diphosphazenes and Re_2O_7 , followed by reaction of the produced oxide with ArNCO ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{iPr}_2$).¹⁷⁵ Protonation of **108** with $\text{CF}_3\text{SO}_3\text{H}$ leads to the structurally characterized amino complex $[(\text{NH}_2^t\text{Bu})\text{Re}(\text{N}^t\text{Bu})_3]\text{O}_3\text{SCF}_3$ (**115**).¹⁷⁴ The amine may be replaced by PPh_3 to give $[(\text{PPh}_3)\text{-Re}(\text{N}^t\text{Bu})_3]\text{O}_3\text{SCF}_3$ (**114**).¹⁷⁴ Monocationic complexes $[\text{LRe}(\text{NR})_3]^+$, e.g., **114**, do not have a counterpart in the $\text{Re}(\text{VII})$ oxo chemistry where the only cationic species are of type $[\text{L}_3\text{ReO}_3]^+$. This fact simply mirrors the already mentioned π -donation capability

of the NR ligand which is strong enough to cause electronic saturation of the metal in these cations.

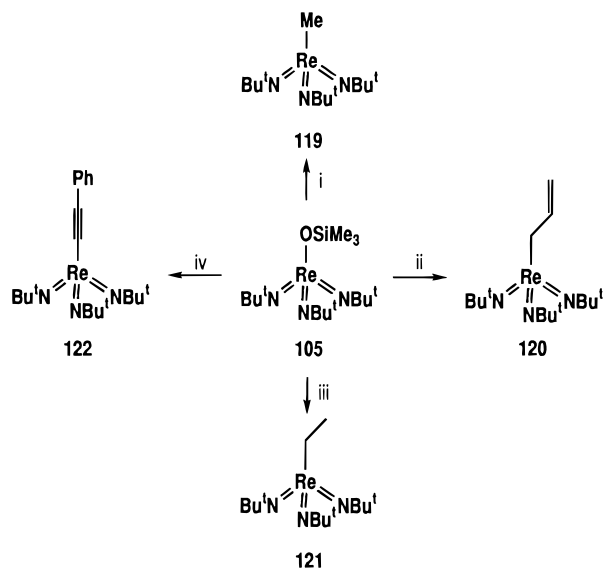
Another species without a counterpart in the Re(VII) oxo chemistry is the hydride $\text{HRe}(\text{NAr})_3$ **117**, alternatively formulated as $\text{Re}(\text{NAr})_2(\text{NHAr})$ ¹⁷³ readily and quantitatively obtained upon protonation of $[\text{Re}(\text{NAr})_3]^-$ (**116**) by $[\text{Et}_2\text{NH}_2][\text{OTf}]$. The resonance of the hydride in the ¹H NMR spectrum is observed at δ 7.22 ppm and varies slightly with temperature between +20 and -80 °C.¹⁷³ Compound **116** abstracts oxygen from Me_3NO to give the mixed oxo-imino analogue of perrhenate $[\text{Re}(\text{NAr})_3(\text{O})]^-$ (**118**).¹⁷³ The synthesis and other reactions of **116** are described below in Scheme 41.

B. The Organic $\text{RRe}(\text{NR})_3$ Derivatives

The first reported compounds of this type were synthesized with bulky aryls $(\text{Ar})\text{Re}(\text{N}^t\text{Bu})_3$ ($\text{Ar} = o\text{-tol, xyl, and mes}$) by action of the corresponding Grignard reagents on $\text{Me}_3\text{SiORe}(\text{N}^t\text{Bu})_3$.¹⁶⁸ The importance of the steric stabilization may be seen in the fact that both the phenyl and *p*-tolyl analogues could not be prepared in this way. Alkylation of $\text{Me}_3\text{SiORe}(\text{NAr})_3$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{Pr}_2, 2,6\text{-C}_6\text{H}_3\text{Me}_2, 2,6\text{-C}_6\text{H}_3\text{Cl}_2$) gives the neopentyl derivatives $(\text{Me}_3\text{CCH}_2)\text{-Re}(\text{NAr})_3$,¹⁷² and following the same synthetic approach, reaction of **105** with RMgCl (or $\text{LiC}\equiv\text{CPh}$) produced a series of hydrocarbonyl derivatives $\text{RRe}(\text{N}^t\text{Bu})_3$ (**119–122**; $\text{R} = \text{Me, Et, } \eta^1\text{-C}_3\text{H}_5, \text{C}\equiv\text{CPh}$) as shown in Scheme 37.⁸⁰

The η^1 coordination mode of the allyl ligand in **120** may be the result of the high electron density at the metal provided by the three imido ligands although orbital symmetry reasons also exist as argued for $(\eta^1\text{-C}_3\text{H}_5)\text{ReO}_3$.⁸¹ However, in contrast to the analogue RReO_3 complexes, no adduct $\text{RRe}(\text{NR})_3\cdot\text{L}_n$ is formed on treatment with donor ligands. The purple methyl derivative $\text{MeRe}(\text{NAr})_3$ (**119**), prepared from MTO and excess ArNCO (>3 equiv) ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{Pr}_2$) is monomeric in hydrocarbon solvents but dimerizes in DME or CDCl_3 .⁸⁰ Use of 1.5 or 2 equiv of ArNCO leads to mixed oxo-imido compounds (see below). A similar complex $\text{MeRe}(\text{NAr})_3$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{Me}_2$) is

Scheme 37^a



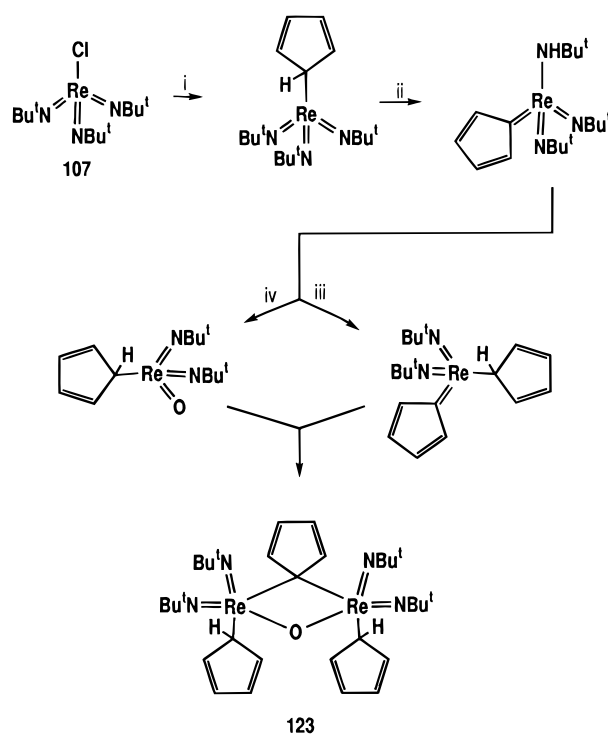
^a (i) MeMgCl ; (ii) $\text{C}_3\text{H}_5\text{MgCl}$; (iii) $\text{C}_2\text{H}_5\text{MgCl}$; (iv) $\text{LiC}\equiv\text{CPh}$.

obtained from MTO and the corresponding isocyanate, in refluxing toluene.¹⁷⁶

Reaction of $[\text{Re}(\text{NAr})_3][\text{Et}_4\text{N}]$ (**116**) with a number of alkyl halides leads to the corresponding alkyl derivatives $[\text{RRe}(\text{NAr})_3]$ (**119**) [$\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{Pr}_2$; $\text{R} = \text{Me, CH}_2\text{-}2,4,6\text{-C}_6\text{H}_2\text{Me}_3$; $\text{CH}_2\text{Cl, CH}(\text{Ph})\text{Cl}$] but double substitution to give $\{\text{Re}(\text{NAr})_3\}_2(\mu\text{-CHR})$ was not achieved (Scheme 41).¹⁷³ The corresponding hydrocarbon-bridged dinuclear species $\{\text{ReO}_3\}_2(\mu\text{-CHR})_n$ are also unknown with the exception of $(\text{O}_3\text{-Re})\text{C}\equiv\text{C}(\text{ReO}_3)$.

Considering all the examples that point out to the electronic saturation of the Re in the Re(VII) tris-imido complexes, the impossibility of preparing the hypothetical $\text{Cp}^*\text{Re}(\text{NR})_3$ or $\text{CpRe}(\text{NR})_3$ seems rather justifiable. In one such attempt NaCp was reacted with $\text{ClRe}(\text{N}^t\text{Bu})_3$. Instead of $\text{CpRe}(\text{N}^t\text{Bu})_3$, the rather unusual dimer **123** was isolated and structurally characterized by X-ray crystallography. The bridging alkylidene ligand $\text{C}_5\text{H}_4^{2-}$ was characterized for the first time.¹⁷⁷ Besides this important new type of ligand, the most interesting feature of this reaction is the loss of a N^tBu ligand. The tentative mechanism proposed which accounts both for the N^tBu loss and the formation of the $\text{C}_5\text{H}_4^{2-}$ ligand is summarized in Scheme 38.¹⁷⁴

Scheme 38



^a (i) NaCp ; (iii) NaCp (NaNH^tBu); (iv) THF ($-\text{C}_4\text{H}_6, -^t\text{BuNH}_2$).

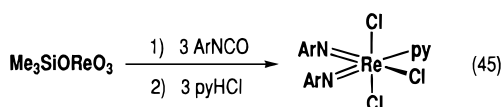
C. The Inorganic $\text{X}_3\text{Re}(\text{NR})_2$ Derivatives

The first example of these compounds, $\text{Cl}_3\text{Re}(\text{N}^t\text{Bu})_2$ (**124**), was obtained in >85% yield upon reaction of $\text{Me}_3\text{SiO}(\text{N}^t\text{Bu})_3$ with 4 equiv of HCl .¹⁷⁸

This kind of protonation is the most important type of reaction of all the $\text{XRe}(\text{NR})_3$ compounds and represents the most accessible pathway for the release of the excess electronic charge on the complex. In agreement with the 18-electron rule, only two of

the imido ligands can simultaneously donate their electron pair to the metal.⁷

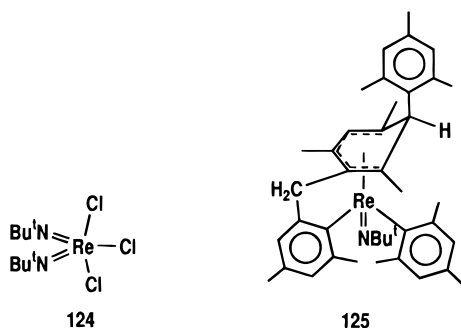
The crystal structure of this compound reveals a slightly distorted TBP geometry with equatorial imido ligands similar to the one observed for the oxo analogues.¹⁷¹ The bromide, $\text{Br}_3\text{Re}(\text{N}^t\text{Bu})_2$, was prepared by reaction of the chloride with Me_3SiBr .¹⁷⁸ These halides add pyridine to give octahedral complexes of general formula $\text{X}_3\text{Re}(\text{NR})_2(\text{py})$. One such example is $\text{Cl}_3\text{Re}(\text{NAr})_2\text{py}$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{iPr}_2$) which results from the combined two-step preparation of eq 45.¹⁷² The chemistry of this complex as precursor of other imido complexes is further described in sections VI.D and VI.H.



Protonation of $\text{RRe}(\text{NR})_3$ compounds with HX gives alkyl halide derivatives $\text{RX}_2\text{Re}(\text{NR})_2$ discussed in the next section.

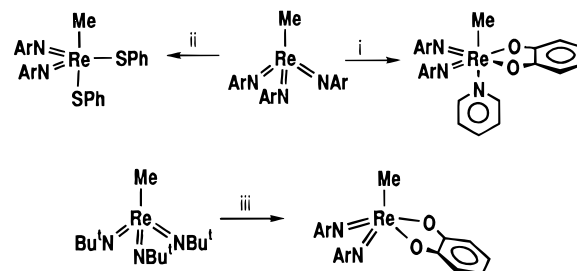
D. The Organic $\text{R}_3\text{Re}(\text{NR})_2$ Derivatives

The discovery of this family of organometallic derivatives of $\text{Re}(\text{VII})$ actually preceded the tris-imido $\text{RRe}(\text{NR})_3$ complexes already presented. The first examples, $\text{R}_3\text{Re}(\text{N}^t\text{Bu})_2$ ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}, \text{CH}_2\text{SiMe}_3$) were obtained by reaction of the parent trichlorides with the appropriate alkylating agents.¹⁷⁸ The aryl derivative (*o*-tol) $_3\text{Re}(\text{N}^t\text{Bu})_2$ was similarly prepared.¹⁷¹ However, the attempted preparation of its mesityl and xylyl analogues resulted in reduction to the paramagnetic $\text{Re}(\text{VI})$ species $(\text{Ar})_2\text{Re}(\text{N}^t\text{Bu})_2$, ($\text{Ar} = \text{xyl}, \text{mes}$) in close parallel to the formation of $(\text{Ar})_2\text{ReO}_2$ ($\text{Ar} = \text{o-tol}, \text{xyl}$) from $\text{Me}_3\text{SiOREo}_3$ and the respective Grignard reagents.^{168,179} Oxidation of $(\text{Ar})_2\text{Re}(\text{N}^t\text{Bu})_2$ ($\text{Ar} = \text{xyl}, \text{mes}$) with Ag^+ or ferrocenium salts gave the $\text{Re}(\text{VII})$ diamagnetic cations $[(\text{Ar})_2\text{Re}(\text{N}^t\text{Bu})_2]^+$ which insert one molecule of isocyanide (RCN ; $\text{R} = \text{xyl}, ^t\text{Bu}$) to give $\{(\text{N}^t\text{Bu})_2\text{Re}(\text{mes})[\eta^2\text{-RN}=\text{C}(\text{mes})]\}^+$.^{171,179} The rather unusual compound **125** resulted from the reaction of **124** with a large excess of mesMgCl in THF.¹⁷⁹



There are two main synthetic routes to the mixed alkyl halides, $\text{R}_n\text{X}_{3-n}\text{Re}(\text{NR})_2$: protonation of $\text{RRe}(\text{NR})_3$ compounds with loss of NRH_2 or partial alkylation of the trichlorides $\text{Cl}_3\text{Re}(\text{NR})_2$. Exemplifying the former route are the syntheses of $\text{Cl}_2\text{ArRe}(\text{N}^t\text{Bu})_2$ ($\text{Ar} = \text{o-tol}, \text{xyl}, \text{and mes}$) from $(\text{Ar})\text{Re}(\text{N}^t\text{Bu})_3$ and excess HCl in ether,¹⁶⁸ and the condensation reactions depicted in Scheme 39 which result from

Scheme 39



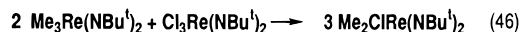
^a (i) 1,2-(HO) $_2\text{C}_6\text{H}_4$ (catechol) + py; (ii) HSPH; (iii) catechol. Ar = 2,6- $\text{C}_6\text{H}_3\text{Me}_2$.

the facile protonation of $\text{MeRe}(\text{NR})_3$ ($\text{R} = ^t\text{Bu}, 2,6\text{-C}_6\text{H}_3\text{Me}_2$) by catechol or PhSH to give the $\text{MeRe}(\text{NR})_2\text{X}_2$ type derivatives ($\text{X}_2 = 1,2\text{-O}_2\text{C}_6\text{H}_4$; SPh).¹⁷⁶ It is interesting to note that in the case of the MeReO_3 , double, rather than monocondensation occurs with HSPH.

Further examples are given by the reaction of $\text{MeRe}(\text{NAr})_3$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{Me}_2$) with HCl , in hexane, which yields the octahedral, structurally characterized ionic complex $[\text{MeCl}_3\text{Re}(\text{NAr})_2][\text{NArH}_3]$. Use of 2 equiv of pyHX lead to $[\text{MeX}_2\text{Re}(\text{NAr})_2(\text{py})]$ ($\text{X} = \text{Cl}, \text{Br}$).¹⁷⁶ Note, in both cases, the prompt formation of octahedral adducts by the complexes $\text{RX}_2\text{Re}(\text{NAr})_2$.

The second route to mixed alkyl halide complexes $\text{R}_n\text{X}_{3-n}\text{Re}(\text{NR})_2$ is exemplified by the alkylation of $\text{ReCl}_3(\text{NAr})_2\text{py}$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{iPr}_2$) with $\text{Zn}(\text{CH}_2\text{-CMe}_3)_2$ to form $(\text{Me}_3\text{CCH}_2)\text{Cl}_2\text{Re}(\text{NAr})_2$ which is a central compound for the synthesis of a number of alkylidene complexes.¹⁷²

The mixed aryl halides $\text{Cl}_2\text{ArRe}(\text{N}^t\text{Bu})_2$ ($\text{Ar} = \text{o-tol}, \text{xyl}, \text{and mes}$) similarly synthesized by reaction of **124** with 1 equiv of the Grignard reagent (see below).¹⁶⁸ $\text{ClAr}_2\text{Re}(\text{N}^t\text{Bu})_2$ ($\text{Ar} = \text{o-tol}$)¹⁷⁹ and $\text{Cl}(\text{CH}_2\text{SiMe}_3)_2\text{Re}(\text{N}^t\text{Bu})_2$ ¹⁷⁸ were produced in a similar way with the appropriate stoichiometry.¹⁷⁹ A particular case is the redistribution reaction of **124** and $\text{Me}_3\text{Re}(\text{N}^t\text{Bu})_2$ that gives $\text{Me}_2\text{ClRe}(\text{N}^t\text{Bu})_2$ according to the stoichiometry of eq 46.¹⁷⁸



The *o*-tol derivative $\text{Cl}_2\text{ArRe}(\text{N}^t\text{Bu})_2$ was structurally characterized. It reveals a bent *N*(*o*-tol) ligand at the axial site of a square-pyramidal structure. This is a somewhat surprising result in view of the usually assigned equatorial position of the imido ligands in TBP structures of many $\text{X}_3\text{Re}(\text{NAr})_2$ and $\text{R}_3\text{Re}(\text{NR})_2$ compounds and seems to be due to a particular kind of stabilization in the solid state. In fact, the structure of the parent Ph derivative, $\text{Cl}_2\text{PhRe}(\text{N}^t\text{Bu})_2$ and the trichloride $\text{Cl}_3\text{Re}(\text{N}^t\text{Bu})_2$ are trigonal bipyramidal with both imido ligands on the equatorial plane.¹⁷¹

Reaction of **124** with LiOH forms the dihydroxo complex $\text{Cl}(\text{OH})_2\text{Re}(\text{N}^t\text{Bu})_2$ which can be transformed into $(\text{mes})\text{Re}(\text{N}^t\text{Bu})_2(\text{O})$ (see below).¹⁷⁹

Another interesting family of complexes in this class are the mixed-alkyl derivatives $\text{RR}'_2\text{Re}(\text{NR})_2$. They can be easily made by alkylation of the parent $\text{RX}_2\text{Re}(\text{NR})_2 \cdot \text{L}$ derivative as in the case of the synthesis of $\text{Me}(\text{Me}_3\text{CCH}_2)_2\text{Re}(\text{NAr})_2$ from $\text{Me}_3\text{CCH}_2\text{-MgCl}$ and $[\text{MeX}_2\text{Re}(\text{NAr})_2(\text{py})]$ ($\text{X} = \text{Cl}, \text{Br}$). Two

isomers are obtained depending on the nature of X. The crystal structure of the predominant isomer (75:25) formed for X = Br, shows that the equatorial sites of the TBP structure are occupied by the methyl and both NAr ligands.¹⁷⁶ The Me group is at an apical site in the other isomer which is predominant for X = Cl (60:40 from NMR data). The reason for these subtle differences remains unclear.

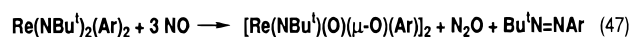
Considering the alkyne ligand as a dianion, the complexes $\text{XR}(\text{NAr})_2(\eta^2\text{-C}_2\text{R}_2)$ (X = H, Cl, Me, $\text{CH}_2\text{-2,4,6-C}_6\text{H}_2\text{Me}_3$) may be regarded as Re(VII) species and, therefore, members of this family. The analogy is useful but has to be taken cautiously as the C_2R_2 ligands are readily displaced by phosphines, as expected from a Re(V) complex. The synthesis of these complexes is discussed below.

E. Miscellaneous Polynuclear and Mixed Imido and Oxo–Imido Derivatives

The trinuclear compound $\text{Re}_3(\text{N}^t\text{Bu})_4\text{O}_5(\text{OSiMe}_3)$ (**106**) was structurally characterized and is formed when deficiency of $^t\text{BuNHSiMe}_3$ is used in its synthesis. The ReO_4^- bridge can be replaced by bridging CF_3COO^- on reaction with $\text{Ag}(\text{O}_2\text{CCF}_3)$.¹⁷⁴

A by product of the protonation of $(\text{NH}^t\text{Bu})\text{Re}(\text{N}^t\text{Bu})_3$ with $\text{CF}_3\text{SO}_3\text{H}$ (reaction iii in Scheme 36) was shown by crystallography to possess a rather complex tetrameric structure.¹⁸⁰

When the paramagnetic complex $\text{Ar}_2\text{Re}(\text{N}^t\text{Bu})_2$ is treated with 1 equiv of NO, a diamagnetic adduct of composition $\text{Ar}_2\text{Re}(\text{N}^t\text{Bu})_2(\text{NO})$ (Ar = xyl) is formed. Upon treatment with another equivalent of NO, $(\text{xyl})\text{-ReO}(\text{N}^t\text{Bu})_2$ is formed.¹⁷⁹ However, rapid bubbling of excess NO through a solution of $\text{Ar}_2\text{Re}(\text{N}^t\text{Bu})_2$ leads to a high yield of the crystallographically characterized dimers $[\text{Re}(\text{N}^t\text{Bu})\text{O}(\mu\text{-O})\text{Ar}]_2$, with the stoichiometry of eq 47:¹⁷⁹



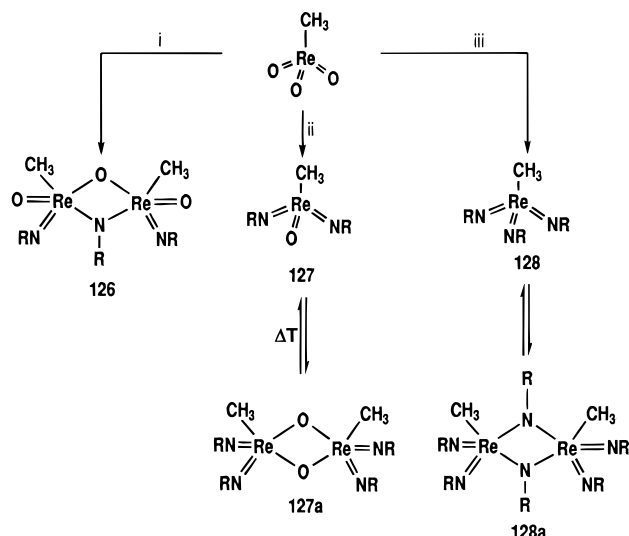
The reason for the dimerization may probably be found in the higher electronic richness of the oxygen atoms in the monomer $\text{ArRe}(\text{N}^t\text{Bu})\text{O}_2$ as compared to the oxo congeners ArReO_3 which are highly Lewis acidic and strongly coordinate to donor solvents as discussed in section II.B.5.

The reactions of MTO with ArNCO are summarized in Scheme 40. If only 1.5 equiv of ArNCO are used (reaction i) the dimer $\text{MeReO}(\text{NAr})(\mu\text{-O})(\mu\text{-NAr})$ (**126**) is formed. Increasing the proportion of ArNCO to 2 equiv results in the mixed $\text{MeReO}(\text{NAr})_2$ (**127**). Full oxide replacement to give **128** only occurs with excess ArNCO . Both **127** and **128** dimerize when cooled to low temperatures and can be isolated as dimers.⁸⁰

The related mixed imido–oxo compound, $(\text{mes})\text{-Re}(\text{N}^t\text{Bu})_2\text{O}$ was prepared by treatment of $\text{Cl}(\text{OH})_2\text{Re}(\text{N}^t\text{Bu})_2$ with mesMgBr or reaction of $\text{ArCl}_2\text{Re}(\text{N}^t\text{Bu})_2$ with Ag_2O .¹⁷⁹

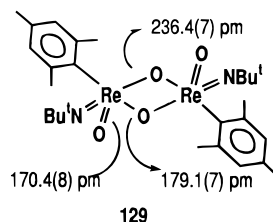
These compounds exhibit rather unsymmetric bridges as shown in the picture for the mesityl derivative $(\text{mes})\text{Re}(\text{N}^t\text{Bu})_2\text{O}$ (**129**). The longer bridge

Scheme 40^a



^a (i) ArNCO (1.5 equiv; Ar = 2,6- $\text{C}_6\text{H}_3\text{iPr}_2$); (ii) ArNCO (2 equiv); (iii) ArNCO (3 equiv).

is the one *trans* to the imido ligand. They dissociate easily in the gas phase.



Several dimers of general formula $\text{Re}_2\text{O}_x(\text{NAr})_{7-x}$ result from the reaction of $\text{Me}_3\text{SiReO}_3$ with ArNCO (Ar = 2,6- $\text{C}_6\text{H}_3\text{iPr}_2$; 2,6- $\text{C}_6\text{H}_3\text{Me}_2$). Of these, $(\text{ArN})_3\text{-Re-O-Re}(\text{O})(\text{NAr})_2$ and $(\text{ArN})_3\text{-Re-O-Re}(\text{NAr})_3$ were characterized.¹⁷² These are useful precursors for the preparation of imido alkylidene derivatives $\text{XRe}(\text{NAr})_2(\text{CH}^t\text{Bu})$ (X = Cl, OR).¹⁷² A more complex mixed oxo–imido tetramer resulted from the reaction of $^t\text{Bu}_2\text{Si}(\text{OREO}_3)_2$ with ArNCO (Ar = 2,6- $\text{C}_6\text{H}_3\text{iPr}_2$) and was structurally characterized.¹⁸¹

F. The $\text{X}_5\text{Re}(\text{NR})$ Derivatives

No complex is known that strictly corresponds to this stoichiometry and formal oxidation state (+7). However, accepting the description of the bonding of an alkyne as a dianion formally brings the complexes $\text{XRe}(\text{NAr})(\eta^2\text{-C}_2\text{R}_2)_2$ (X = H, Cl, Me, $\text{CH}_2\text{-2,4,6-C}_6\text{H}_2\text{-Me}_3$) under this heading. Their syntheses are presented and discussed in section VI.H.1 (Scheme 43).

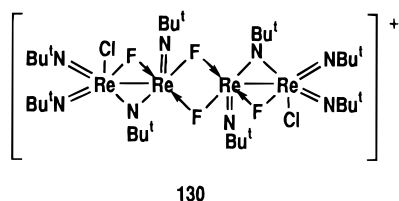
Some octahedral Re(VI) complexes of this stoichiometry have been reported, namely $[\text{Re}(\text{NPh})\text{Cl}_4\text{L}]$ (L = THF, MeCN) and $[\text{Re}(\text{NPh})\text{Cl}_5][\text{Me}_4\text{N}]$. The parent complex for these species, $[\text{Re}(\text{NPh})\text{Cl}_4]_2$ is obtained by reaction of ReOCl_4 with PhNCO .¹⁸² No oxidation of any of these complexes to a Re(VII) species was reported.

G. Reactions of $\text{XRe}(\text{NR})_3$ Complexes

Unlike their oxo congeners, these complexes do not undergo addition of two-electron donor ligands to form adducts. On the other hand, the easy protonation of one imido ligand in the $\text{XRe}(\text{NR})_3$ complexes

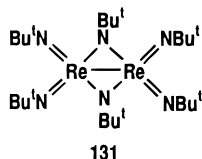
is a general characteristic which normally leads to $L_n\text{Re}(\text{NR})_2$ complexes, e.g., $\text{X}_3\text{Re}(\text{NR})_2$ as described in the preceding section. This reactivity is, of course, extensive to Lewis acids other than the proton. A straightforward example is the reaction of SbCl_5 with $\text{ClRe}(\text{N}^t\text{Bu})_3$ (**107**) in MeCN solvent, whereby one (N^tBu) ligand is abstracted forming the cation $[\text{Re}(\text{N}^t\text{Bu})_2\text{Cl}_2(\text{MeCN})_2][\text{SbCl}_6]$ and ${}^t\text{BuN}=\text{SbCl}_3$.¹⁷⁴ An alternative preparation of this cationic compound involves chloride abstraction from $\text{Cl}_3\text{Re}(\text{N}^t\text{Bu})_2$ with SbCl_5 , in MeCN.¹⁷⁴

In many other cases reduction may also take place simultaneously. By interaction of **107** with AgBF_4 (or AgPF_6) in CH_2Cl_2 , imido groups are lost and partial reduction takes place to give the tetramer **130**.



Reduction also takes place when $\text{Me}_3\text{SiORe}(\text{N}^t\text{Bu})_3$ reacts with $\text{Ag}(\text{O}_2\text{CCF}_3)$ to give a Re(V) dimer $[(\text{N}^t\text{Bu})_2\text{Re}]_2(\mu\text{-OSiMe}_3)(\mu\text{-O}_2\text{CCF}_3)$.¹⁷⁴ The cluster $\text{ReCo}_3(\text{N}^t\text{Bu})_2(\text{CO})_{10}$ contains the metal atoms in a butterfly-type core structure with $\mu_3\text{-N}^t\text{Bu}$ and CO bridges.^{174b}

Reduction of $\text{Me}_3\text{SiORe}(\text{N}^t\text{Bu})_3$ with Na/Hg, in hexane, gives the Re(VI) homoleptic, hexane soluble dimer $({}^t\text{BuN})_2\text{Re}(\mu\text{-}{}^t\text{BuN})_2\text{Re}(\text{N}^t\text{Bu})_2$ (**131**),¹⁷¹ with a weak Re–Re bond. It is a formal analogue of ReO_3 , which, however, has a very different polymeric perovskite structure.



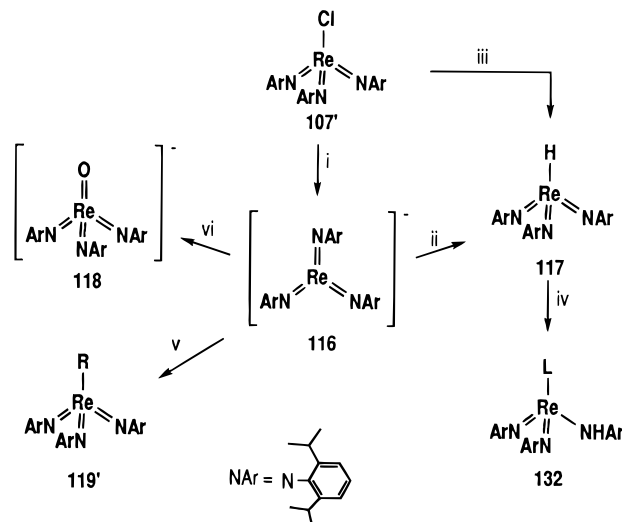
Reduction of $\text{ClRe}(\text{NAr})_3$ (**107'**) with Na/Hg first gives $\text{Hg}[\text{Re}(\text{NAr})_3]_2$ (X-ray structure) and, with a second equivalent, the Re(V) trigonal planar anion $[\text{Re}(\text{NAr})_3]^-$ (**116**) structurally characterized as the PPN^+ salt (Scheme 41).

The steric bulk of the aryl substituents is the decisive factor in the stabilization of **116**. In fact, similar attempts to synthesize the analogue $[\text{Re}(\text{N}^t\text{Bu})_3]^-$ ¹⁷⁴ and $[\text{Re}(\text{NAr})_3]^-$ ($\text{Ar} = \text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-Me}_2$) failed and led to dimers like **131**.

Although $\text{HRe}(\text{NAr})_3$ reacts with CCl_4 to give $\text{ClRe}(\text{NAr})_3$, as expected for a *de bona fide* hydride, an alternative formulation of the compound as $\text{Re}(\text{NAr})_2(\text{NHAr})$ or as an agostic species in between both extremes cannot be entirely ruled out on the basis of its reactions with π -acceptor ligands that lead to $\text{Re}(\text{NAr})_2(\text{NHAr})\text{L}$ (**132**) species ($\text{L} = \text{C}_2\text{H}_2$, C_2Me_2 , OCHCMe_3 , C_2H_4 , norbornene).¹⁷³

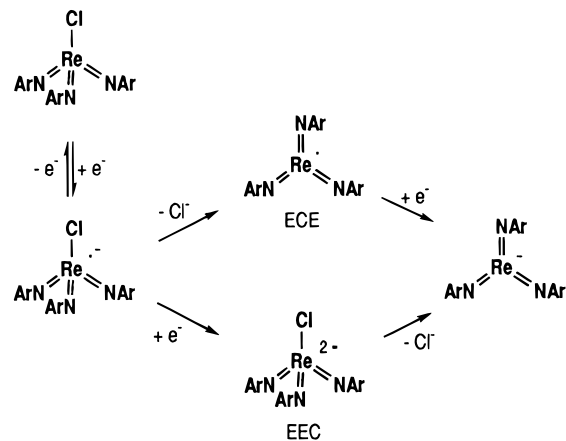
The cyclovoltammetric study of the reduction of **107'** has been interpreted according to the Scheme

Scheme 41^a



^a (i) Na/Hg (2 equiv) in THF (isolated as $\text{Na}(\text{THF})_2$, PPN , and Et_4N salt); (ii) $[\text{Et}_2\text{NH}_2]\text{OTf}$; (iii) CCl_4 ; (iv) $\text{L} = \text{C}_2\text{H}_2$, C_2Me_2 , OCHCMe_3 , C_2H_4 , norbornene, PMe_3 ; (v) MeI ; RCl ($\text{R} = \text{Me}$, $\text{CH}_2\text{-2,4,6-C}_6\text{H}_2\text{Me}_3$; CH_2Cl , $\text{CH}(\text{Ph})\text{Cl}$); (vi) Me_3NO .

Scheme 42



42 and represents the only electrochemical study of Re(VII) imido complexes.

H. Reactions of $\text{X}_3\text{Re}(\text{NR})_2$ and Derivatives

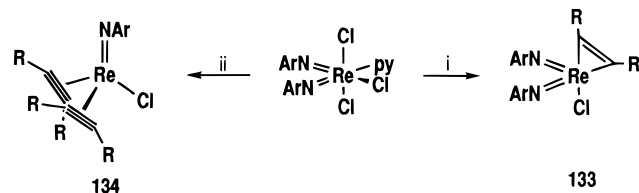
Besides their alkylation reactions (section VI.D), the formation of adducts with two-electron donors, e.g., $\text{X}_3\text{Re}(\text{NAr})_2\text{-L}$ and Cl^- abstraction from $\text{Cl}_3\text{Re}(\text{N}^t\text{Bu})_2$ (section VI.G) these complexes are useful precursors for a number of other imido derivatives, either by way of intramolecular α -elimination reactions of some trialkyl derivatives or by way of reduction. These important reactions are described in this section.

1. The Imido–Alkyne $\text{XR}(\text{NAr})_x(\eta^2\text{-C}_2\text{R}_2)_{3-x}$ Complexes

Reduction of $\text{Cl}_3\text{Re}(\text{NAr})_2\text{-py}$ with 2 equiv of Na/Hg in the presence of acetylenes, $\text{RC}\equiv\text{CR}$, gives $\text{ClRe}(\text{NAr})_2(\eta^2\text{-C}_2\text{R}_2)$ (**133**) ($\text{R} = \text{Me}$, Np), as shown in Scheme 43.

The structure is rigid and the alkyne ligands do not rotate, thus supporting the formal Re(VII) structure as drawn. Reduction of $\text{Cl}_3\text{Re}(\text{NAr})_2\text{-py}$ with Zn powder and 2 equiv of $\text{NpC}\equiv\text{CNp}$ gives the isoelectronic monoimido complex $\text{ClRe}(\text{NAr})(\eta^2\text{-C}_2\text{Np}_2)_2$ (**134**).

Scheme 43



The alkyne ligands undergo neither rotation nor exchange with excess alkyne like their oxo analogues $\text{XReO}(\eta^2\text{-C}_2\text{R}_2)_2$ ($\text{X} = \text{I}, \text{R}$). Like the tris-imido complex $\text{ClRe}(\text{NAr})_3$, both $\text{ClRe}(\text{NAr})_2(\eta^2\text{-C}_2\text{Np}_2)$ and $\text{ClRe}(\text{NAr})(\eta^2\text{-C}_2\text{Np}_2)_2$ can be reduced to their anions which undergo the same reactions described for $[\text{Re}(\text{NAr})_3]^-$ in Scheme 41.

In fact, the strikingly similar reactivity pattern that exists among the $\text{XR}(\text{NAr})_x(\eta^2\text{-C}_2\text{R}_2)_{3-x}$ complexes themselves and their oxo analogues $\text{XRO}_x(\eta^2\text{-C}_2\text{R}_2)_{3-x}$ is only limited by the tendency toward dimerization of their reduced species evidenced for the oxo and the NR complexes with less bulky R groups.¹⁷³

2. The Imido-Alkylidene and Imido-Alkylidyne Complexes

The very successful role of oxo-alkylidene and imido-alkylidene complexes of Mo and W in olefin metathesis reactions prompted the study of similar species in Re(VII) chemistry, having in mind the well-recognized importance of the latter metal in metathesis of functionalized olefins.

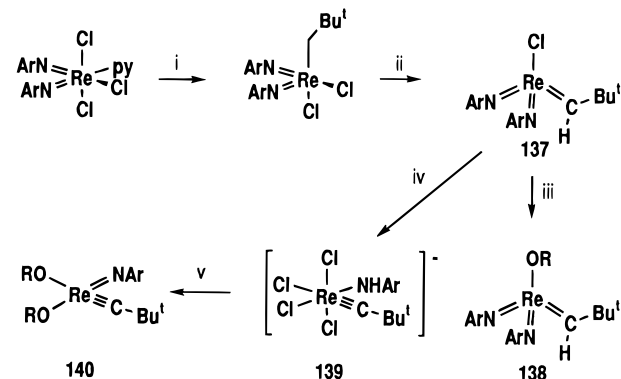
Attempted preparation of the tris-neopentyl derivative $\text{Np}_3\text{Re}(\text{N}^t\text{Bu})_2$ from $\text{Cl}_3\text{Re}(\text{N}^t\text{Bu})_2$ and Np-MgCl gave a 70% yield of the alkylidene $(\text{Me}_3\text{CCH}_2)\text{Re}(\text{N}^t\text{Bu})_2(\text{C}(\text{H})\text{CMe}_3)$ (**135**) as a distillable oil. A similar compound, $(\text{Me}_3\text{SiCH}_2)\text{Re}(\text{N}^t\text{Bu})_2(\text{C}(\text{H})\text{SiMe}_3)$ (**136**) was prepared by light irradiation of $(\text{Me}_3\text{SiCH}_2)_3\text{Re}(\text{N}^t\text{Bu})_2$.¹⁷⁸ Both instances reproduce the findings already described for their Re(VII) oxo congeners (section III.B) and their generation methods are examples of α -hydrogen elimination reactions also common to the chemistry of Mo and W in high-oxidation states. The corresponding benzylidene and methylene analogues could not be thoroughly identified in the photolytic decomposition of $\text{R}_3\text{Re}(\text{N}^t\text{Bu})_2$ ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}$).¹⁷⁸

These alkylidene complexes, **135** and **136**, which are isoelectronic and isostructural with both RReO_3 and $\text{RRe}(\text{NR})_3$, do not catalyze olefin metathesis reactions. In the hope of achieving catalytic activity for this type of reaction, more electron-deficient analogues of the type $\text{XRe}(\text{NAr})_2(\text{CH}^t\text{Bu})$, e.g., **137** and **138**, ($\text{X} = \text{Cl}, \text{OCH}(\text{CF}_3)_2, \text{OCMe}(\text{CF}_3)_2, \text{O-2,6-C}_6\text{H}_3\text{Pr}_2$) have been prepared according to Scheme 44.^{172,183} The formation of **137** by reaction ii in this scheme represents the quantitative dehydrohalogenation of $\text{NpReCl}_2(\text{NAr})_2$ with DBU, an example of a rare reaction type.¹⁷²

Even in spite of their enhanced Lewis acidity, complexes of type **137** and **138** still remain inactive in olefin metathesis and are unable to polymerize norbornene.¹⁷²

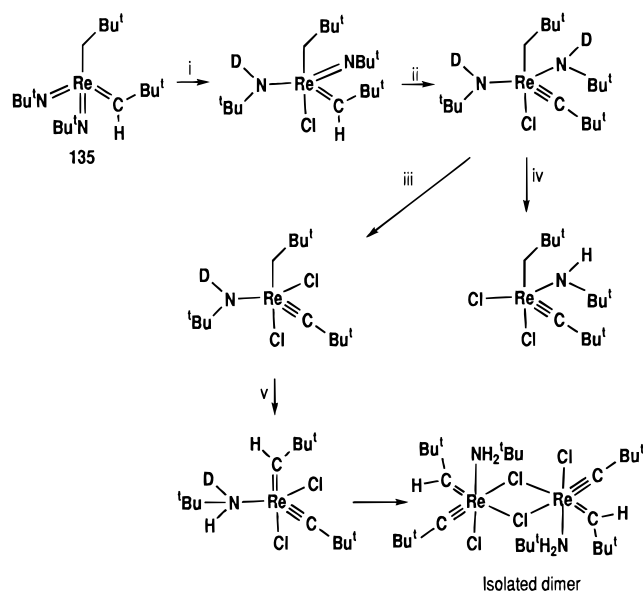
The alkylidene complexes **135**–**138** are preferentially protonated at one of the imido ligands rather than at the alkylidene. Following this protonation,

Scheme 44



^a (i) $\text{Zn}(\text{CH}_2^t\text{Bu})_2$ (0.65 equiv); (ii) DBU; (iii) LiOR ($\text{R} = \text{OCH}(\text{CF}_3)_2, \text{OCMe}(\text{CF}_3)_2, \text{O-2,6-C}_6\text{H}_3\text{Pr}_2$); (iv) $3\text{HCl}/\text{Et}_2\text{O}$; (v) 3LiOR .

a rearrangement takes place involving the transfer of the neopentylidene proton to a nitrogen atom leading ultimately to alkylidyne complexes like the anion **139**.^{183a} The reaction mechanism proposed on the basis of labeling studies with the ^tBuN derivative, **135**, is shown in Scheme 45.¹⁷⁸

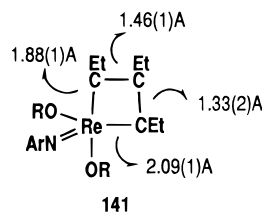
Scheme 45^a

^a (i) LutDCl; (iii) LutDCl ($-0.5\text{Me}_3\text{CND}_2\text{HCl}$); (iv) LutDCl ($-0.5\text{Me}_3\text{CND}_3\text{Cl}$).

By taking advantage of this reaction pathway, a number of alkylidyne complexes were synthesized from **137** and HCl, in ether (Scheme 44).¹⁸³ The initially formed **139** is treated with 3 equiv of LiOR to give the 4-coordinate, pentane soluble, 16-electron complexes $\text{Re}(\text{OR})_2(\text{C}^t\text{Bu})(\text{NAr})$ (**140**).¹⁸³ Simple dehydrohalogenation (with DBU) of $\text{Cl}_3\text{Re}(\text{C}^t\text{Bu})(\text{NAr})(\text{py})$, a neutral analogue of **139** with py instead of Cl^- as the sixth ligand, leads to the dichloro analogues of **140** with two pyridine ligands (two isomers) $\text{Cl}_2\text{Re}(\text{C}^t\text{Bu})(\text{NAr})(\text{py})_2$.^{183c} A related method gives the more versatile and reactive DME derivative $\text{Cl}_2\text{Re}(\text{C}^t\text{Bu})(\text{NAr})(\text{DME})$ (**140'**).

The complexes **140** with $\text{R} = \text{CMe}(\text{CF}_3)_2, \text{CH}(\text{CF}_3)_2$ react readily with internal acetylenes. The rhenacyclobutadiene species **141** was isolated in the reaction with 3-hexyne and structurally characterized (R

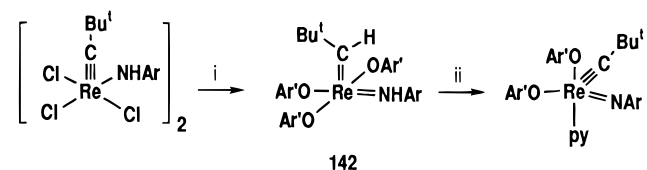
= CMe(CF₃)₂). It can be considered as having a TBP structure with the N, O, and C ligand with the longer Re–C distance on the equatorial plane. The 4-membered ring is clearly asymmetric and bent at C_β. (The dihedral angle between the C/Re/C and C/C/C planes of the 4-membered ring is 34°.)^{183c}



Compound **141** metathesizes other alkynes. Other similar rhenacyclobutadiene complexes were carefully characterized, thereby identifying the key structural and reactivity features of these metallacycles in the alkyne metathesis reaction.^{183c} The steric bulk of both the OR ligand and the substituents at the metallacycle is necessary to increase the reactivity of these toward acetylene loss and achieve further alkyne metathesis. β -H abstraction from the metallacycle, by RO[−], leads to reduced, Re(V), catalytically inactive metallacycles with *exo* C=C double bonds.^{183c}

When [Cl₃Re(C^tBu)(NHAr)]₂, a synthetic analogue of **139**, is treated with relatively less basic alkoxides, the outcome of the reaction v) in Scheme 44 is no longer the imido alkylidynes **140** but the imido alkylidenes (Ar'O)₃Re(CH^tBu)(NAr) (**142**) (Ar' = OC₆F₅, O-2,6-C₆H₃Cl₂, OC₆Cl₅; Ar = 2,6-C₆H₃ⁱPr₂), as in Scheme 46.¹⁸⁶

Scheme 46^a

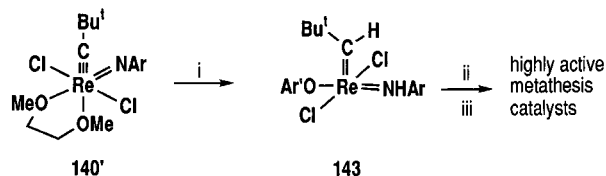


^a (i) Ar'OK (6 equiv) (Ar' = C₆F₅, 2,6-C₆H₃Cl₂, C₆Cl₅); (ii) pyridine, excess.

The square-pyramidal structure of the derivative **142** with Ar' = O-2,6-C₆H₃Cl₂ should better be regarded as octahedral due to intramolecular Cl–Re interactions in the position *trans* to the alkylidene ligand, as discussed in section VI.I. Similarly, this *trans* position is occupied by THF in the structurally characterized octahedral adduct of this solvent with **142** (Ar' = C₆F₅).¹⁸⁶ Therefore, the lack of reactivity of complexes **142** in olefin metathesis reactions is probably due to the fact that the olefin coordinates in a position *trans* to the Re=CH^tBu ligand rendering the formation of the necessary metallacyclobutane ring impossible without further isomerization steps.

As could be expected, bases like pyridine deprotonate the neopentylidene ligand of **142** to give the neopentylidyne derivatives (Ar'O)₂Re(C^tBu)(NAr)(py) as shown in reaction ii of Scheme 46. Conversely, the neopentylidyne complexes Cl₂Re(C^tBu)(NAr)-(DME) (**140'**), which are readily made from **139** and a base in DME solvent, react with a variety of phenols with protonation of the neopentylidyne ligand to give the imido–alkylidene analogues of **142** namely,

Scheme 47^a

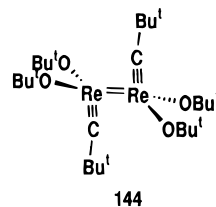


(i) Ar'OH (1 equiv in CH₂Cl₂) (Ar' = 2,6-C₆H₃Cl₂, 2,6-C₆H₃Me₂, 2,6-C₆H₃ⁱPr₂, 2,6-C₆H₃(OMe)₂); (ii) pyridine; (iii) GaBr₃ (20 mol %).

Cl₂(Ar'O)Re(CH^tBu)(NAr) (**143**) (Ar' = O-2,6-C₆H₃-Me₂, O-2,6-C₆H₃ⁱPr₂, O-2,6-C₆H₃Cl₂, O-2,6-C₆H₃(OMe)₂; Ar = 2,6-C₆H₃ⁱPr₂) as in Scheme 47.¹⁸⁶ The deprotonation of **143** with excess pyridine reverts to the expected neopentylidyne complexes Cl₂Re(C^tBu)(NAr)(py)₂ (Scheme 47; **140'** with py instead of DME).

Complexes **143** are incapable of metathesizing olefins by themselves. However, addition of a Lewis acid turns them into very active catalysts for this reaction. This is suggestive of the formation of a highly electrophilic 4-coordinate imido–alkylidene cation, [Cl(Ar'O)Re(CH^tBu)(NAr)]⁺ where no more stereochemical limitations hamper the formation of the metallacyclobutane ring necessary for metathesis as with the well-characterized isoelectronic Mo and W congeners. GaBr₃ has the right acidity for this purpose since stronger acids (AlCl₃, AlBr₃, or GaCl₃) also exchange phenoxide for Cl ligands, and SnCl₄ does not cause any activation.¹⁸⁶

For the sake of completeness mention should be made of a number of alkylidene–alkylidyne complexes X₂Re(C^tBu)(CH^tBu) (X = OR, CH₂^tBu) and derivatives thereof which are isoelectronic with the imido species (RO)₂Re(C^tBu)(NAr) (**140**), and are active in the metathesis of terminal and internal olefins, much in parallel with the activity of their isoelectronic Mo and W complexes, M(NR)(CHR)-(OR)₂.^{184,185} The structurally analogous dimers **144** with a double, unsupported, Re=Re bond, are formed upon reaction of (RO)₂Re(C^tBu)(CH^tBu) with excess CH₂=CHOEt. Their structure has a right angle (90°) between the alkylidyne and the Re=Re bond, as seen in the case where R = ^tBu.¹⁸⁴



I. Structural Studies

The structurally characterized monomeric Re(VII) imido complexes are listed in Table 17 whereas the dimeric and polymeric imido and mixed oxo-imido complexes of Re(VII) are listed in Table 18. Due to the possible variations in bond angles and distances, the imido complexes are more difficult to compare with each other than their oxo congeners. As we have seen, the Re–O bond distance in terminal oxo complexes of Re(VII) shows little dependence on the electronic richness of the Re center even in spite of the several possible bond multiplicity formalisms derived from the 18-electron rule. In the case of the

Table 17. Monomeric Re(VII) Imido Complexes with Known Structures

compound	CN	ref
[Re(N ^t Bu) ₄][LiTMEDA]	4	171b
ClRe(N ^t Bu) ₃	4	171a
mesRe(N ^t Bu) ₃	4	179
PhRe(N-2,6-C ₆ H ₃ ⁱ Pr ₂) ₃	4	35a
Ph ₃ SiORe(N-2,6-C ₆ H ₃ ⁱ Pr ₂) ₃	4	35a
Ph ₃ SiORe(N-2,6-C ₆ H ₃ Me ₂) ₃	4	35a
Ph ₃ SiORe(N ^t Bu) ₃	4	35a
Me ₃ SiORe(N ^t Bu) ₃	4	171a
(Ph ₂ P)Re(N ^t Bu) ₃	4	174a
[(^t BuNH ₂)Re(N ^t Bu) ₃][O ₃ SCF ₃]	4	174a
MeNp ₂ Re(N-2,6-C ₆ H ₃ Me ₂) ₂	5 (tbp)	176
Cl ₃ Re(N ^t Bu) ₂	5 (tbp)	171a
PhCl ₂ Re(N ^t Bu) ₂	5 (tbp)	171a
(<i>o</i> -tol)Cl ₂ Re(N ^t Bu) ₂	5 (sp)	168
(Me(CF ₃) ₂ CO) ₂ Re(C ₃ Et ₃)(N-2,6-C ₆ H ₃ ⁱ Pr ₂)	5 (tbp)	183c
[Cl ₃ MeRe(N-2,6-C ₆ H ₃ Me ₂) ₂][2,6-C ₆ H ₃ Me ₂ NH ₃]	6	176
[Cl ₃ (^t BuNH ₂) ₂ Re(NPh)]	6	182
(O-2,6-Cl ₂ C ₆ H ₃) ₃ Re(N-2,6-C ₆ H ₃ ⁱ Pr ₂)(CH ^t Bu)	6	186
(C ₆ F ₅ O) ₃ Re(N-2,6-C ₆ H ₃ ⁱ Pr ₂)(CH ^t Bu)(THF)	6	186

Table 18. Known Structures of Dimeric and Polymeric Re(VII) Complexes with Imido and Other Ligands

compound	CN	ref
Re ₃ (N ^t Bu) ₄ O ₅ (OSiMe ₃) ₃	6/6/4	170a
[Re(N ^t Bu) ₂ (OSiMe ₃) ₂ (<i>μ</i> -O)(<i>μ</i> -OSiMe ₃)-(<i>μ</i> -O ₂ CCF ₃)	6/6	174
[Re(N ^t Bu)(O)(<i>μ</i> -O)(xyl)] ₂	5	179
[Re(N ^t Bu)(O)(<i>μ</i> -O)(mes)] ₂	5	179
Re ₄ (N ^t Bu) ₈ (<i>μ</i> -O) ₂ (<i>μ</i> -O) ₂ (O ₃ SCF ₃) ₄	6/5	180
[Re(NAr)O] ₂ [Re(NAr) ₂ O] ₂ (<i>μ</i> -O) ₄ (<i>μ</i> -O) ₂ (<i>μ</i> -O ₂ Si ^t Bu) ₂ ^a	6	181
[Re(N ^t Bu) ₂ (<i>η</i> ¹ -C ₅ H ₅) ₂ (<i>μ</i> -C ₅ H ₄)(<i>μ</i> -O)]	5	177
[Re{(NP(Ph) ₂ N) ₂ }(NAr) ₂] ₂ ^a	4	175
Re{NP(Ph) ₂ NC(O)NAr}(NAr) ₂ ^a	5	175
ReCo ₃ (<i>μ</i> -N ^t Bu) ₂ (<i>μ</i> -CO) ₂ (CO) ₈	8	174b

^a Ar: 2,6-C₆H₃ⁱPr₂.

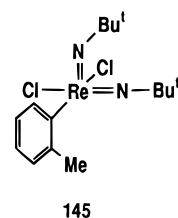
imido complexes, different bond multiplicities imply, in principle, both different Re–N bond distances and Re–N–C angles. The double Re=NR bond, corresponding to a 4-electron count for the imido ligand, implies a bent Re–N–C angle, whereas a linear Re–N–R arrangement is to be expected in the case of the formal triple bond Re≡NR which corresponds to a 6-electron count. Of course, such simplistic pictures are easily obscured by intra or intermolecular (crystal packing) forces that may distort the expected bond angles and/or bond distances and it is usually very difficult to assign the distortions to one electronic or steric cause. Further changes may also result from bond delocalization and bond order averaging or, more obviously in the cases of bridging through the imido ligands.

One such example is given by the formal imido analogue of perrhenate, in [Re(N^tBu)₄][LiTMEDA]. The expected tetrahedral structure of the anion is distorted by the coordination to the [LiTMEDA]⁺ cation along one edge of the ReN₄ tetrahedron.^{171b} All four imido ligands are bent at the N atom with the bridging ones showing the smaller C–N–Re angles and the (slightly) longer Re–N bonds. According to the 18-electron rule, [Re(N^tBu)₄][–] requires three bent and one linear imido ligand. However, one might expect that the unperturbed [Re(N^tBu)₄][–] anion would present four slightly bent imido ligands there-

fore, averaging the triple bond over the four Re–N bonds, which would really become of order 2.25. The bending of all four ligands in the actual structure still shows some of that averaging.

The mononuclear tris-imido complexes XRe(NR)₃ have a distorted tetrahedral structure. The degree of distortion varies with the nature of X and the bulk of both X and R substituents. This is clearly illustrated by the structural variations observed in the series of siloxo derivatives R₃SiORe(NR)₃. Indeed, the Si–O–Re angle varies from 180° in Ph₃SiORe(N-2,6-C₆H₃ⁱPr₂)₃ down to 138–139° in Me₃SiORe(N^t-Bu)₃ and Ph₃SiORe(N-2,6-C₆H₃Me₂)₃, the intermediate value of ~152° being found for Ph₃SiORe(N^tBu)₃. The Re–N bond distances range between 168.3 pm (in ClRe(N^tBu)₃) and 176.1(5) pm in PhRe(N-2,6-C₆H₃ⁱPr₂)₃ but the more commonly found values lie within the 173–175 pm interval. These Re–N bond lengths are shorter than those of the bulkier derivatives like [Re(N^tBu)₄][–] (177(2) pm – 187(3) pm) and [(^tBuNH₂)Re(N^tBu)₃]⁺ (172.4(8)–184.9(9) pm). The simplest example, the chloride ClRe(N^tBu)₃, has a broader range of Re–N bond distances (168.3–175.0 pm) than the siloxo analogues R₃SiORe(NR)₃. The only organometallic derivatives RRe(NR)₃ structurally characterized, so far, are the aryls PhRe(N-2,6-C₆H₃ⁱPr₂)₃,^{35a} and mesRe(N^tBu)₃.¹⁷⁹

The 5-coordinate bis-imido complexes X₃Re(NR)₂ may either have trigonal-bipyramidal (TBP) or square-planar (SP) structures. In this case, solution NMR on a number of organometallic derivatives R₃Re(NR)₂ favored the TBP structures.^{168,178,183b} This was confirmed for the crystal structure of MeNp₂Re(N-2,6-C₆H₃Me₂)₂ where both NAr ligands are linear and lie on the equatorial plane. Probably due to steric reasons, these Re–N bonds are on the upper range (174–176 pm). However, subtle effects are capable of altering this picture, as it happened first in the case of (*o*-tol)Cl₂Re(N^tBu)₂ (**145**) which has a typical SP structure with one apical, bent, and one basal (linear) imido group.



145

In contrast, the related trichloride Cl₃Re(N^tBu)₂ possesses a typical TBP structure with both N^tBu groups on the equatorial plane. Not unexpectedly, the structure of PhCl₂Re(N^tBu)₂ reveals an intermediate degree of distortion between both SP and TBP extremes.

The imido–alkylidene analogue (O-2,6-C₆H₃Cl₂)₃-Re(CH^tBu)(N-2,6-C₆H₃ⁱPr₂) (**142**) also adopts a square-pyramidal structure with the Re=C bond at the apical position and a nearly linear basal imido ligand.¹⁸⁶ However, intramolecular coordination of one of the Cl substituents at the position *trans* to the Re=C bond is very likely (Re–Cl = 283.2(5) pm), therefore, rendering this complex just another example of 6-coordinate species like [Cl₃MeRe(NAr)₂][–] and (C₆F₅O)₃Re(CH^tBu)(NAr)(THF).¹⁸⁶

The dimeric and polymeric complexes in Table 18 display a variety of structural motifs the most common feature being the fact that whenever there is a choice, the bridges are made by oxygen atoms instead of the bulky imido ligands. The phosphazene derivatives and the Re–Co–carbonyl cluster represent unique examples in their classes.

VII. Conclusions

Heptavalent rhenium has received focal attention in the past 10 years in inorganic and organometallic chemistry. A plethora of oxides and imido complexes have been synthesized from well-available, simple precursor compounds such as dirhenium heptaoxide. Of key importance in this development, methyl trioxorhenium(VII) and related imido complexes of formula $RRe(=NR')_3$ have unfolded versatile chemical reactivity yielding catalytic applications. As a matter of fact, methyl trioxorhenium(VII) is presently the most efficient catalyst in olefin epoxidation, but it also applies to olefin metathesis, aldehyde olefination, Baeyer–Villiger oxidation, and oxidation of aromatic compounds as well as oxidation of waxes. The secret of this particular compound is its molecular structure with a low-coordinate heptavalent rhenium of pronounced Lewis acidity; in addition, the compound exhibits an unexpectedly strong rhenium–carbon bond.

In the course of recent research regarding high-valent rhenium chemistry, several aspects related to basic synthesis and structural chemistry have been highlighted. For example, the ester-type carboxylato complexes of formula $(RCOO)ReO_3$ were not only easily synthesized; they also proved to be outstanding precursors for alkylation and arylation reactions. Furthermore, a straightforward alkylation of perrhenate to yield methyl trioxorhenium(VII) has recently been developed.

In spite of a rich body of chemistry being available now, this area is far from being mature. Beyond that, related high-valent metals such as molybdenum(VI), tungsten(VI), and osmium(VI/VII) warrant application of the basic knowledge that has been accumulated in the chemistry of rhenium(VII). We particularly believe that organometal oxides and imido congeners in rhenium's neighborhood of the periodic table will improve the catalytic strength of these classes of compounds.

VIII. Abbreviations

bipy	2,2'-bipyridine
^t Bupy	4- <i>tert</i> -butylpyridine
Bu	butyl
Bz	benzyl
Cp	cyclopentadienyl
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dien	diethylenetriamine
DMA	dimethylacetamide
DME	1,2-dimethoxyethane
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
Et	ethyl
HMPT	hexamethylphosphortriamide
Ind	indenyl
Lut	lutidine

Me	methyl
Me ₃ tacn	1,4,7-trimethyltriazacyclononane
mes	mesityl, 2,4,6-trimethylphenyl
moa	methoxyaniline
Np	neopentyl
Ph	phenyl
phen	1,10-phenanthroline
PMDT	<i>N, N, N, N, N', N'</i> -pentamethyldiethylenetriamine
PPN	bis(triphenylphosphine)iminium
Pr	propyl
py	pyridine
pz	pyrazolate
quinuc	quinuclidine
rt	room temperature
SP	square pyramidal
tacn	1,4,7-triazacyclononane
TBP	trigonal bipyramidal
^t Bubipy	4,4'-ditertbutyl-2,2'-bipyridine
terpy	2,2':6',2''-terpyridine
THF	tetrahydrofuran
TMEDA	<i>N,N,N,N'</i> -tetramethylethylenediamine
TMS	trimethylsilyl
<i>o</i> -tol	2-methylphenyl
tpb	1,1,1-hydrotrispyrazolylborate, HB(pz) ₃
tpm	1,1,1-trispyrazolylmethane, HC(pz) ₃
Tröger's base	[5 <i>R</i> ,11 <i>R</i>]-(+)-2,8-dimethyl-6 <i>H</i> ,12 <i>H</i> -5,11-methanodibenzo[b,f][1,5]diazocine
ttcn	1,4,7-trithiacyclononane
xyl	2,6-dimethylphenyl

IX. Acknowledgments

The authors thank the European Network "Selective Processes and Catalysis" as well as the INIDA/DAAD and Açções Integradas exchange programs for the financial support that made possible the necessary mutual visits, contacts, and discussions.

X. References

- (1) Herrmann, W. A. *J. Organomet. Chem.* **1990**, *382*, 1.
- (2) Rouschias, G. *Chem. Rev.* **1974**, *74*, 531.
- (3) Conner, K. A.; Walton, R. A. *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J., Eds; Pergamon: Oxford, 1987; Vol. 4, p 125.
- (4) Peacock, R. D. *Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., et al., Eds; Pergamon: Oxford, 1973; Vol. 3, p 940.
- (5) (a) Boag, N. M.; Kaez, H. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 4, p 161. (b) Romão, C. C. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; J. Wiley & Sons: New York, 1994; Vol. 6, p 3437. (c) Hoffman, D. M. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1995; Vol. 6, p 231.
- (6) (a) Herrmann, W. A. *J. Organomet. Chem.* **1995**, *500*, 149. (b) Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169.
- (7) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.
- (8) Melaven, A. D.; Fowle, J. N.; Brickell, W.; Hiskey, C. F. *Inorg. Synth.* **1950**, *3*, 188.
- (9) (a) Chiswell, B.; McKenzie, E. D.; Lindoy, L. F. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J., Eds.; Pergamon: Oxford, 1987; Vol. 4, p 110. (b) Griffith, W. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J., Eds.; Pergamon: Oxford, 1987; Vol. 4, p 588. (c) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 1984; pp 509 and 549 [Re_2O_7 and $Re_2O_7 \cdot (H_2O)_2$]; pp 531 and 543 [(OsO_4)]; p 553 [Mn_2O_7]; p 549 [(Tc_2O_7)].
- (10) (a) Krebs, B.; Müller, A.; Beyer, H. H. *Inorg. Chem.* **1969**, *8*, 436. (b) Krebs, B.; Müller, A.; Beyer, H. H. *Chem. Commun.* **1968**, 263. (c) Krebs, B., *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 308.
- (11) (a) Kiprof, P.; Herrmann, W. A.; Kühn, F. E.; Scherer, W.; Kleine, M.; Elison, M.; Rypdal, K. Volden, H. V.; Gundersen, S.; Haaland, A. *Bull. Soc. Chim. Fr.* **1992**, *129*, 655. (b) Vinogradov, V. S.; Ugarov, V. V.; Rambidi, N. G. *Zh. Struk. Khim.* **1972**, *13*,

715. (c) Vinogradov, V. S.; Ugarov, V. V.; Rambidi, N. G. *J. Struct. Chem.* **1972**, *13*, 661.
- (12) (a) Peacock, R. D. *The Chemistry of Technetium and Rhenium*; Elsevier: Amsterdam, 1966. (b) Krebs, B.; Müller, A. *Z. Naturforsch.* **1968**, *23b*, 415. (c) Emel'yanov, D. E.; Gukova, Y. Y.; Karyakin, Y. V.; Ermolaev, M. I. *Russ. J. Inorg. Chem.* **1968**, *7*, 308.
- (13) (a) Beyer, H.; Glemser, O.; Krebs, B.; Wagner, G. *Z. Anorg. Allg. Chem.* **1970**, *376*, 87. (b) Beyer, H.; Glemser, O.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 295. (c) Fischer, D.; Krebs, B. *Z. Anorg. Allg. Chem.* **1982**, *491*, 73. (d) Krebs, B.; Fischer, D.; Paul, G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 448. (e) Herrmann, W. A.; Correia, J. D. G.; Kühn, F. E.; Artus, G. R. J.; Romão, C. C. *Chem. Eur. J.* **1996**, *2*, 168.
- (14) (a) Roesky, H. W.; Hesse, D.; Noltemeyer, M. *Eur. J. Solid State Inorg. Chem.* **1990**, *28*, 809. (b) Herrmann, W. A.; Roesky, P. W.; Kühn, F. E.; Elison, M.; Scherer, W.; Artus, G. R. J.; Romão, C. C.; Lopes, A. D.; Basset, J. M. *Inorg. Chem.* **1995**, *34*, 4701.
- (15) (a) Johnson, J. W.; Brody, J. F.; Ansell, G. B.; Zentz, S. *Acta Crystallogr.* **1984**, *C40*, 2024. (b) Johnson, J. W.; Brody, J. F.; Ansell, G. B.; Zentz, S. *Inorg. Chem.* **1984**, *23*, 2415.
- (16) Sundermeyer, J.; Weber, K.; Peters, K.; v. Schnering, H. G. *Organometallics* **1994**, *13*, 2560.
- (17) Aynsley, E. E.; Hair, M. L. *J. Chem. Soc. (London)* **1958**, 3747.
- (18) (a) Selig, H.; El-Gad, U. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3517. (b) Lotspeich, J. F.; Javan, A.; Engelbrecht, A. *J. Chem. Phys.* **1959**, *31*, 633. (c) Engelbrecht, A.; Grosse, A. V. *J. Am. Chem. Soc.* **1954**, *76*, 2042.
- (19) (a) Gerlach, U.; Ringel, C. *Z. Chem.* **1977**, 306. (b) Huppmann, P. Ph.D. Thesis, Free University of Berlin, Germany, 1983.
- (20) (a) Bruckl, A.; Ziegler, K. *Monatsh. Chem.* **1933**, *63*, 329. (b) Miller, F. A.; Carlson, G. L. *Spectrochim. Acta* **1960**, *16*, 1148. (c) Ovchinnikov, K. V.; Mel'nikov, L. B.; Kolbin, N. I. *Zh. Obshch. Khim.* **1973**, *43*, 699; *Chem. Abstr.* **1973**, *79*, 26600b. (d) Colton, R.; Wilkinson, G. *Chem. Ind. (London)* **1959**, 1314. (e) Zavalishin, N. J.; Mikhailova, L. G.; Drobot, D. V.; Mal'tsev, A. A. *Zh. Neorg. Khim.* **1978**, *23*, 685. (f) Drobot, D. V.; Mikhailova, L. G.; Korshunov, B. G.; Kravchenko, V. V.; Makarova V. M.; *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* **1975**, *18*, 605; *Chem. Abstr.* **1975**, *83*, 107551w.
- (21) (a) Ringel, C.; Lehmann, H. A. *Z. anorg. allg. Chem.* **1967**, *353*, 158. (b) Lehmann, H. A.; Ringel, C. *Z. anorg. allg. Chem.* **1969**, *366*, 73. (c) Ringel, C. *Z. Chem.* **1969**, *9*, 461. (d) Guest, A.; Lock, C. J. L. *Can. J. Chem.* **1971**, *49*, 603. (e) Gerlach, U.; Ringel, C. *Z. anorg. allg. Chem.* **1978**, *442*, 144.
- (22) (a) Wolf, C. J.; Clifford, A. F.; Johnston, W. H. *J. Am. Chem. Soc.* **1957**, *79*, 4257. (b) Edwards, P. G.; Wilkinson, G.; Hursthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2467. (c) Dehnicke, K.; Liese, W. *Chem. Ber.* **1977**, *110*, 3959.
- (23) Gerlach, U.; Ringel, C. *Z. anorg. allg. Chem.* **1974**, *408*, 180.
- (24) (a) Lis, T. *Acta Crystallogr.* **1983**, *C39*, 961. (b) Lis, T. *Acta Crystallogr.* **1979**, *B35*, 1230.
- (25) Weber, R.; Dehnicke, K.; Müller, U. *Z. anorg. allgem. Chem.* **1984**, *516*, 214.
- (26) Grove, D. E.; Johnson, N. P.; Wilkinson, G. *Inorg. Chem.* **1969**, *8*, 1196.
- (27) Tisley, D. G.; Walton, R. A. *J. Mol. Struct.* **1973**, *17*, 401.
- (28) Herrmann, W. A.; Thiel, W. R.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 271.
- (29) Herrmann, W. A.; Kühn, F. E.; Romão, C. C.; Kleine, M.; Mink, J. *Chem. Ber.* **1994**, *127*, 47.
- (30) Addison, C. C.; Davis, R.; Logan, N. *J. Chem. Soc. (A)* **1967**, 1449.
- (31) (a) Lössberg, R.; Dehnicke, K. *Z. Naturforsch. B* **1979**, *34*, 1040. (b) Dehnicke, K.; Liese, W. *Z. Naturforsch. B* **1979**, *34*, 111. (c) Edwards, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2419.
- (32) (a) *Chem. Ber.* **1959**, *92*, 2667. (b) Schmidt, M.; Schmidbaur, H. *Inorg. Synth.* **1967**, *4*, 149. (c) Sheldrick, G. M.; Sheldrick, W. S. *J. Chem. Soc. (A)* **1969**, 2160.
- (33) Herrmann, W. A.; Wojtczak, W. A.; Artus, G. R. J.; Kühn, F. E.; Mattner, M. R. *Inorg. Chem.* **1997**, *36*, 465.
- (34) Herdtweck, E.; Kiprof, P.; Herrmann, W. A.; Kuchler, J. G.; Degnan, I. *Z. Naturforsch.* **1990**, *45b*, 937.
- (35) (a) Schoop, T.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **1993**, *12*, 571. (b) Roesky, H. W.; Mazzah, A.; Hesse, D.; Noltemeyer, M. *Chem. Ber.* **1991**, *124*, 519. (c) Winkhofer, N.; Roesky, H. W.; Noltemeyer, M.; Robinson, W. T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 599.
- (36) Ringel, C.; Boden, G. *Z. anorg. allgem. Chem.* **1972**, *393*, 65.
- (37) Edwards, P.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1984**, 2695.
- (38) Suhan, M.; Kennedy, R. M. *Tetrahedron Lett.* **1992**, *33*, 5299, 5303, 7823.
- (39) Stravropoulos, P.; Edwards, P. G.; Wilkinson, G.; Motevalli, M.; Abdul Malik, K. M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 2167.
- (40) Cai, S.; Hoffman, D. M.; Huffman, J. C.; Wierda, D. A.; Woo, H.-G. *Inorg. Chem.* **1987**, *26*, 3693.
- (41) Herrmann, W. A.; Romão, C. C.; Kiprof, P.; Behm, J.; Cook, M. R.; Taillefer, M. *J. Organomet. Chem.* **1991**, *413*, 11.
- (42) Cai, S.; Hoffman, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Commun.* **1988**, 313.
- (43) (a) McGilligan, B. S.; Arnold, J.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2465. (b) Roesky, H. W.; Hesse, D.; Rietzel, M.; Noltemeyer, M. *Z. Naturforsch.* **1990**, *45b*, 72–76.
- (44) Herrmann, W. A.; Thiel, W. R.; Kühn, F. E.; Fischer, R. W.; Kleine, M.; Herdtweck, E.; Scherer, W. *Inorg. Chem.* **1993**, *32*, 5188.
- (45) (a) Wieghardt, K.; Pomp, C.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1659. (b) Pomp, C.; Wieghardt, K. *Polyhedron* **1988**, *7*, 2537. (c) Böhm, G.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 787. (d) Böhm, G.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1991**, *30*, 3464.
- (46) (a) Conry, R.; Mayer, J. M. *Inorg. Chem.* **1990**, *29*, 4862. (b) Thomas, J. A.; Davison, A. *Inorg. Chim. Acta* **1991**, *190*, 231. (c) DuMez, D. D.; Mayer, J. M. *Inorg. Chem.* **1995**, *34*, 6396. (d) Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091. (e) Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12119. (f) DuMez, D. D.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12416.
- (47) (a) Küppers, H. J.; Nuber, B.; Weiss, J.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1990**, 979. (b) Banbery, H. J.; Hussain, W.; Evans, I. G.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A.; Schulte, H.-J.; Engles, B.; Kläui, W. *Polyhedron* **1990**, *9*, 2549.
- (48) (a) Degnan, I. A.; Herrmann, W. A.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 1347. (b) Coe, B. J. *Polyhedron* **1992**, *11*, 1085.
- (49) (a) Domingos, A.; Marçalo, J.; Paulo, A.; de Matos, A. P.; Santos, I. *Inorg. Chem.* **1993**, *32*, 5114. (b) Paulo, A.; Domingos, A.; Marçalo, J.; de Matos, A. P.; Santos, I. *Inorg. Chem.* **1995**, *34*, 2113. (c) Paulo, A.; Domingos, A.; Santos, I. *Inorg. Chem.* **1996**, *35*, 1798.
- (50) Herrmann, W. A.; Roesky, P. W.; Kühn, F. E.; Scherer, W.; Kleine, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1714.
- (51) El Essawi, M.; Dehnicke, K. *Z. Naturforsch.* **1979**, *34b*, 746.
- (52) Ara, I.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 1429.
- (53) (a) Xiao, J.; Puddephatt, R. J.; Manojlovic-Muir, L.; Torabi, A. A. *J. Am. Chem. Soc.* **1994**, *116*, 1129. (b) Xiao, J.; Hao, L.; Puddephatt, R. J.; Manojlovic-Muir, L.; Muir, K. W.; Torabi, A. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2221. (c) Hao, L.; Xiao, J.; Vittal, J. J.; Puddephatt, R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 346.
- (54) Costas, M.; Poblet, J. M.; Rohmer, M.-M.; Bénard, M. *Inorg. Chem.* **1995**, *34*, 176.
- (55) (a) Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899. (b) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571. (c) Artus, G. R. J. Ph.D. Thesis, Technical University of Munich, 1996.
- (56) (a) Sergienko, V. S.; Khodashova, T. S.; Porai-Koshits, M. A.; Butman, L. A. *Sov. J. Coord. Chem.* **1977**, *3*, 822. (b) Kühn, F. E. Ph.D. Thesis, Technical University Munich, 1994. (c) Heidrich, J.; Loderer, D.; Beck, W. *J. Organomet. Chem.* **1986**, *12*, 329.
- (57) Herrmann, W. A.; Kühn, F. E.; Roesky, P. W. *J. Organomet. Chem.* **1995**, *485*, 243.
- (58) Edwards, P. G.; Skapski, A. C.; Slawin, A. M. Z.; Wilkinson, G. *Polyhedron* **1984**, *3*, 1083.
- (59) Danopoulos, A. A.; Wong, A. C. C.; Wilkinson, G.; Hursthouse, M. B.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1990**, 315.
- (60) Beattie, I. R.; Jones, P. J. *Inorg. Chem.* **1979**, *18*, 2318.
- (61) (a) Bosma, R. H. A.; v. d. Aardweg, J. C. *J. Organomet. Chem. Commun.* **1985**, 631. (b) Xiaoding, X.; Mol, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, 631.
- (62) (a) Herrmann, W. A.; Kuchler, J. G.; Felixberger, J. K.; Herdtweck, E.; Wagner, W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 394. (b) Fischer, R. W. Ph.D. Thesis, Technical University Munich, 1994.
- (63) (a) Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 6527. (b) Herrmann, W. A.; Scherer, W.; Fischer, R. W.; Blümel, J.; Kleine, M.; Mertin, W.; Gruhn, R.; Mink, J.; Boysen, H.; Wilson, C. C.; Ibberson, R. M.; Bachmann, L.; Mattner, M. *J. Am. Chem. Soc.* **1995**, *117*, 3231.
- (64) Scherer, W. Ph.D. Thesis, Technical University of Munich, 1994.
- (65) (a) Herrmann, W. A.; Kuchler, J. G.; Weichselbaumer, G.; Herdtweck, E.; Kiprof, P. *J. Organomet. Chem.* **1989**, *372*, 351. (b) Takacs, J.; Cook, M. R.; Kiprof, P.; Kuchler, J. G.; Herrmann, W. A. *Organometallics* **1997**, *10*, 316. (c) Herrmann, W. A.; Kuchler, J. G.; Kiprof, P.; Riede, J. *J. Organomet. Chem.* **1990**, *395*, 55.
- (66) (a) Herrmann, W. A.; Weichselbaumer, G.; Herdtweck, E. *J. Organomet. Chem.* **1989**, *372*, 371; (b) Roesky, P. W. Ph.D. Thesis, Technical University of Munich, 1994. (c) Herrmann, W. A.; Kühn, F. E.; Mattner, M. R.; Artus, G. R. J.; Geisberger, M.; Correia, J. D. G. *J. Organomet. Chem.* **1997**, *538*, 203. (d) Herrmann, W. A.; Correia, J. D. G.; Rauch, M. U.; Artus, G. R. J.; Kühn, F. E. *J. Mol. Catal.* **1997**, *118*, 33. (e) Geisberger, M., Ph.D. Thesis, Technical University of Munich, 1997.
- (67) Kunkely, H.; Türk, T.; Teixeira, C.; Bellefon, C. de Méric de; Herrmann, W. A.; Vogler, A. *Organometallics* **1991**, *10*, 2090.

- (68) Kuchler, J. G., Ph.D. Thesis, Technical University of Munich, 1990.
- (69) (a) Herrmann, W. A.; Fischer, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 3223. (b) Genin, H. S.; Lawler, K. A.; Hoffmann, R.; Herrmann, W. A.; Fischer, R. W.; Scherer, W. *J. Am. Chem. Soc.* **1995**, *117*, 3244. (c) Köstlmeier, S.; Pachioni, G.; Herrmann, W. A.; Rösch, N. *J. Organomet. Chem.* **1996**, *514*, 111.
- (70) Herrmann, W. A.; Ladwig, M.; Kiprof, P.; Riede, J. *J. Organomet. Chem.* **1989**, *371*, C13.
- (71) Herrmann, W. A.; Romão, C. C.; Fischer, R. W.; Kiprof, P.; Bellefon, C. M. de M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 185.
- (72) de Bellefon, C. M.; Herrmann, W. A.; Kiprof, P.; Whitaker, C. R. *Organometallics* **1992**, *11*, 1072.
- (73) Herrmann, W. A.; Kühn, F. E.; Romão, C. C.; Huy, H. T.; Wang, M.; Fischer, R. W.; Scherer, W.; Kiprof, P. *Chem. Ber.* **1993**, *126*, 45.
- (74) (a) Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Catal.* **1994**, *86*, 243. (b) Herrmann, W. A.; Kühn, F. E.; Rauch, M. U.; Correia, J. D. G.; Artus, G. *Inorg. Chem.* **1995**, *34*, 2914.
- (75) Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. U. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1157.
- (76) (a) Cai, S.; Hoffman, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1489. (b) Cai, S.; Hoffman, D. M.; Wierda, D. A. *Inorg. Chem.* **1989**, *28*, 3784.
- (77) (a) Herrmann, W. A.; Kühn, F. E.; Fischer, R. W.; Thiel, W. R.; Romão, C. C. *Inorg. Chem.* **1992**, *31*, 4431. (b) Herrmann, W. A.; Kratzer, R.; Fischer, R. W. *Angew. Chem., Int. Ed. Engl.*, in press.
- (78) (a) Neumann, W. P. *Die Organische Chemie des Zinns*; Ferdinand Enke: Stuttgart, 1967 and references cited therein. (b) Ingham, R. K.; Rosenberg, S. D.; Gilman, H. *Chem. Rev.* **1960**, *60*, 459.
- (79) Herrmann, W. A.; Kühn, F. E.; Romão, C. C.; Huy, H.-T. *J. Organomet. Chem.* **1994**, *481*, 227.
- (80) (a) Herrmann, W. A.; Weichselbaumer, G.; Paciello, R. A.; Fischer, R. A.; Herdtweck, E.; Okuda, J.; Marz, D. W. *Organometallics* **1990**, *9*, 489; (b) Herrmann, W. A.; Ding, H.; Kühn, F. E.; Scherer, W. Unpublished results
- (81) (a) Mealli, C.; Lopez, J. A.; Calhorda, M. J.; Romão, C. C.; Herrmann, W. A. *Inorg. Chem.* **1994**, *33*, 1139–1143. (b) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9275.
- (82) (a) Grasselli, R. K.; Burrington, J. D. *Adv. Catal.* **1981**, *30*, 134. (b) Chan, D. M. T.; Fultz, W. C.; Nugent, W. A.; Roe, D. C.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 251. (c) Chan, D. M. T.; Nugent, W. A. *Inorg. Chem.* **1985**, *24*, 1422.
- (83) (a) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, 1996. (b) Belgacem, J.; Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 1501. (c) Belgacem, J.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1125
- (84) Atagi, L. M.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 1483.
- (85) Herrmann, W. A.; Kühn, F. E.; Romão, C. C. *J. Organomet. Chem.* **1995**, *495*, 209.
- (86) Ewing, D. F. *Org. Magn. Reson.* **1979**, *12*, 499.
- (87) (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297. (b) Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165. (c) Herrmann, W. A.; Okuda, J. *J. Mol. Catal.* **1987**, *41*, 109. (d) Herrmann, W. A. *J. Organomet. Chem.* **1986**, *300*, 111.
- (88) Riedel, A. Diploma Thesis, Technical University of Munich, Germany, 1963.
- (89) (a) Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 383; (b) Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1984**, *3*, 1313.
- (90) (a) Herrmann, W. A.; Voss, E.; Flöel, M. *J. Organomet. Chem.* **1985**, *297*, C5. (b) Wallis, J. M.; Kochi, J. K. *Inorg. Chim. Acta* **1989**, *160*, 217. (c) Wolowiec, S.; Kochi, J. K. *Inorg. Chem.* **1991**, *30*, 1215. (d) Gable, K. P.; Phan, T. N. *J. Organomet. Chem.* **1994**, *466*, C5. (e) Thiel, W. R.; Fischer, R. W.; Herrmann, W. A. *J. Organomet. Chem.* **1993**, *459*, C9.
- (91) Herrmann, W. A.; Serrano, R.; Schäfer, A.; Küsthardt, U.; Ziegler, M. L.; Guggolz, E. *J. Organomet. Chem.* **1984**, *272*, 55.
- (92) (a) Okuda, J.; Herdtweck, E.; Herrmann, W. A. *Inorg. Chem.* **1988**, *27*, 1254. (b) Burrell, A. K.; Cotton, F. A.; Daniels, L. M.; Petricek, V. *Inorg. Chem.* **1995**, *34*, 4253. (c) Masciocchi, N.; Cairati, P.; Saiano, F.; Sironi, A. *Inorg. Chem.* **1996**, *35*, 4060.
- (93) Jung, K. A. Ph.D. Thesis, Technical University of Munich, 1990.
- (94) Herrmann, W. A.; Taillefer, M.; de Méric de Bellefon, C.; Behm, J. *Inorg. Chem.* **1991**, *30*, 3247.
- (95) Kühn, F. E.; Herrmann, W. A.; Hahn, R.; Elison, M.; Blümel, J.; Herdtweck, E. *Organometallics* **1994**, *13*, 1601.
- (96) (a) Szyperski, T.; Schwerdtfeger, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1128. (b) Wiest, R.; Leininger, T.; Jeung, G. H.; Bénard, M. *J. Phys. Chem.* **1992**, *96*, 10800. (c) Köstlmeier, S.; Häberlen, O. D.; Rösch, N. *Organometallics* **1996**, *15*, 1872.
- (97) Flessner, U. N. Ph.D. Thesis, Technical University of Munich, 1992.
- (98) Herrmann, W. A.; Kühn, F. E.; Romão, C. C. *J. Organomet. Chem.* **1995**, *489*, C56.
- (99) (a) Kiprof, P. *Ph.D. Thesis*; Technical University of Munich, 1991. (b) Behm, J. *Ph.D. Thesis*; Technical University of Munich, 1992.
- (100) Mink, J.; Keresztury, G.; Stirling, A.; Herrmann, W. A. *Spectrosc. Chim. Acta* **1994**, *50A*, 2039.
- (101) Herrmann, W. A.; Roesky, P. W.; Scherer, W.; Kleine, M. *Organometallics* **1994**, *13*, 4536.
- (102) Costas, M.; Leininger, T.; Jeung, G. H.; Bénard, M. *Inorg. Chem.* **1992**, *31*, 3317.
- (103) Albach, R. Ph.D. Thesis, Technical University of Munich, 1992.
- (104) Herrmann, W. A.; Kühn, F. E.; Fiedler, D. A.; Mattner, M. R.; Geisberger, M. R.; Kunkely, H.; Vogler, A.; Steenken, S. *Organometallics* **1995**, *14*, 5377.
- (105) Kunkely, H.; Vogler, A. *J. Organomet. Chem.* **1996**, *506*, 175.
- (106) (a) Herrmann, W. A.; Fischer, R. W.; Scherer, W. *Adv. Mater.* **1992**, *4*, 653. (b) Mattner, M. R.; Herrmann, W. A.; Berger, R.; Gerber, C.; Gimzewski, J. K. *Adv. Mater.* **1996**, *8*, 654.
- (107) (a) Herrmann, W. A.; Wachter, W.; Kühn, F. E.; Kleine, M.; Fischer, R. W. *J. Organomet. Chem.*, in press. (b) Wachter, W. Ph.D. Thesis, Technical University of Munich, 1996.
- (108) Herrmann, W. A.; Wachter, W.; Geisberger, M. Unpublished results.
- (109) Gable, K. P.; Juliette, J. J.; Li, C.; Nolan, S. P. *Organometallics* **1996**, *15*, 5250.
- (110) (a) Herrmann, W. A.; Serrano, R.; Ziegler, M. L.; Pfisterer, H.; Nuber, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 50. (b) Herrmann, W. A.; Serrano, R.; Küsthardt, U.; Guggolz, E.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1985**, *287*, 329. (c) Küsthardt, U. Ph.D. Thesis, Technical University of Munich, Germany, 1986.
- (111) de Boer, E. J. M.; de With, J.; Orpen, A. G. *J. Am. Chem. Soc.* **1986**, *108*, 8271.
- (112) Bursten, B. E.; Cayton, R. H. *Organometallics* **1987**, *6*, 2004.
- (113) Herrmann, W. A.; Fischer, R. A.; Amslinger, W.; Herdtweck, E. *J. Organomet. Chem.* **1989**, *362*, 333.
- (114) Felixberger, J. K.; Kuchler, J. G.; Herdtweck, E.; Paciello, R. A.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 946.
- (115) Takacs, J.; Kiprof, P.; Herrmann, W. A. *Polyhedron* **1990**, *9*, 2211.
- (116) (a) Herrmann, W. A.; Marz, D.; Herdtweck, E.; Schäfer, A.; Wagner, W.; Kneuper, H.-J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 462. (b) Herrmann, W. A.; Flöel, M.; Kulpe, J.; Felixberger, J. F.; Okuda, J.; Herdtweck, E. *J. Organomet. Chem.* **1988**, *355*, 297.
- (117) Herberhold, M.; Jin, G.-X.; Millius, W. *J. Organomet. Chem.* **1993**, *459*, 257.
- (118) Herrmann, W. A.; Küsthardt, U.; Ziegler, M. L.; Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 860.
- (119) Herrmann, W. A.; Alberto, R.; Kiprof, P.; Baumgärtner, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 189 and references cited therein.
- (120) (a) Schröder, M. *Chem. Rev.* **1980**, *80*, 187. (b) Hentges, S. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 4263; (c) Jacobsen E. N.; Markó, I.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968. (d) Göbel, T.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1329. (e) Veldkamp, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 4937. (f) Herrmann, W. H.; Eder, S. J.; Scherer, W. *Chem. Ber.* **1993**, *126*, 39.
- (121) Gable, K. P.; Phan, T. N. *J. Am. Chem. Soc.* **1993**, *115*, 3036.
- (122) Gable K. P. *Organometallics* **1994**, *13*, 2486.
- (123) Gable, K. P.; Phan, T. N. *J. Am. Chem. Soc.* **1994**, *116*, 833.
- (124) Herrmann, W. A.; Marz, D. W. *J. Organomet. Chem.* **1989**, *362*, C5.
- (125) Degnan, I. A.; Behm, J.; Cook, M. R.; Herrmann, W. A. *Inorg. Chem.* **1991**, *30*, 2165.
- (126) (a) Herrmann, W. A.; Felixberger, J. K.; Kuchler, J. G.; Herdtweck, E. *Z. Naturforsch.* **1990**, *45b*, 876. (b) Herrmann, W. A.; Roesky, P.; Wang, M.; Scherer, W. *Organometallics* **1994**, *13*, 4531. (c) Ciani, G. F.; D'Alfonso, G.; Romiti, P. F.; Sironi, A.; Freni, M. *Inorg. Chim. Acta* **1983**, *72*, 29. (d) Abu-Omar, M. M.; Appelman, E. H.; Espenson, J. H. *Inorg. Chem.* **1996**, *35*, 7751.
- (127) (a) Takacs, J.; Kiprof, P.; Kuchler, J. G.; Herrmann, W. A. *J. Organomet. Chem.* **1989**, *369*, C1. (b) Takacs, J.; Kiprof, P.; Riede, J.; Herrmann, W. A. *Organometallics* **1990**, *9*, 783. (c) Takacs, J.; Cook, M. R.; Kiprof, P.; Kuchler, J. G.; Herrmann, W. A. *Organometallics* **1991**, *10*, 316. (d) Herrmann, W. A.; Watzlowik, P.; Kiprof, P. *Chem. Ber.* **1991**, *124*, 1101.
- (128) Zhu, Z.; Al-Ajlouni, A. M.; Espenson, J. H. *Inorg. Chem.* **1996**, *35*, 1408.
- (129) Jørgensen, K. A. *Chem. Rev.* **1989**, *89*, 447.
- (130) (a) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638.
- (131) Herrmann, W. A.; Correia, J. D. G.; Artus, G. R. J.; Fischer, R. W.; Romão, C. C. *J. Organomet. Chem.* **1996**, *520*, 139.
- (132) (a) Yamazaki, S.; Espenson, J. H.; Huston, P. *Inorg. Chem.* **1993**, *32*, 4683. (b) Sundermeyer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1144. (c) Pestovsky, O.; van Eldik, R.; Huston, P.; Espenson,

- J. H. *J. Chem. Soc., Dalton Trans.* **1995**, 133. (d) Schröder, D.; Fiedler, A.; Herrmann, W. A.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2636. (e) Hatzopoulos, I.; Brauer, H.-D.; Geisberger, M.; Herrmann, W. A. *J. Organomet. Chem.* **1996**, *520*, 201.
- (133) Abu-Omar, M. M.; Hansen, P. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 4966.
- (134) (a) Al-Ailoun, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 9243. (b) Herrmann, W. A. In *Organic Peroxygen Chemistry*; Herrmann, W. A., Ed.; Springer Verlag: Berlin, 1993; Vol. 164, p 130. (c) Boehlow, T. R.; Spilling, C. D. *Tetrahedron Lett.* **1996**, *37*, 2717. (d) Murray, R. W.; Singh, M.; Williams, B. L.; Moncrieff, H. M. *Tetrahedron Lett.* **1995**, *36*, 2437. (e) Al-Ajlouni, A. M.; Espenson, J. H. *J. Org. Chem.* **1996**, *61*, 3969. (e) Adam, W.; Mitchell, C. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 533.
- (135) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 7728.
- (136) (a) Adam, W.; Herrmann, W. A.; Lin, J.; Saha-Möller, C. R.; Fischer, R. W.; Correia, J. D. G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2475. (b) Karasevich, E. I.; Nikitin, A. V.; Rubailo, V. L. *Kinet. Katal.* **1994**, *35*, 810; *Kinetika i Kataliz* **1994**, *35*, 878. (c) Yamazaki, S. *Chem. Lett.* **1995**, 127. (d) Adam, W.; Herrmann, W. A.; Lin, J.; Saha-Möller, C. R. *J. Org. Chem.* **1994**, *59*, 8281. (e) Adam, W.; Herrmann, W. A.; Saha-Möller, C. R.; Shimizu, M. *J. Mol. Catal.* **1995**, *97*, 15.
- (137) (a) Vassell, K. A.; Espenson, J. H. *Inorg. Chem.* **1994**, *33*, 5491. (b) Adam, W.; Mitchell, C. M.; Saha-Möller, C. R. *Tetrahedron* **1994**, *50*, 13121. (c) Yamazaki, S. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2955. (d) Beddoes, R. L.; Painter, J. E.; Quayle, P.; Patel, P. *Tetrahedron Lett.* **1996**, *37*, 9385; (e) Brown, K. N.; Espenson, J. H. *Inorg. Chem.* **1996**, *35*, 7211. (f) Huston, P.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1993**, *32*, 4517.
- (138) Abu-Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272.
- (139) (a) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 1326. (b) Murray, R. W.; Iyanar, K.; Chen, J.; Wearing, J. T. *Tetrahedron Lett.* **1996**, *37*, 805.
- (140) (a) Espenson, J. H.; Pestovsky, O.; Huston, P.; Staudt, S. *J. Am. Chem. Soc.* **1994**, *116*, 2869. (b) Hansen, P. J.; Espenson, J. H. *Inorg. Chem.* **1995**, *34*, 5389.
- (141) Murray, R. W.; Iyanar, K.; Chen, J.; Wearing, J. T. *Tetrahedron Lett.* **1995**, *36*, 6415.
- (142) Rietveld, M. H. P.; Nagelholz, L.; Grove, D. M.; Veldman, N.; Spek, A. L.; Rauch, M. U.; Herrmann, W. A.; von Koten, G. *J. Organomet. Chem.* **1997**, *530*, 159.
- (143) (a) Herrmann, W. A.; Fischer, R. W.; Correia, J. D. G. *J. Mol. Catal.* **1994**, *94*, 213. (b) Abu-Omar, M. M.; Espenson, J. H. *Organometallics* **1996**, *15*, 3543.
- (144) (a) Herrmann, W. A.; Wang, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1641. (b) Zhu, Z.; Espenson, J. H. *J. Mol. Catal.* **1995**, *103*, 87. (c) Abu-Omar, M. M.; Espenson, J. H. *Inorg. Chem.* **1995**, *34*, 6239.
- (145) (a) Herrmann, W. A.; Rauch, M. U.; Roesky, P. W. *J. Organomet. Chem.* **1996**, *511*, 299. (b) Herrmann, W. A.; Rauch, M. U.; Artus, G. R. *J. Inorg. Chem.* **1996**, *35*, 1988.
- (146) (a) Mol, J. C.; Woerlee, E. F. G. *J. Chem. Soc., Chem. Commun.* **1979**, 330. (b) Verkuiljen, E.; Kapsteijn, F.; Mol, J. C.; Boelhouwer, C. *J. Chem. Soc., Chem. Commun.* **1977**, 198. (c) Mol, J. C.; Woerlee, E. F. G. *J. Chem. Soc., Chem. Commun.* **1979**, 330. (d) Mol, J. C. *J. Mol. Catal.* **1982**, *15*, 35.
- (147) Herrmann, W. A.; Wagner, W.; Flessner, U. N.; Volkhardt, U.; Komber, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1636.
- (148) (a) Buffon, R.; Aurox, A.; Lefebvre, F.; Leconte, M.; Choplin, A.; Basset, J.-M.; Herrmann, W. A. *J. Mol. Catal.* **1992**, *76*, 287. (b) Buffon, R.; Choplin, A.; Leconte, M.; Basset, J. M.; Touroude, R.; Herrmann, W. A. *J. Mol. Catal.* **1992**, *72*, L7.
- (149) (a) Borvornwattanought, A.; Bein, T. *J. Phys. Chem.* **1992**, *96*, 9446. (b) Huber, C.; Wu, G. C.; Möller, K.; Bein, T. *Abstr. Pap. Am. Chem. Soc.* **1995**, *209*, 172. (c) Malek, A.; Ozin, G. *Adv. Mater.* **1995**, *7*, 160.
- (150) Commereuc, D. *J. Chem. Soc., Chem. Commun.* **1995**, 791.
- (151) (a) Correia, J. D. G. Ph.D. Thesis, Technical University of Munich, 1996. (b) Kholopov, A. B.; Nikitin, A. V.; Rubailo, V. L. *Kinet. Catal.* **1995**, *36*, 101; *Kinetika i Kataliz* **1995**, *36*, 111. (c) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 7090. (d) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1996**, *61*, 324. (e) Zhu, Z.; Espenson, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 9901.
- (152) (a) Kennedy, R. M.; Tang, S. *Tetrahedron Lett.* **1992**, *33*, 3729. (b) Kennedy, R. M.; Tang, S. *Tetrahedron Lett.* **1992**, *33*, 5299. (c) Kennedy, R. M.; Tang, S. *Tetrahedron Lett.* **1992**, *33*, 5299. (d) Tang, S.; Kennedy, R. M. *Tetrahedron Lett.* **1992**, *33*, 7823.
- (153) McDonald, F. E.; Towne, T. B. *J. Org. Chem.* **1995**, *60*, 5750.
- (154) Laurency, G.; Lukács, F.; Roulet, R.; Herrmann, W. A.; Fischer, R. W. *Organometallics* **1996**, *15*, 845.
- (155) (a) Ainsley, E. E.; Peacock, R. D.; Robinson, P. L. *J. Chem. Soc.* **1950**, 1622. (b) Holloway, J. H.; Selig, H.; Claassen, H. H. *J. Chem. Phys.* **1971**, *54*, 4305. (c) Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1991**, *11*, 3127.
- (156) (a) Turowsky, L.; Seppelt, K. *Z. Anorg. allg. Chem.* **1990**, *590*, 37. (b) Selig, U.; Karpas, Z. *Isr. J. Chem.* **1971**, *9*, 53.
- (157) Schrobilgen, G. J.; Holloway, J. H.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1984**, 1411.
- (158) (a) Peacock, R. D. *J. Chem. Soc.* **1955**, 602. (b) Yagodin, G. A.; Dudin, A. S.; Rakov, E. G.; Opalovskii, A. A. *Russ. J. Inorg. Chem.* **1980**, *25*, 170.
- (159) (a) Huppmann, P.; Labischinski, H.; Lentz, D.; Pritzkow, H.; Seppelt, K. *Z. anorg. allg. Chem.* **1982**, *487*, 7. (b) Casteel, W. J., Jr.; MacLeod, D. M.; Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.* **1996**, *35*, 7279.
- (160) Glukhov, I. A.; El'manova, N. A.; Eliseev, S. S.; Temurova, M. T. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1974**, *19*, 168.
- (161) Makhmadurov, A. M.; Temurova, M. T.; El'manova, N. A.; Glukkhov, I. A. *Dokl. Akad. Nauk. Tadzh. SSR* **1992**, *25(4)*, 225.
- (162) Bol'shakov, A. M.; Glushkova, M. A.; Buslaev, Yu. A. *Dokl. Akad. Nauk. SSR* **1983**, *273*, 1134.
- (163) Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1488.
- (164) Cai, S.; Hoffman, D. M.; Lappas, D.; Woo, H.-G.; Huffman, J. C. *Organometallics* **1987**, *6*, 2273.
- (165) Cai, S.; Hoffman, D. M.; Wierda, D. A. *Organometallics* **1988**, *7*, 2069.
- (166) Heyn, B.; Hoffmann, R. *Z. Chem.* **1976**, *16*, 195.
- (167) Cai, S.; Hoffman, D. M.; Wierda, D. A. *Organometallics* **1996**, *15*, 1023.
- (168) Longley C. J.; Savage, P. D.; Wilkinson, G.; Hussain, B.; Hursthouse, M. *Polyhedron* **1988**, *7*, 1079.
- (169) (a) Spaltenstein, E.; Erikson, T. K. G.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 617. (b) Conry, R. R.; Mayer, J. M. *Organometallics* **1993**, *12*, 3179. (c) Mayer, J. M.; Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 7454. (d) Spaltenstein, E.; Mayer, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7744.
- (170) (a) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1105. (b) Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965. (c) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.
- (171) (a) Danopoulos, A. A.; Longley, C. J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. *Polyhedron* **1989**, *8*, 2657. (b) Danopoulos, A. A.; Wilkinson, G.; Hussain, B.; Hursthouse, M. *J. Chem. Soc., Dalton Trans.* **1989**, 896.
- (172) Horton, A. D.; Schrock, R. R.; Freudenberger, J. H. *Organometallics* **1987**, *6*, 893.
- (173) Williams, D. S.; Schrock, R. R. *Organometallics* **1993**, *12*, 1148.
- (174) Saboonchian, V.; Danopoulos, A. A.; Gutierrez, A.; Wilkinson, G.; Williams, D. J. *Polyhedron* **1991**, *10*, 2241. (b) Saboonchian, V.; Gutierrez, A.; Wilkinson, G.; Bates, B. H.; Hursthouse, M. B. *Polyhedron* **1991**, *10*, 1423.
- (175) Hasselbring, R.; Roesky, H. W.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 601.
- (176) Cook, M. R.; Herrmann, W. A.; Kiprof, P.; Takacs, J. *J. Chem. Soc., Dalton Trans.* **1991**, 797.
- (177) Danopoulos, A. A.; Wilkinson, G.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 181.
- (178) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505.
- (179) Gutierrez, A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1990**, *9*, 2081.
- (180) Lam, H.-W.; Wilkinson, G.; Williams, D. J. *Polyhedron* **1991**, *10*, 2647.
- (181) Roesky, H. W.; Hesse, D.; Bohra, R.; Noltemeyer, M. *Chem. Ber.* **1991**, *124*, 1913.
- (182) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *Polyhedron* **1988**, *7*, 117.
- (183) (a) Schrock, R. R.; Weinstock, I. A.; Horton, A. D.; Liu, A. H.; Schofield, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 2686. (b) Horton, A. D.; Schrock, R. R. *Polyhedron* **1988**, *7*, 1841. (c) Weinstock, I. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1991**, *113*, 135.
- (184) (a) Toreki, R.; Schrock, R. R.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 3610. (b) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 127. (c) Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Organomet. Chem.* **1996**, *520*, 69.
- (185) LaPointe, A. M.; Schrock, R. R. *Organometallics* **1995**, *14*, 1875.
- (186) Schofield, M. H.; Schrock, R. R.; Park, L. Y. *Organometallics* **1991**, *10*, 1844.