

Review

Methyltrioxorhenium and its applications in olefin oxidation, metathesis and aldehyde olefination

Fritz E. Kühn *, Andrea Scherbaum, Wolfgang A. Herrmann *

Anorganisch-chemisches Institut der Technischen, Universität München, Lichtenbergstrasse 4, D-85747 Garching bei München, Germany

Received 1 July 2004; accepted 2 August 2004

Available online 17 September 2004

Abstract

Organorhenium(VII) oxides, most notably methyltrioxorhenium (MTO) and several of its derivatives gained significant importance as extremely versatile catalysts for olefin oxidation reactions, aldehyde olefination, olefin metathesis, etc. MTO is nowadays available by several straightforward synthetic procedures and found even applications in material sciences, forming the first known polymeric organometallic oxide. In this review, the applications of MTO in oxidation catalysis, olefin metathesis and aldehyde olefination are summarized and conclusions concerning possible future applications of organorhenium oxides and related complexes are drawn.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Aldehyde olefination; Methyltrioxorhenium; Olefin epoxidation; Olefin metathesis

1. Introduction

Organometallic oxides are known since about 40 years due to the pioneering work of the research groups of Fischer and Green [1,2]. Their importance as catalyst models and, more importantly, as real catalysts became clear soon after [3]. Despite attempts to synthesize $(C_5H_5)ReO_3$ in the Fischer group in the early 1960s [4] it was only in 1979 that the first organometallic rhenium oxide, methyltrioxorhenium (MTO, Fig. 1) was synthesized [5].

A couple of years later two groups synthesized $(C_5(CH_3)_5)ReO_3$ independently [6,7]. The rational synthesis of the latter compound by the Herrmann group [8] triggered a broader examination on its reaction chemistry and its derivatives [9,10]. By the early 1990s several

derivatives had been synthesized (Fig. 2) [11–16] and their use as efficient catalysts in olefin metathesis, olefin epoxidation and aldehyde olefination was established [17–19]. During the last 15 years an amazingly broad catalytic applicability, especially of the particularly stable MTO unfolded [20–24]. Additionally, MTO even found its entry into material sciences (see Section 3). This article gives a summary of the synthesis and behavior of MTO and follows the development in the three original fields of catalytic application, namely olefin oxidation, metathesis and aldehyde olefination, with particular attention paid to the more recent findings.

2. Synthesis of methyltrioxorhenium(VII)

MTO was first synthesized in a quite time consuming (weeks) and low scale (milligrams) synthesis [5]. The breakthrough towards possible applications came only about 10 years after its first synthesis, when a more efficient synthetic route was reported [25]. An additional improvement was the preventing of any significant Re

* Corresponding authors. Tel.: +49 89 289 13108; fax: +49 89 289 13473.

E-mail addresses: fritz.kuehn@ch.tum.de (F.E. Kühn), wolfgang.herrmann@ch.tum.de (W.A. Herrmann).

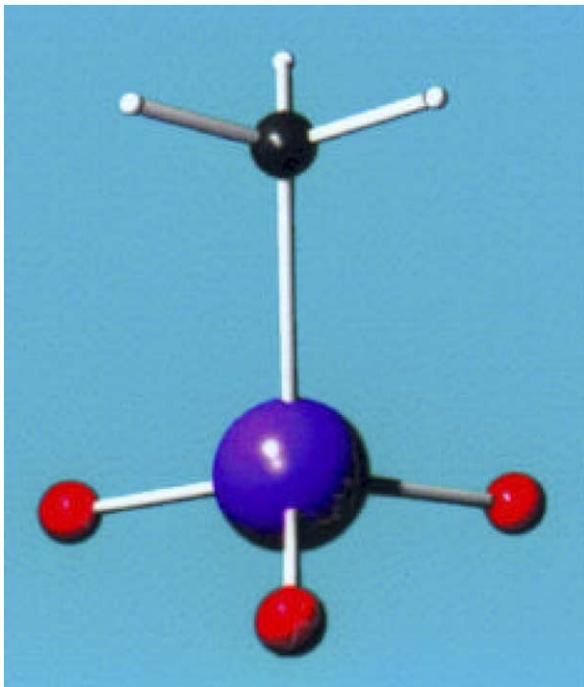


Fig. 1. Methyltrioxorhenium(VII), MTO.

loss as unwanted byproducts [26]. The laboratory pilot-plant stage for MTO synthesis was reached in 1999 [27]. A further modification of the synthesis allows avoiding the moisture sensitive and expensive dirhenium heptaoxide as starting material using instead Re powder or perrhenates [28,29]. This method is of particular additional interest since it allows recycling the catalyst decomposition products from reaction solutions. Scheme 1 describes this latter method. Scheme 1 describes this latter method. A comparative overview on the synthetic pathways to MTO has been given recently [30].

3. Behavior of methyltrioxorhenium in water

MTO hydrolyzes rapidly in basic aqueous solutions and much slower in acidic media. At low concentrations ($\sigma_{\text{MTO}} < 0.008 \text{ M}$) the formation of methane gas and perrhenate was detected. At higher concentrations a second reaction, a faster reversible polymerization–precipitation, takes place to yield a golden colored solid of the empirical composition $\{\text{H}_{0.5}[(\text{CH}_3)_{0.92}\text{ReO}_3]\}$ (poly-MTO) in about 70% yield (Eq. (1)) [31–36]. The reaction

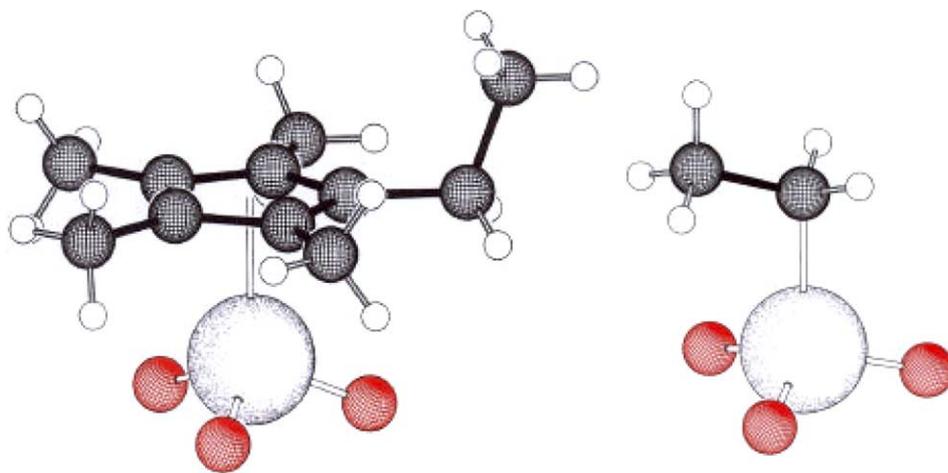
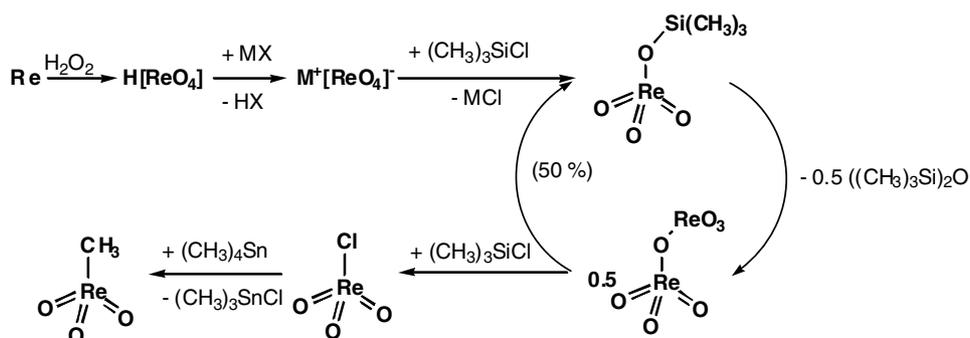
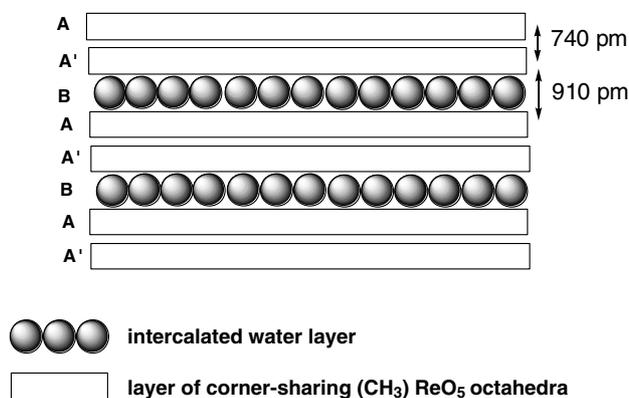


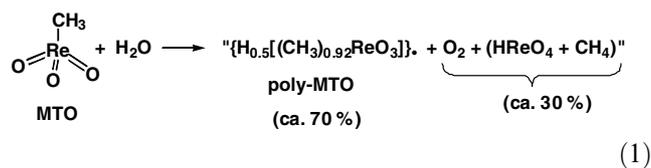
Fig. 2. ((Ethyl)(tetramethyl)pentamethyl)trioxorhenium (left) and ethyltrioxorhenium (right).



Scheme 1.



follows first-order reversible kinetics. The rate of polymerization–precipitation is independent of the concentration of H^+ , and the reaction does not occur in the presence of oxidants [31]. The structure of the crystalline domains of poly-MTO can be described as double layers of corner sharing CH_3ReO_5 octahedra (AA') with intercalated water molecules (B) in a ...AA'BAA'... layer sequence. 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 non-polar methyl groups, which are orientated inside the double layer (Scheme 2). These structural features explain the observed lubricity of poly-MTO. 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 poly-MTO [34,35]. Poly-MTO also contains amorphous areas with a defect stacking of double layers and with smaller content of water. The conductivity of poly-MTO is attributed to occasional demethylation and to the inclusion of extra hydrogen in the lattice. A theoretical study of MTO dimers, trimers and tetramers has been performed. 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 [37]. Terminal oxygens of monomeric MTO seem to be easily available for the formation of bridging oxygens [38].

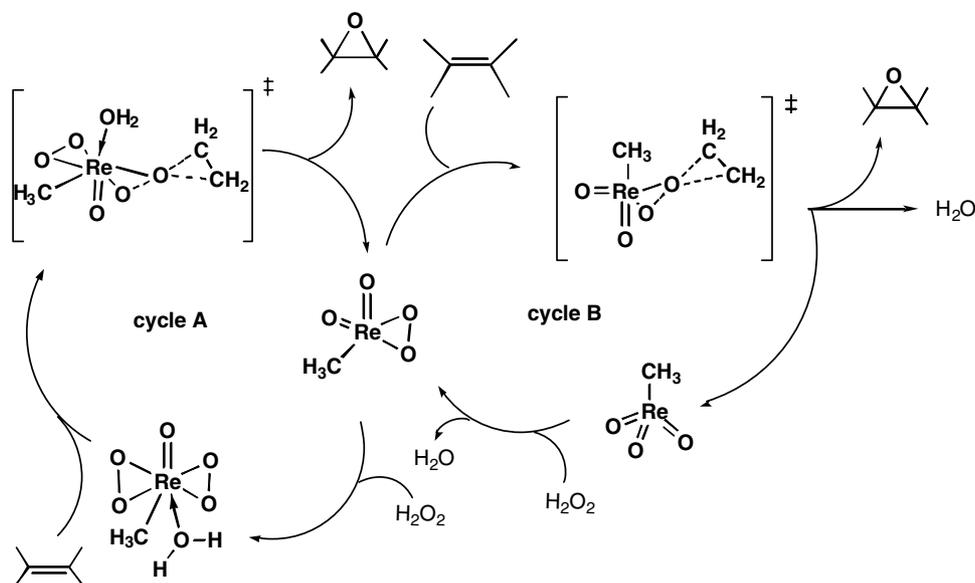


4. MTO as oxidation catalyst

4.1. The active species

The catalytic activity of MTO in the epoxidation of olefins was noticed soon after it was accessible in higher amounts [18]. An important step in the understanding of the role of MTO in oxidation catalysis was the isolation and characterization of the reaction product of MTO with excess H_2O_2 , i.e. a bisperoxo complex of stoichiometry $(CH_3)Re(O_2)_2O \cdot H_2O$ [39]. Its formation takes place in any organic solvent or water. The structures of $(CH_3)Re(O_2)_2O \cdot H_2O$ and $(CH_3)Re(O_2)_2O \cdot (O=P(N(CH_3)_2)_3)$ (X-ray diffraction) were determined, the structure of ligand free complex $(CH_3)Re(O_2)_2O$ is known from the gas phase [39,40].

Experiments with the isolated bis(peroxo)complex $(CH_3)Re(O_2)_2O \cdot H_2O$ have shown that it is an active species in olefin epoxidation catalysis and several other catalytic reactions [39,40]. In situ experiments show that the reaction of MTO with one equivalent of H_2O_2 leads to a monoperoxo complex of the composition $(CH_3)Re(O_2)O_2$ [41,42]. $(CH_3)Re(O_2)O_2$ exists solely in equilibrium with MTO and $(CH_3)Re(O_2)_2O \cdot H_2O$. The monoperoxo complex is also catalytically active in oxidation processes. Kinetic experiments indicate that the rate constants for the transformation of most substrates into their oxidation products by catalysis with the mono and bisperoxo complex are of a comparable order of magnitude [41–43]. These results are supported by density functional calculations [44–46]. The transition states in the olefin epoxidation process starting from $(CH_3)Re(O_2)O_2$ and $(CH_3)Re(O_2)_2O \cdot H_2O$ are not different enough in energy to exclude one of these two catalysts totally from the catalytic process. 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 of the terminal oxygen atoms, which remains on the Re as aqua ligand. The rate of this reaction is not pH-dependent [47]. Two catalytic pathways for the olefin epoxidation may be described depending on the concentration of the hydrogen peroxide used. If 85% hydrogen peroxide is used only $(CH_3)Re(O_2)_2O \cdot H_2O$ appears to be responsible for the epoxidation activity (Scheme 3, cycle A). When a solution of 30 wt% or less H_2O_2 is used, the monoperoxo complex, $(CH_3)Re(O_2)O_2$, is also taking part in the epoxidation process and a second catalytic cycle is involved as shown in Scheme 3, cycle B. For both cycles, a concerted mechanism is suggested in which the electron rich double bond of the alkene attacks a peroxidic oxygen of $(CH_3)Re(O_2)_2O \cdot H_2O$. It has been inferred from experimental data that the system may involve a spiro arrangement [44–49]. The formation and catalytic



Scheme 3.

application of organorhenium(VII) peroxo species as well as possible intermediates and transition states have been reviewed previously [50–54].

4.2. Donor adducts of MTO in catalytic epoxidations

The most important drawback of the MTO catalyzed process is the concomitant formation of diols instead of the desired epoxides, especially in the case of more sensitive substrates [55]. It was quickly detected that the use of Lewis base adducts of MTO (Fig. 3) significantly decreases the formation of diols due to the reduced Lewis acidity of the catalyst system.

However while the selectivity increases, the conversion decreases [55–57]. It was found that biphasic systems (water phase/organic phase) and addition of a significant excess of pyridine as Lewis base not only hamper the formation of diols but also increase the reaction velocity in comparison to MTO as catalyst precursor [58,59]. Additionally it was shown that 3-cyanopyridine and especially pyrazole as Lewis bases are even more effective and less problematic than pyridine itself while pyridine *N*-oxides are less efficient [60–63]. The Brønsted basicity of pyridines lowers the activity of hydronium ions, thus reducing the rate of opening the epoxide ring [64]. MTO forms trigonal-bipyramidal adducts with monodentate N-bases and (distorted) octahedral adducts with bidentate Lewis bases [65–68]. The monodentate Lewis base adducts of MTO react with H₂O₂ to form mono- and bisperoxo complexes analogous to that of MTO, but coordinated by one Lewis base molecule instead of H₂O. From the Lewis base–MTO complexes to the bisperoxo complexes a clear increase in electron deficiency at the Re center can be

observed by spectroscopic methods. The activity of the bisperoxo complexes in olefin epoxidation depends on the Lewis bases, the redox stability of the ligands, and the excess of Lewis base used. The peroxo complexes of the MTO–Lewis bases are, in general, more sensitive to water than MTO itself [65–67]. Furthermore, in the presence of olefins, which are not readily transformed to their epoxides 2,2'-bipyridine can be oxidized to its *N*-oxide by the MTO/H₂O₂-system [69]. Low to moderate stereo induction values (up to about 40% ee with conversions of around 10% at –5 °C reaction temperature) can be achieved when prochiral olefins, e.g. *cis*- β -methylstyrene or α -pinene are epoxidized with chiral amine adducts of MTO [70]. MTO is also successfully applied as chiral epoxidation catalysts in the presence of excess chiral Lewis base ligands derived from pyrazole. Moderate enantiomeric excesses up to ca. 30% can be reached at low reaction temperatures (–30 °C), the conversions however, being quite low (<25%). The reason for this may be the fluctuality of the N-base ligand. Glycolate complexes of MTO, applied under the same conditions reach somewhat higher enantiomeric excesses (up to ca. 40%), however, again associated with low conversions (<30%). In this case the sensitivity of the catalyst to water induced ligand removal as well as ligand exchange with other diols is the most likely reason [71].

4.3. Epoxidations with MTO in ionic liquids

MTO has also been successfully applied as an olefin epoxidation catalyst in ionic liquids [57,72,73]. The values of the rate constants of the formation of the peroxo complexes of MTO have been found to be highly

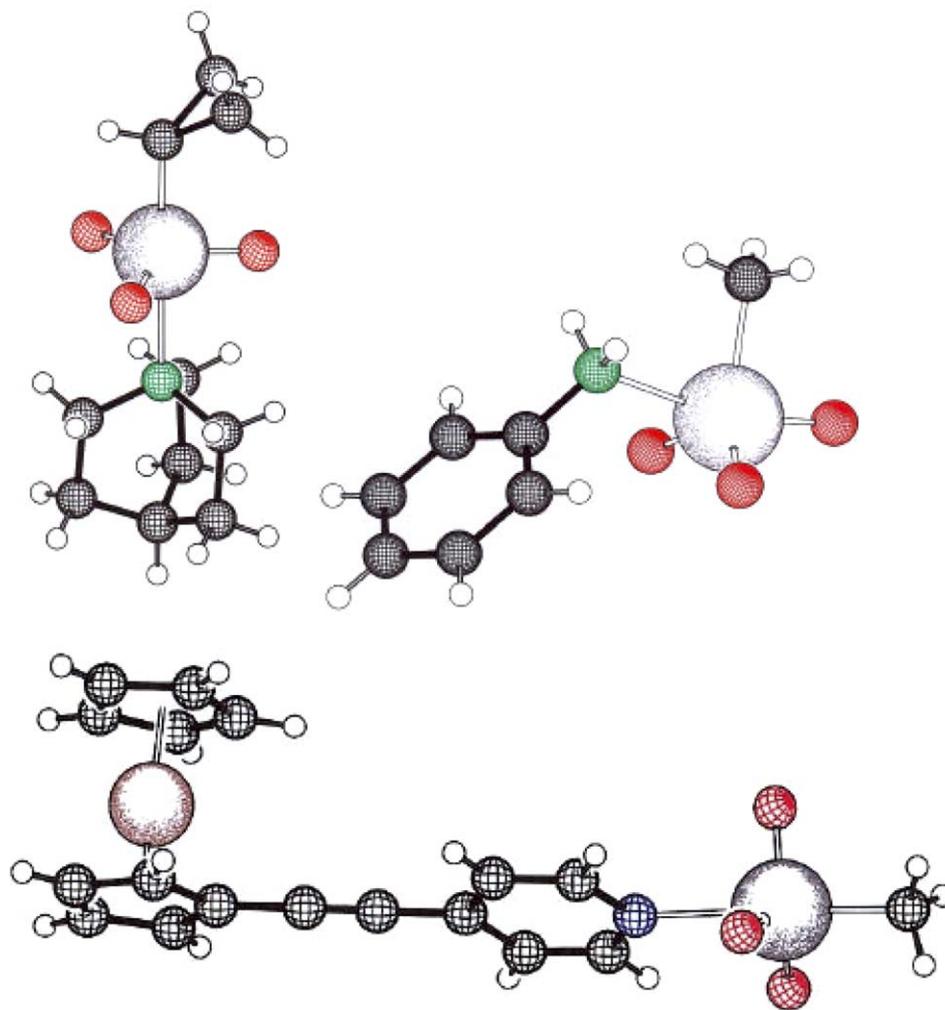


Fig. 3. Aliphatic and aromatic Lewis-base adducts of organorhenium(VII) oxides ((cyclopropyl)trioxorhenium (upper left) and MTO).

dependent on the concentration of water in the solvent. Ionic liquids can behave like organic solvents and aqueous solutions of high salt concentrations.

4.4. Epoxidations with heterogenized MTO as the catalyst

Alternative strategies to improve MTO-catalyzed oxidations have made use of host–guest inclusion chemistry [74–81]. It was found that an urea/hydrogen peroxide (UHP) complex is a very effective oxidant in heterogeneous olefin epoxidations and silane oxidations catalyzed by MTO [74]. Even stereoidal dienes, uracil and purine have been successfully oxidized by the MTO/H₂O₂–urea system [75–77]. The oxidation of the plasmid pBG1 has also been reported as the first example of double-strand DNA cleavage mediated by the catalytic system MTO/H₂O₂ [76]. The epoxidation by urea–hydrogen peroxide catalyzed by MTO on niobia (Nb₂O₅) has also been studied [81]. The reaction rates were found to be more selective than those in homogeneous MTO/hydrogen peroxide solutions.

Using NaY zeolite as host for epoxidations leads to high yields and excellent product selectivities [82]. MTO has also been supported on silica functionalized with polyether tethers [83]. In the absence of an organic solvent, this catalytic assembly catalyzed the epoxidation of alkenes with 30% H₂O₂ in high selectivity compared to the ring-opened products observed in homogeneous media. MTO has additionally been immobilized in the mesoporous silica MCM-41 functionalized with pendant bipyridyl groups of the type [4-(≡Si(CH₂)₄)-4'-methyl-2,2'-bipyridine] [84]. Powder XRD and N₂ adsorption–desorption studies confirm that the regular hexagonal symmetry of the host is retained during the grafting reaction and that the channels remain accessible. The formation of a tethered Lewis base adduct of the type CH₃ReO₃ · (N–N) was confirmed. The XAFS results however indicated that not all rhenium is present in this form and this is consistent with elemental analysis which gave the Re:N ratio to be 1:1.1. It is likely that the excess rhenium is present as un-coordinated MTO molecules assembled in the MCM channels. Furthermore, polymer

supported derivatives of MTO were prepared with poly(4-vinylpyridine) and polystyrene [85]. In the case of poly(4-vinylpyridine)/MTO derivatives, a slightly distorted octahedral conformation of the metal's primary coordination sphere was observed. The Re–N bond was abnormally short in comparison to previously reported homogeneous MTO/pyridine complexes [65], showing a strong coordination of the MTO moiety to the surface. The reticulation grade of the polymer was a crucial factor for the morphology of the particles surface. The polymer supported MTO proved to be an efficient and selective catalyst for the olefin epoxidation. The catalytic activity was reported to be maintained for at least five recycling experiments [85].

4.5. Deactivation of the MTO-derived epoxidation catalysts

A particular important role of water and pH values becomes evident when looking at the catalyst deactivation processes. While MTO and its peroxy complexes are quite stable in acidic media, basic conditions lead to significantly reduced catalyst stabilities. In spite of the extraordinarily strong Re–C bond [86], characteristic of MTO, the cleavage of this bond plays a prominent role in the decomposition processes of these complexes [87–89]. Concerning MTO, the full kinetic pH profile for the base-promoted decomposition to CH_4 and ReO_4^- was examined. Spectroscopic and kinetic data give evidence for mono- and dihydroxo complexes of formulae $\text{CH}_3\text{ReO}_3(\text{OH}^-)$ and $\text{CH}_3\text{ReO}_3(\text{OH}^-)_2$ prior to and responsible for the decomposition process. In the presence of hydrogen peroxide, $(\text{CH}_3)\text{Re}(\text{O}_2)\text{O}_2$ and $(\text{CH}_3)\text{Re}(\text{O}_2)_2\text{O} \cdot \text{H}_2\text{O}$ decompose to methanol and perrhenate with a rate that is dependent on $[\text{H}_2\text{O}_2]$ and $[\text{H}_3\text{O}^+]$. The complex peroxide and pH dependencies are explained by two possible pathways: attack of either hydroxide on $(\text{CH}_3)\text{Re}(\text{O}_2)\text{O}_2$ or HO_2^- on MTO. The bisperoxy complex decomposes much more slowly to yield O_2 and MTO [89]. Thus, critical concentrations of strong nucleophiles have to be avoided, high excess of hydrogen peroxide stabilizes the catalyst. It turned out to be advantageous to keep the steady state concentration of water during the oxidation reaction as low as possible to depress catalyst deactivation.

It has to be noted that quite recently the possibility of MTO catalyzed reactions, utilizing dioxygen from the air instead of H_2O_2 as oxidizing agent has been reported for some special cases [90,91]. Sodium percarbonate has also been successfully applied as an oxygen source for MTO catalyzed epoxidations [92].

4.6. MTO catalyzed epoxidations: an assessment of the current state

Epoxidations with the MTO/ H_2O_2 display several advantages. MTO is easily available, active in low con-

centrations of both MTO (0.05 mol%) and H_2O_2 (<5 wt%), it works with a broad temperature range (–40 to +90 °C) and is stable in water at acidic conditions as well as in basic media in special cases. Furthermore, the MTO/ H_2O_2 system works in a broad variety of solvents, ranging from highly polar solvents (e.g., nitromethane, water) to solvents with low polarity (e.g., toluene). However, the reactions between MTO/ H_2O_2 and alkenes are ca. one order of magnitude faster in semi-aqueous solvents (e.g., 85% H_2O_2) than in methanol. The rate constants for the reaction of MTO/ H_2O_2 with aliphatic alkenes correlate closely with the number of alkyl groups on the alkene carbons. The reactions become significantly slower when electron-withdrawing groups, such as –OH, –CO, –Cl, and –CN are present in the substrates.

A major advantage of MTO is that it does not decompose hydrogen peroxide. This is in striking contrast to many other oxidation catalysts. Turnover numbers (TON) of up to 2500 mol product per mol catalyst (reaction conditions: 0.1 mol% MTO, 5 mol% pyrazole) and turnover frequencies (TOF) of up to 14,000 mol product per mol catalyst per hour have been reported, with typical MTO concentrations of 0.1–1.0 mol%. However, these impressive results have only been reached in perfluorinated alcohols as solvents with cyclohexene as substrate [93,94].

High selectivity (epoxide vs. diol) can be adjusted by temperature control, trapping of water or the use of certain additives, such as aromatic Lewis-base ligands, which additionally accelerate the epoxidation reactions. Selectivities of >95% can be reached.

4.7. Oxidation of conjugated dienes, allylic alcohols and alkynes

Special cases closely related to the topic discussed above are the oxidation of conjugated dienes and the epoxidation of allylic alcohols. Conjugated dienes are oxidized to epoxides or diols, respectively, in the presence of water with the MTO/ H_2O_2 system. The biphasic system MTO/ H_2O_2 / CH_2Cl_2 oxidizes 1,4-polybutadiene efficiently [95,96]. The extension of epoxidation (10–50%) can be modulated by the amount of oxidant added, without significant change in the molecular weight of the polymer [96]. A conjugated linoleic acid isomer, methyl (9Z,11E)-octadecadienolate can also be successfully epoxidized with MTO/hydrogen peroxide [97]. Soybean oil can be oxidized by the MTO/ CH_2Cl_2 / H_2O_2 catalytic biphasic system. Total double bond conversion and 95% selectivity were obtained in two hours at room temperature. The epoxidized soybean oil is reported to remain stable in the absence of stabilizers for up to one month when stored at mild conditions [98]. Fish oils can be epoxidized with MTO in the presence of excess pyridine and 30% H_2O_2 in methylene

chloride. The Norway fish oil ethyl ester can be quantitatively epoxidized in an 86% yield. The Capelin fish oil gives 100% epoxidized fish oil in 72% yield. Decreasing the amounts of MTO and pyridine results in partially epoxidized fish oils [99]. Allylic alcohols are epoxidized to the epoxy alcohols by hydrogen peroxide in the presence of MTO [100,101]. Provided that no acid is added, the product is mostly epoxide, accompanied by minor amounts of triol resulting from acid-catalyzed ring opening. With added acid the triol is obtained. The 1,3-transpositioning of allylic alcohols, also catalyzed by MTO, however, is strongly inhibited by the presence of traces of water [102]. This reaction does not require the presence of peroxides or peroxy complexes. Theoretical investigations on the allylic rearrangement have also been performed [103]. It was also reported that allylic alcohols as well as alkenes can be oxidized in an ambient temperature ionic liquid using MTO and urea hydrogen peroxide [57]. Excellent conversions and selectivities for the epoxides of a wide number of substrates were observed.

The MTO/H₂O₂ system also catalyzes the oxidation of both internal and terminal alkynes. It provides a significantly cleaner and safer method of alkyne epoxidation than the oxidation by organic peracids [104]. Internal alkynes yield carboxylic acids and α -diketones. Rearrangement products were only observed for aliphatic alkynes. Terminal alkynes give carboxylic acids, derivatives thereof and acids as the major products.

4.8. MTO catalyzed formation of aldehydes or ketones from olefins

The advantage of the rhenium catalysts is their ability to activate hydrogen peroxide as cheap and environmentally friendly oxidant without any H₂O₂ decomposition, independent of the concentration of the used hydrogen peroxide (5–85 wt%, see also Section 4.6). Compared to RuCl₃ in the presence of MTO the half-life of H₂O₂ is 20000 times higher, analogously compared to MnO₂ by a factor of 50, Na₂WO₄ by a factor of 20, and even Re₂O₇ by a factor of 2 [105]. In this light, MTO appears as a first class catalyst for an efficient activation of hydrogen peroxide. Dependent on the reaction conditions MTO can be tuned into an epoxidation catalyst (low temperature, presence of co-ligands, correct stoichiometry of oxidant and olefin, see above), dihydroxylation catalysts (ambient temperature and higher, presence of water), or catalysts for the cleavage of C=C double bonds. A mild asymmetric H₂O₂-based dihydroxylation of olefins can be achieved by the MTO/OsO₄ couple. The MTO is catalyzing the H₂O₂ oxidation of the chiral ligand to its *N*-oxide, which in turn re-oxidizes Os-VI to Os-VIII. (DHQD)(2)PHAL plays a dual role serving as the chiral inductor as well as the tertiary amine generating the *N*-oxide required

for the recycling of osmium. This catalytic system gives vicinal diols in good isolated yields and enantiomeric excesses up to 99% ee [106]. Cleavage of double bonds can be achieved under nearly water free conditions, the right choice of solvent, and a defined excess of hydrogen peroxide (olefin/oxidant/catalyst = 1/>4/0.01). To turn MTO into a C=C double bond cleaving catalyst it is necessary to trap the formed water with MgSO₄, *ortho*-esters, or by azeotropic distillation during the course of the oxidation reaction to increase activity and to avoid catalyst hydrolysis. This increases the catalyst lifetime at the required higher reaction temperature of 60 °C. Under these conditions olefins are converted into aldehydes in fair to high yields. Special aprotic solvents like *t*-butyl methyl ether (mtbe) allow higher water concentrations, without being essential to trap H₂O₂ from the reaction mixture. Addition of non-coordinating Brønsted acids like HBF₄ or HClO₄ as co-catalysts increases the yield of aldehyde from olefin oxidation from 68% to 85% under two phase conditions, e.g. with chloroform as the organic phase [107]. Drop wise addition of 30% aqueous hydrogen peroxide to a variety of diols using MTO as the catalyst leads selectively to the corresponding 1,2-diketones. The C–C single bond is maintained in this case [108].

4.9. Acid formation from olefins with MTO/co-catalyst systems

A strong solvent effect was discovered by the application of the oxidation system mtbe/H₂O₂/HBF₄/MTO, which oxidizes the primary formed aldehydes further to their corresponding carboxylic acids in 60% selectivity at complete conversion. In contrast, in mtbe as solvent without addition of HBF₄ only aldehyde formation is observed.

The right combination of aprotic solvent (mtbe) and co-catalyst (HBF₄) leads to a one-pot transformation of olefinic double bonds to aliphatic as well as aromatic carboxylic acids. Thus according to the reaction conditions used, MTO can be freely tuned, dependent on the desired reaction pathway. Besides, simple olefins also long chain olefins, waxes, and fatty acid derivatives can be cleaved by the aforesaid manner to the aldehydes and carboxylic acids applying co-catalyst systems. A C₃₀ wax fraction (Mw 564 g/mol; chain lengths between C₂₆ and C₅₄; Chevron) is cleaved by MTO (0.5 mol%)/H₂O₂ to 57% aldehydes and 43% *vic*-diols at full conversion of the substrate mixture. 2-Alkyl-1-alkene compounds are oxidized to the ketones. Under HBF₄ conditions further oxidation to the carboxylic acid is observed. At the reaction temperature the wax is completely soluble in mtbe, after cooling to ambient temperature the catalyst solution (mtbe/MTO/H₂O₂) is easily separated from the solid reaction products by filtration [107].

Furthermore, the MTO/H₂O₂ system catalyzes the oxidation of cyclic β-diketones to carboxylic acids [109]. Conversions are usually above 85%, the product selectivity is nearly quantitative. The reaction is performed in a 1:1 water acetonitrile solution at room temperature. It has been assumed that enolic forms, which exist in solution are initially epoxidized. After a rearrangement step the C–C bond is cleaved and an oxygen atom is inserted. Then a α-diketone intermediate forms, which is finally oxidized to the carboxylic acid [109].

4.10. Oxidation of alcohols and ethers

Very closely related to the topics discussed previously and therefore mentioned for sake of completeness in this review is the oxidation of alcohols and ethers. Since alcohols, in particular diols can be generated by MTO catalysis from olefins (see above), the further fate of alcohols in the presence of MTO – under the special conditions described below – will be discussed here as well. Primary and secondary alcohols are oxidized using the MTO/H₂O₂ catalyst system to aldehydes and ketones, respectively [110–114]. The addition of a catalytic quantity of bromide ions, such as HBr or NaBr, significantly enhances the reaction rate [111]. The bromide is oxidized to the hypobromite ion, BrO[−], which combines with additional bromide to give bromine. Bromine oxidises the alcohols to aldehydes and ketones. The system MTO/H₂O₂/HBr/TEMPO (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy) catalyses the selective oxidation of terminal alcohols to the corresponding aldehydes with excellent selectivities and yields [112]. The system allows the oxidation of alcohols either selectively to aldehydes or to the corresponding acids depending on the reaction parameters. This technique is especially applicable to the oxidation of carbohydrates [112]. The MTO hydrogen peroxide system oxidatively cleaves furans in yields usually >70% to enediones. Substituted pyranones are obtained from furans with hydroxymethyl groups at the 2-position. The yields, in this case, are >75%. Acetonitrile as solvent leads to the fastest reactions although the work-up is reported to be easier with CH₂Cl₂ [113]. Silyl enol ethers are oxidized to α-hydroxy ketones by MTO/H₂O₂ with subsequent desilylation with KF [114]. Yields are usually >90%. In the case of conjugated systems, the yields are significantly lower.

4.11. Oxidation of aromatic compounds

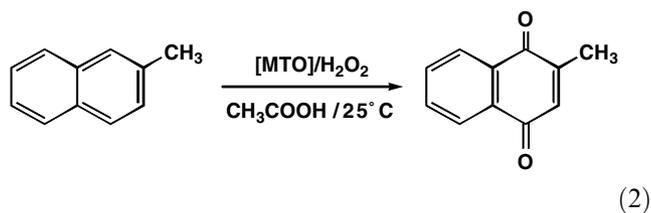
In general, the oxidation of arenes is more difficult than that of alkynes and alkenes. The oxidation of benzenes is harder to achieve than that of polycyclic arenes. Arenes are oxidized to *para*-benzoquinones by hydrogen peroxide with MTO as catalyst in glacial acetic acid and usually at elevated temperatures [115]. The role of the

acetic acid seems to be one of increasing the electrophilicity of the peroxy complex by protonation of a peroxy oxygen atom [51].

Since water is an inhibitor, concentrated (85 wt%) H₂O₂ is also preferred. Alternatively, commercially available 35% H₂O₂ in acetic anhydride can be employed; a considerable regioselectivity is obtained with this system. The conversion is higher for electron-rich arenes (nearly 100%) and selectivities of greater than 85% have been reached [115–126]. Biphenylene can be oxidized with the MTO system in chloroform affording an *o*-quinone product (83% conversion) [116]. Hydroxy substituted arenes can be oxidized by aqueous hydrogen peroxide (85 wt%) in acetic acid to afford the corresponding *p*-quinones in isolated yields of up to 80% [119]. It has been shown that using a mixture of acetic acid and acetic anhydride further improves the product yield [122,123]. Instead of acetic acid, HBF₄ in EtOH may also be used [119,120]. Anisol was also found to undergo selective oxidation with the MTO/H₂O₂ system to yield *o*- and *p*-methoxyphenols. There is no need to use a solvent in this case. The hydrogen peroxide/MTO system has also been reported for the catalytic preparation of *ortho*- and *para*-benzoquinones of cardanol derivatives [124]. Bidentate Lewis base adducts of halogeno rhenium(VII) oxides also catalyze the arene oxidation in the presence of H₂O₂ [121]. Heterogeneous poly(4-vinylpyridine)MTO systems have also been described for the oxidation of substituted phenol and anisole derivatives to benzoquinones. In the oxidation of some natural phenols such as cardanol derivatives higher conversions and yields of benzoquinones were observed with respect to MTO in homogeneous phase suggesting a support-mediated molecular recognition process based on hydrogen-bonding interactions [125].

Concerning the mechanism of the arene oxidation it is assumed that the first reaction step results in the formation of a phenol. Phenols and methoxy arenes, being more electron rich than arenes, react faster with the peroxorhenium compounds. Therefore, the subsequent steps in the oxidation occur more rapidly than the first [123,126].

Benzaldehydes with hydroxy or methoxy substituents in *ortho* or *para* positions are reported to be oxidized to the corresponding phenols (carboxylic acids are formed as by-products) in good yields [118]. The yield is temperature and solvent dependent.



Some of the quinones obtained are of industrial interest, e.g. the synthesis of vitamin K₃ (2-methyl-1,4-naphthoquinone, see Eq. (2)) [115]. Vitamine K₃ is produced on an industrial scale as a supplement for animal feed. 2,3-dimethoxy-5-methyl-*p*-benzoquinone is a key intermediate in the synthesis of coenzyme Q [122].

5. Aldehyde olefination catalyzed by MTO and derivatives

In 1991, Herrmann et al. [19] reported on an aldehyde olefination catalyzed by MTO (see above). The aldehyde olefination reaction with MTO was carried out at room temperature by adding diazo alkane dissolved in benzene or tetrahydrofuran (THF) drop wise to a solution of stoichiometric amounts of aldehyde and triphenyl phosphine and a catalytic amount of MTO (1–10 mol%) in the same solvent (Eq. (3)). The reaction temperature (–20 to +80 °C) has little effect on the product distribution. Ethyldiazo acetate and diazo malonate have been applied together with both saturated and α,β -unsaturated aldehydes and triphenyl phosphine or tri-*n*-butylphosphine. Dependent on the aldehyde used, yields up to 98% and *E:Z* ratios of up to 97:3 could be reached within 20 min reaction time at 20 °C. The more catalyst is present, the worse is the selectivity towards *trans* product and the less azines, RCH=N–N=CHR are produced. Electron withdrawing substituents on the aldehyde favor the olefination in contrast to the Mo-based catalytic system established previously by Schwartz and co-workers [127] and Lu et al. [128]. Another important difference is that olefins derived from diazomalonnate are received with MTO as a catalyst but not with [MoO₂{S₂CN(C₂H₅)₂}₂]. Instead a stable phosphorus ylide, (C₆H₅)₃P=C(CO₂CH₃)₂, is formed in the latter case, which does not react with aldehydes in a Wittig reaction. Therefore, a significant advantage of the MTO catalyzed system is that the synthesis of olefins from otherwise un-reactive precursor compounds is possible. The mechanistic implications of this observation are discussed below in some detail. Some cyclic ketones also undergo the olefination reaction with MTO as the catalyst. However, the yields and activities are in this case considerably lower. The predominant side reaction here is a metal catalysed formation of the symmetric olefin from the diazoalkane.

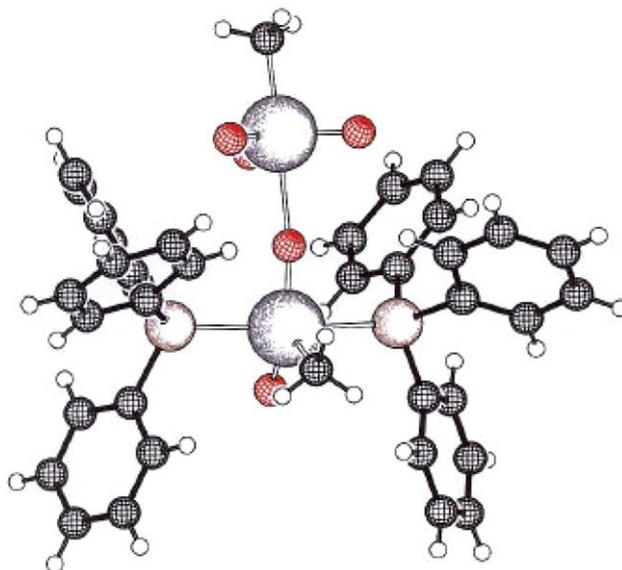
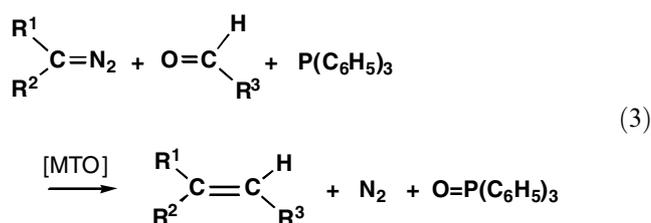
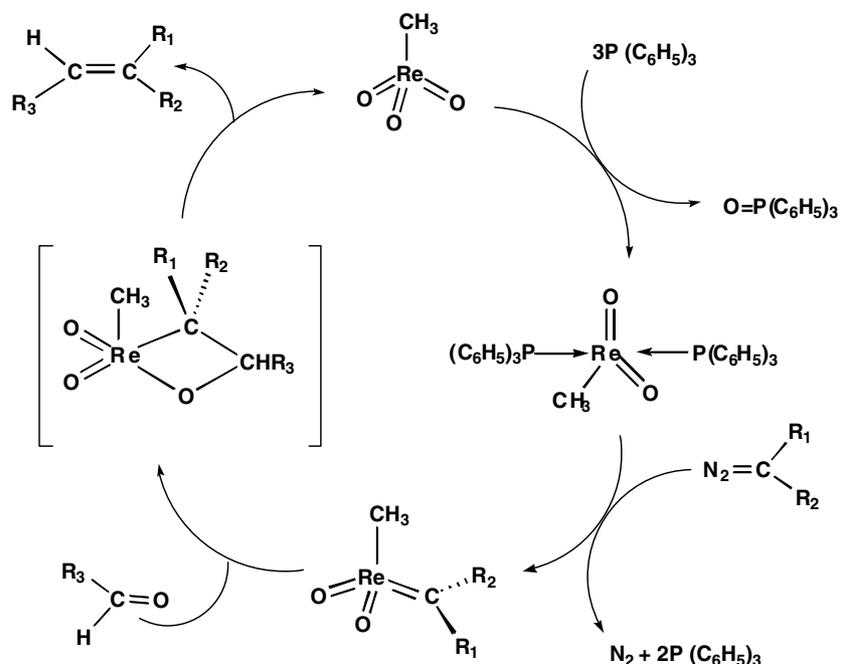


Fig. 4. Adduct of MDO and MTO, found to act as catalytically active species in aldehyde olefination.

Since it was already known that MTO reacts readily with phosphines, it was assumed that in a first step of the catalytic reaction one of the terminal oxo atoms originally bound the rhenium centre is abstracted by the phosphine, forming a compound of the composition CH₃ReO₂ · O=PPh₃, which then would react in a further step with the diazo acetate under liberation of both phosphine oxide and dinitrogen [19,129]. A follow up work showed, that the catalytically active species really was a rhenium(V) complex based on methyldioxorhenium(V), abbreviated as “MDO” (methyldioxorhenium) (Fig. 4) [130].

This compound is formed, as it has been previously anticipated, via reduction of MTO with the phosphine under formation of phosphine oxide. It was assumed that in the catalytic cycle, after the formation of the Re(V) species, in a second step a rhenium carbene complex is formed by the reaction of MDO with the diazo complex under extrusion of dinitrogen gas. The carbene would then react with the aldehyde and form a metallacycle, which finally reforms MTO (with oxygen from the aldehyde) and olefin [129–131]. The whole reaction cycle is shown in Scheme 4. However, neither the rhenium carbene nor the metallacycle could be directly observed. However, rhenium(VII) carbenes could be generated independently already before, but have never been applied as catalysts or carbene transfer reagents for the aldehyde olefination [132–135]. Therefore, based on the work of Espenson et al. [136–138] another mechanistic suggestion was made for the MTO/MDO based olefination of aldehydes by Abu-Omar et al. (Scheme 5) [24]. However, a closer examination of the different steps of this alternative mechanism shows, that the decisive

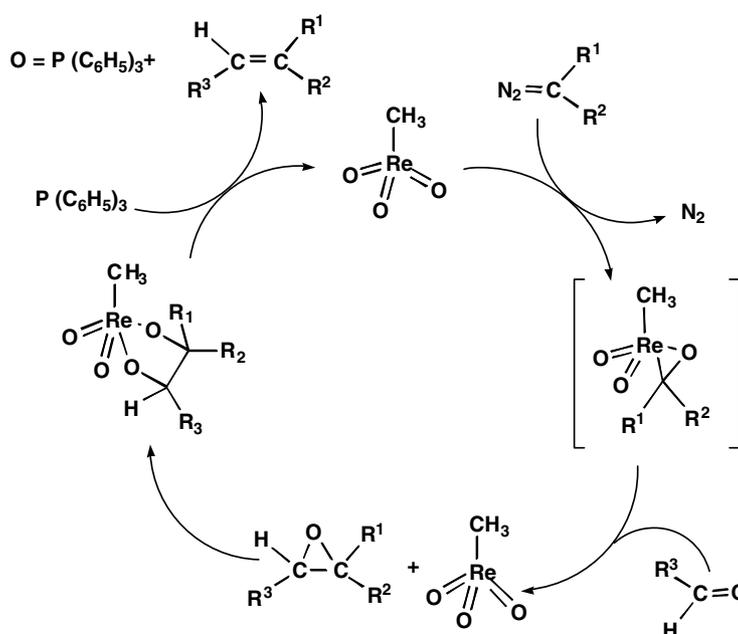


Scheme 4. Catalytic aldehyde olefination mechanism with MTO as the catalyst according to Herrmann et al. [21].

steps of this mechanism – despite being all plausible in itself and some of them being observed under different reaction conditions – would be too slow under the conditions applied for the aldehyde olefination with the MTO/MDO system to play a major role.

More recently, two studies with other Re catalyst systems performed independently by Romão et al., [129,139] and by Zhang and co-workers [139] and by Zhang and Chen [140] proved the presence of Re carbe-

nes under the applied reaction conditions by NMR and MS techniques. The first group used several stable derivatives of MDO, such as $\text{CH}_3\text{ReO}_2(\text{PhC}\equiv\text{CPh})$ [141,142] as catalysts for the aldehyde olefination. It was found that the formation of a phosphazene prior to the reaction with the Re(V) catalyst seems to be a decisive step of the reaction. Abstraction of an oxygen from the MDO moiety by the positively polarized phosphine (observed by ^{17}O NMR spectroscopy) leads to the



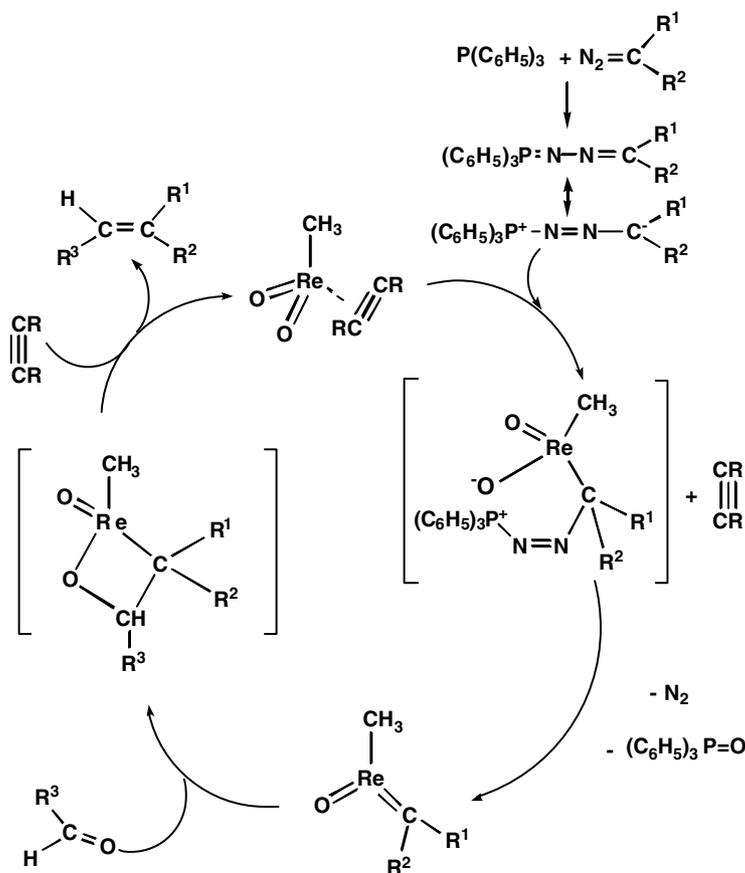
Scheme 5. Catalytic aldehyde olefination mechanism with MTO as the catalyst according to Abu-Omar et al. [24].

formation of a labile Re(V) carbene complex (observed by ^{13}C NMR) and phosphine oxide (Scheme 6). Addition of excess alkyne lead to a significant slowing down of the reaction, probably due to a competition between phosphazine and alkyne for the coordination to the MDO moiety [139]. In the work of Chen et al. ionic catalyst systems based on Lewis-base adducts of dirheniumheptoxide (Re_2O_7) were used [140]. In the gas phase evidence for Re carbene species has been found by ESI-MS spectroscopy. However, both groups originally did not find evidence for the formation of a “rhena-oxethane” intermediate. Chen et al. observed Re bound ylides in the gas phase and by NMR spectroscopy in solution and assumed the Re catalyzed formation of ylides. Since the observed *E/Z*-relationships are dependent on the phosphine used, it is assumed that PR_3 cannot only be a de-oxygenation agent [140]. However, in a follow-up work Chen et al. [143] also reported experiments pointing to an intermediary formation of rhenacycles (rhena-oxethanes) in the related reactions.

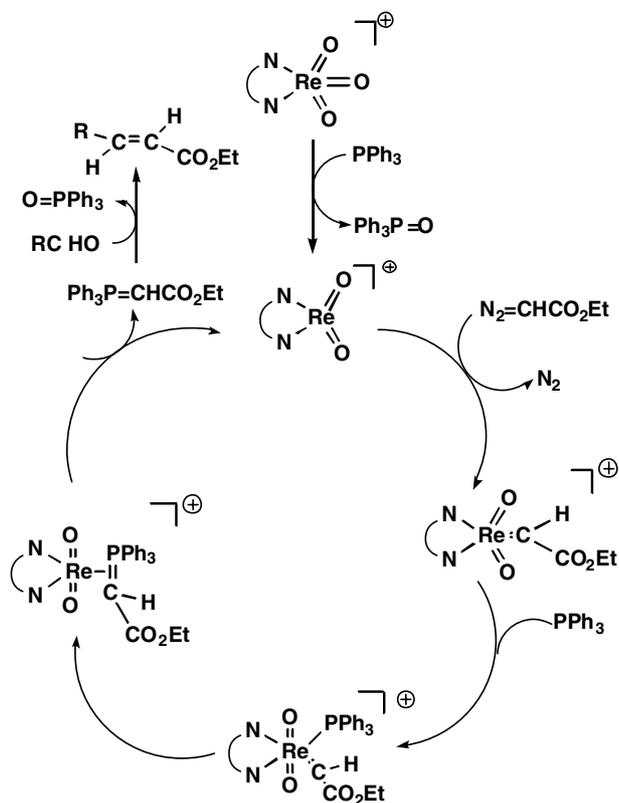
It has been assumed by several groups that the catalytic formation of ylides is the most important role played by the catalysts in aldehyde olefination. However, an interesting detail in the context of the Re catalyzed aldehyde olefination is the following observation:

While the stable phosphorus ylide $(\text{C}_6\text{H}_5)_3\text{P}=\text{C}(\text{CO}_2\text{CH}_3)_2$ does not even react with aldehydes in boiling benzene, the reaction takes place at room temperature in the presence of MTO. Under these conditions olefins of the formula $\text{RCH}=\text{C}(\text{CO}_2\text{CH}_3)_2$ are formed. MTO in benzene does not catalyze olefin formation from ylides and phosphazines (without aldehyde being present) at room temperature [19]. MTO therefore implements the Wittig olefination of aldehydes with otherwise un-reactive phosphorus ylides. With respect to the mechanism, this latter observation may indicate that MTO either catalyzes the aldehyde olefination according to Scheme 4 or catalyses the formation of ylides in a similar way as suggested by Chen et al. for ReO_3^+ derivatives (Scheme 7) [140,143–145] and afterwards, in a second step, catalyses the classical Wittig reaction with the previously formed ylide and the aldehyde. However, these mechanistic questions still remain unsettled. It is also possible that both mechanisms play a role, dependent on the starting materials involved. More work is necessary to elucidate the reaction mechanism.

Another Re(V) complex, $\text{Cl}_3(\text{O})\text{Re}(\text{PPh}_3)_2$, was also found to catalyse the aldehyde olefination showing higher *cis/trans* selectivity than the MTO/MDO-based system [129,130]. However, several derivatives of MTO,



Scheme 6. Mechanism of the catalytic aldehyde olefination with MDO as the catalyst according to Romão et al., [139].



Scheme 7. ReO_3^+ catalyzed formation of ylides according to Chen et al. [140].

namely $(\text{C}_5\text{H}_5)\text{ReO}_3$, $(\text{C}_5(\text{CH}_3)_5)\text{ReO}_3$, and $(t\text{-bu}_2\text{bipy})(\text{CH}_3)\text{ReO}_3$ show low activity [129,130]. $(\text{C}_5(\text{CH}_3)_5)\text{Re}(\text{CO})_3$, $\text{BrRe}(\text{CO})_5$, $\text{Re}_2(\text{CO})_{10}$, and both ionic and covalent perrhenates, such as $[\text{NH}_4]\text{ReO}_3$ and $\text{Me}_3\text{SnOReO}_3$ are completely inactive as catalysts in the aldehyde olefination [130]. The reason for the low activity of CpReO_3 and its derivatives is the different $\text{Re}=\text{O}$ bond strength in comparison to MTO. In MTO the $\text{Re}=\text{O}$ bond is so strong that an oxygen can not be totally abstracted by PR_3 as it is the case as in $(\text{C}_5(\text{CH}_3)_5)\text{ReO}_3$. As outlined above, in MTO the $\text{Re}-\text{O}$ bond is activated through a phosphine base, resulting in $\text{CH}_3\text{ReO}_2 \cdot \text{OPR}_3$ or the isolated $\text{CH}_3\text{ReO}_2 (\text{PR}_3)_2 \cdot (\text{O}=\text{Re}(\text{CH}_3)\text{O}_2)$ [130]. In $(\text{C}_5(\text{CH}_3)_5)\text{ReO}_3$ OPR_3 is extruded, the resulting $(\text{C}_5(\text{CH}_3)_5)\text{ReO}_2$ is stabilized by dimerization to $((\text{C}_5(\text{CH}_3)_5)\text{ReO}_2)_2(\mu\text{-O})_2$ [8–10]. DFT-calculations indicate that dimer-formation is exothermic for $(\text{C}_5(\text{CH}_3)_5)\text{ReO}_3$ and $(\text{C}_5\text{H}_5)\text{ReO}_2$, but endothermic for $\text{CH}_3\text{ReO}_2 \cdot \text{OPR}_3$ [146]. The OPR_3 , however, can be easily abstracted when surface fixed phosphine is used in the presence of alkyne to generate $\text{CH}_3\text{ReO}_2(\text{PhC}\equiv\text{CPh})$ [141,142,147], which is also an aldehyde olefination catalyst, as described above [129,139]. The chemistry of $(t\text{-bu}_2\text{bipy})(\text{CH}_3)\text{ReO}_3$ [148] and other closely related bidentate Lewis-base adducts of MTO resembles more that of $(\text{C}_5(\text{CH}_3)_5)\text{ReO}_3$

than the chemistry of free MTO, explaining their low activity in the aldehyde olefination reaction.

The use of MTO as aldehyde olefination catalyst as first described by Herrmann et al. has, according to some other authors [149] – notwithstanding the mechanistic debate – some practical drawbacks, among them being the use of dry solvents, the formation of OPPh_3 as co-product, which can often complicate product isolation and purification, and the catalyst itself, which had to be prepared from expensive Re_2O_7 [150]. Carreira et al. therefore set out to develop a variation based on $\text{Cl}_3(\text{O})\text{Re}(\text{PPh}_3)_2$ as catalyst (1 mol%), which could be performed in reagent grade solvents without purification of any reagent prior to use. Good yields (ca. 85%) and diastereoselectivities of 20:1 have been reached by replacing PPh_3 by $\text{P}(\text{OEt})_3$. The by product $\text{OP}(\text{OEt})_3$ can be easily removed by aqueous work up [149]. Since then the synthesis of MTO has also been significantly modified, so that it can be directly synthesized from Re powder (see Section 2). This is a particularly straightforward and inexpensive way to get to this stable and easy to handle compound. From the cost, stability and preparative point of view, no other $\text{Re}(\text{VII})$ compound is nowadays a match for MTO (see above). However, in the meantime some other, not Re-based aldehyde olefination catalysts have been described, which rival the Re based systems both in selectivity and activity [151].

6. MTO as catalyst in 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 and its activity can be further increased by the addition of tetra alkyl tin compounds [152–155]. This observation led to the methyl tin based synthesis of MTO [25].

Since tin containing co-catalysts are essential for the metathesis of functionalized olefins [156,157], it was soon discovered that MTO supported on acidic metal oxides forms metathesis catalysts that are active without additives, even for functionalized olefins [17]. 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 (for surface fixed MTO see also Section 4.4) [158–160]. 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 [17,158,159,161]. 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 [17]. The carbene species, which is implied in the metathesis catalytic cycle does not appear to originate from the methyl group of MTO [155]. It has been shown, however, that matrix-isolated MTO tautomerizes to $\text{H}_2\text{C}=\text{Re}(\text{OH})\text{O}_2$ under the influence of UV light; the carbene has been characterised in its normal, D- and ^{13}C -enriched isotopic forms by IR spectroscopy with results in good agreement with quantum chemical calculations [162]. DFT calculations indicate that $\text{H}_2\text{C}=\text{Re}(\text{OH})\text{O}_2$ lies nearly 90 kJ/mol higher in energy than MTO, and hence is inaccessible under normal thermal conditions. Using the complex $\text{CH}_3\text{ReO}_2\{(\eta^2\text{-OSiH}_2)_2\text{O}\}$ as a model, i.e. the condensation product of MTO with disilanol, $\{\text{H}_2\text{Si}(\text{OH})\}_2\text{O}$, shows that the tautomeric H-atom transfer occurs preferentially to an Re–O–Si bridging oxygen rather than to an Re=O unit. The resulting carbene species, $\text{H}_2\text{C}=\text{ReO}_2\{(\text{OSiH}_2)(\text{O})(\text{SiH}_2\text{OH})\}$, is effectively stabilized by nearly 50 kJ/mol relative to $\text{CH}_3\text{ReO}_2\{(\eta^2\text{-OSiH}_2)_2\text{O}\}$. This alternative H-atom transfer to the Re–O–Si bridge is considered to be a more plausible mechanism for carbene formation on supported MTO [162,163].

It was possible to encapsulate MTO in a zeolite and still maintain 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 [164,165]. There is evidence in the case of zeolite Y that the loading level of MTO corresponds to four molecules per supercage. The still intact molecules of MTO can either hydrogen bond to Brønsted acid sites or interact with extra framework cationic sites in the supercages of M56Y, 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 de-aggregation of the guest molecules. Thermal treatment (~ 120 °C) is found to yield methane and water together with the formation of an intrazeolite cluster species containing Re–Re bonds [166].

7. Conclusions

More than 40 years ago, in the early days of high oxidation state organometallic chemistry, first attempts to synthesize organorhenium(VII) oxides have been undertaken. Though not succeeding at that time, later success-

ful attempts opened the way towards an extremely rich chemistry, particularly with respect to catalytic applications. Methyltrioxorhenium(VII) became one of the most versatile catalysts ever examined and is close to its industrial application. Its chemistry and applicability is not an isolated case, however. Related high oxidation state organometallic compounds, particularly of molybdenum and tungsten, which are known since several years [2,167–171] are now also being examined for their catalytic applications in more detail [52,172–174]. Theoretical work to compare the high oxidation state organometallics and to understand their behavior is also being performed [54,175–179]. Several questions, however, particularly with respect to the reaction mechanisms are still unanswered and await to be addressed. Of particular interest are stable, chiral high oxidation state organometallics, which would allow easy chirality transfer in oxidation catalysis. Although some excellent catalytic systems already exist [180–183], they remain isolated cases and a much broader variety of chiral high oxidation state catalysts seems still to be ahead. Chiral derivatives or adducts of MTO and other high oxidation state organometallics may play an important part in this still largely undiscovered area.

References

- [1] E.O. Fischer, S. Vigoureux, *Chem. Ber.* 91 (1958) 1342.
- [2] M. Cousins, M.L.H. Green, *J. Chem. Soc.* (1963) 889.
- [3] B.S. Lane, K. Burgess, *Chem. Rev.* 103 (2003) 2457.
- [4] A. Riedel, Diploma Thesis, Universität München, 1963.
- [5] I.R. Beattie, P.J. Jones, *Inorg. Chem.* 18 (1979) 2318.
- [6] W.A. Herrmann, R. Serrano, U. Küsthardt, M. Ziegler, E. Guggolz, T. Zahn, *Angew. Chem. Int. Ed.* 23 (1984) 515.
- [7] A.H. Klahn-Oliva, D. Sutton, *Organometallics* 3 (1984) 1313.
- [8] J. Okuda, E. Herdtweck, W.A. Herrmann, *Inorg. Chem.* 27 (1988) 1254.
- [9] W.A. Herrmann, *J. Organomet. Chem.* 300 (1986) 111.
- [10] W.A. Herrmann, *Angew. Chem. Int. Ed.* 27 (1988) 1297.
- [11] For Alkylrhenium(VII) oxides see: W.A. Herrmann, F.E. Kühn, C.C. Romão, H.T. Huy, M. Wang, R.W. Fischer, W. Scherer, P. Kiprof, *Chem. Ber.* 126 (1993) 45.
- [12] For Alkenylrhenium(VII) oxides see: W.A. Herrmann, F.E. Kühn, C.C. Romão, H.T. Huy, *J. Organomet. Chem.* 481 (1994) 227.
- [13] For Alkylrhenium(VII) oxides see: W.A. Herrmann, F.E. Kühn, C.C. Romão, *J. Organomet. Chem.* 495 (1995) 209.
- [14] For Arylrhenium(VII) oxides see: C.M. de Bellefon, W.A. Herrmann, P. Kiprof, C.R. Whitaker, *Organometallics* 11 (1992) 1072.
- [15] For cyclopentadienylrhenium(VII) oxides, see: F.E. Kühn, W.A. Herrmann, R. Hahn, M. Elison, J. Blümel, E. Herdtweck, *Organometallics* 13 (1994) 1601.
- [16] For indenylrhenium(VII) oxide, see: W.A. Herrmann, F.E. Kühn, C.C. Romão, *J. Organomet. Chem.* 489 (1995) C56.
- [17] For olefin metathesis, see: W.A. Herrmann, W. Wagner, U.N. Flessner, U. Volkhardt, H. Komber, *Angew. Chem. Int. Ed.* 30 (1991) 1636.
- [18] For olefin epoxidation, see: W.A. Herrmann, R.W. Fischer, D.W. Marz, *Angew. Chem. Int. Ed.* 30 (1991) 1638.

- [19] For aldehyde olefination, see: W.A. Herrmann, M. Wang, *Angew. Chem. Int. Ed.* 30 (1991) 1641.
- [20] W.A. Herrmann, F.E. Kühn, *Acc. Chem. Res.* 30 (1997) 169.
- [21] C.C. Romão, F.E. Kühn, W.A. Herrmann, *Chem. Rev.* 97 (1997) 3197.
- [22] J.H. Espenson, M.M. Abu-Omar, *ACS Adv. Chem.* 253 (1997) 3507.
- [23] F.E. Kühn, R.W. Fischer, W.A. Herrmann, *Chem. unserer Zeit.* 33 (1999) 192.
- [24] G.S. Owens, J. Arias, M.M. Abu-Omar, *Catal. Today* 55 (2000) 317.
- [25] W.A. Herrmann, J.G. Kuchler, J.K. Felixberger, E. Herdtweck, W. Wagner, *Angew. Chem. Int. Ed. Engl.* 27 (1988) 394.
- [26] W.A. Herrmann, F.E. Kühn, R.W. Fischer, W.R. Thiel, C.C. Romão, *Inorg. Chem.* 31 (1992) 4431.
- [27] W.A. Herrmann, second. ed., in: B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, vol. 3, Wiley-VCH, Weinheim, 2002, p. 1319.
- [28] W.A. Herrmann, R.M. Kratzer, R.W. Fischer, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2652.
- [29] W.A. Herrmann, R.M. Kratzer, *Inorg. Synth.* 33 (2002) 110.
- [30] F.E. Kühn, C.C. Romão, W.A. Herrmann, in: T. Imamoto (Ed.), *Houben-Weyl Science of Synthesis, Category 1, Organometallics*, vol. 2, Georg Thieme Verlag, Stuttgart, New York, 2003, pp. 128–130.
- [31] G. Laurenczy, F. Lukács, R. Roulet, W.A. Herrmann, R.W. Fischer, *Organometallics* 15 (1996) 848.
- [32] W.A. Herrmann, R.W. Fischer, W. Scherer, *Adv. Mater.* 4 (1992) 653.
- [33] W.A. Herrmann, R.W. Fischer, *J. Am. Chem. Soc.* 117 (1995) 3223.
- [34] W.A. Herrmann, W. Scherer, R.W. Fischer, J. Blümel, M. Kleine, W. Mertin, R. Gruehn, J. Mink, C.C. Wilson, R.M. Ibberson, L. Bachmann, M.R. Mattner, *J. Am. Chem. Soc.* 117 (1995) 3231.
- [35] H.S. Genin, K.A. Lawler, R. Hoffmann, W.A. Herrmann, R.W. Fischer, W. Scherer, *J. Am. Chem. Soc.* 117 (1995) 3244.
- [36] M.R. Mattner, W.A. Herrmann, R. Berger, C. Gerber, J.K. Gimzewski, *Adv. Mater.* 8 (1996) 654.
- [37] S. Köstlmeier, G. Pacchioni, W.A. Herrmann, N. Rösch, *J. Organomet. Chem.* 514 (1996) 111.
- [38] P. Gisdakis, N. Rösch, E. Bencze, I.S. Gonçalves, F.E. Kühn, *Eur. J. Inorg. Chem.* (2001) 989.
- [39] W.A. Herrmann, R.W. Fischer, W. Scherer, M.U. Rauch, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1157.
- [40] W.A. Herrmann, J.D.G. Correia, G.R.J. Artus, R.W. Fischer, C.C. Romão, *J. Organomet. Chem.* 520 (1996) 139.
- [41] A. Al-Ajlouni, H. Espenson, *J. Am. Chem. Soc.* 117 (1991) 9234.
- [42] J.H. Espenson, *J. Chem. Soc. Chem. Commun.* (1999) 479.
- [43] W. Adam, C.R. Saha-Möller, O. Weichold, *J. Org. Chem.* 65 (2000) 5001.
- [44] P. Gisdakis, N. Rösch, *Eur. J. Org. Chem.* 4 (2001) 719.
- [45] P. Gisdakis, I.V. Yudanov, N. Rösch, *Inorg. Chem.* 40 (2001) 3755.
- [46] C. di Valentin, R. Gandolfi, P. Gisdakis, N. Rösch, *J. Am. Chem. Soc.* 123 (2001) 2365.
- [47] O. Pestovski, R.v. Eldik, P. Huston, J.H. Espenson, *J. Chem. Soc. Dalton Trans.* (1995) 133.
- [48] P. Gisdakis, W. Antonczak, S. Köstlmeier, W.A. Herrmann, N. Rösch, *Angew. Chem. Int. Ed. Engl.* 37 (1998) 2211.
- [49] W. Adam, C.M. Mitchell, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 533.
- [50] F.E. Kühn, W.A. Herrmann, *Struct. Bond.* 97 (2000) 213.
- [51] W. Adam, C.M. Mitchell, C.R. Saha-Möller, O. Weichold, *Struct. Bond.* 97 (2000) 237.
- [52] F.E. Kühn, A.M. Santos, I.S. Gonçalves, C.C. Romão, A.D. Lopes, *Appl. Organomet. Chem.* 15 (2001) 43.
- [53] Y. Ren, W.D. Wu, A.M. Tian, *Chin. J. Org. Chem.* 21 (2001) 413.
- [54] D.V. Deubel, *J. Am. Chem. Soc.* 125 (2003) 15308.
- [55] W.A. Herrmann, R.W. Fischer, M.U. Rauch, W. Scherer, *J. Mol. Catal.* 86 (1994) 243.
- [56] W. Adam, C.M. Mitchell, C.R. Saha-Möller, *J. Org. Chem.* 64 (1999) 3699.
- [57] G.S. Owens, M.M. Abu-Omar, *J. Chem. Soc. Chem. Commun.* (2000) 1165.
- [58] J. Rudolph, K.L. Reddy, J.P. Chiang, K.B. Sharpless, *J. Am. Chem. Soc.* 119 (1997) 6189.
- [59] H. Adolfsson, A. Converso, K.B. Sharpless, *Tetrahedron Lett.* 40 (1999) 3991.
- [60] C. Copéret, H. Adolfsson, K.B. Sharpless, *J. Chem. Soc. Chem. Commun.* (1997) 1565.
- [61] W.A. Herrmann, H. Ding, R.M. Kratzer, F.E. Kühn, J.J. Haider, R.W. Fischer, *J. Organomet. Chem.* 549 (1997) 319.
- [62] W.A. Herrmann, F.E. Kühn, M.R. Mattner, G.R.J. Artus, M. Geisberger, J.D.G. Correia, *J. Organomet. Chem.* 538 (1997) 203.
- [63] H. Adolfsson, C. Copéret, J.P. Chiang, A.K. Yudin, *J. Org. Chem.* 65 (2000) 8651.
- [64] W.D. Wang, J.H. Espenson, *J. Am. Chem. Soc.* 120 (1998) 11335.
- [65] F.E. Kühn, A.M. Santos, P.W. Roesky, E. Herdtweck, W. Scherer, P. Gisdakis, I.V. Yudanov, C. Di Valentin, N. Rösch, *Chem. Eur. J.* 5 (1999) 3603.
- [66] P. Ferreira, W.M. Xue, É. Bencze, E. Herdtweck, F.E. Kühn, *Inorg. Chem.* 40 (2001) 5834.
- [67] A.M. Santos, F.E. Kühn, W.M. Xue, E. Herdtweck, *J. Chem. Soc. Dalton Trans.* (2000) 3570.
- [68] S.M. Nabavizadeh, *Inorg. Chem.* 42 (2003) 4204.
- [69] M. Nakajima, Y. Sasaki, H. Iwamoto, S.I. Hashimoto, *Tetrahedron Lett.* 39 (1998) 87.
- [70] M.J. Sabatier, M.E. Domine, A. Corma, *J. Catal.* 210 (2002) 192.
- [71] J.J. Haider, R.M. Kratzer, W.A. Herrmann, Jin Zhao, F.E. Kühn, *J. Organomet. Chem.* (in press).
- [72] G.S. Owens, M.M. Abu-Omar, *J. Mol. Catal. A* 187 (2002) 215.
- [73] G.S. Owens, A. Durazo, M.M. Abu-Omar, *Chem. Eur. J.* 8 (2002) 3053.
- [74] W. Adam, C.M. Mitchell, C.R. Saha-Möller, O. Weichold, *J. Am. Chem. Soc.* 121 (1999) 2097.
- [75] D. Sica, D. Musumeci, F. Zollo, S. de Marino, *Eur. J. Org. Chem.* 19 (2001) 373.
- [76] R. Saladino, P. Carlucci, M.C. Danti, C. Crestini, E. Mincione, *Tetrahedron* 56 (2000) 10031.
- [77] D. Sica, D. Musumeci, F. Zollo, S. de Marino, *J. Chem. Soc. Perkin Trans. 1* (2001) 1889.
- [78] R. Buffon, U. Schuchardt, J. Braz, *Chem. Soc.* 14 (2003) 347.
- [79] A.O. Bouh, J.H. Espenson, *J. Mol. Catal. A* 200 (2003) 43.
- [80] R. Bernini, E. Mincione, M. Cortese, R. Saladino, G. Gualandi, M.C. Belfiore, *Tetrahedron Lett.* 44 (2003) 4823.
- [81] M. Li, J.H. Espenson, *J. Mol. Catal. A* 208 (2004) 123.
- [82] W. Adam, C.R. Saha-Möller, O. Weichold, *J. Org. Chem.* 65 (2000) 2897.
- [83] R. Neumann, T.J. Wang, *J. Chem. Soc. Chem. Commun.* (1997) 1915.
- [84] C.D. Nunes, M. Pillinger, A.A. Valente, I.S. Gonçalves, J. Rocha, P. Ferreira, F.E. Kühn, *Eur. J. Inorg. Chem.* (2002) 1100.
- [85] R. Saladino, V. Neri, A.R. Pelliccia, R. Caminiti, C. Sadun, *J. Org. Chem.* 67 (2002) 1423.
- [86] C. Mealli, J.A. Lopez, M.J. Calhorda, C.C. Romão, W.A. Herrmann, *Inorg. Chem.* 33 (1994) 1139.
- [87] K.A. Brittingham, J.H. Espenson, *Inorg. Chem.* 38 (1999) 744.

- [88] J.H. Espenson, H. Tan, S. Mollah, R.S. Houk, M.D. Eager, *Inorg. Chem.* 37 (1998) 4621.
- [89] M.M. Abu Omar, P.J. Hansen, J.H. Espenson, *J. Am. Chem. Soc.* 118 (1996) 4966.
- [90] V.B. Sharma, S.L. Jain, B. Sain, *Tetrahedron Lett.* 44 (2003) 2655.
- [91] V.B. Sharma, S.L. Jain, B. Sain, *Tetrahedron Lett.* 44 (2003) 3235.
- [92] A.R. Vaino, *J. Org. Chem.* 65 (2000) 4210.
- [93] M.C.A. van Vliet, I.W.C.E. Arends, R.A. Sheldon, *J. Chem. Soc. Chem. Commun.* (1999) 821.
- [94] J. Iskra, D. Bonnet-Delpon, J.P. Begue, *Tetrahedron Lett.* 43 (2002) 1001.
- [95] H. Tan, J.H. Espenson, *Inorg. Chem.* 37 (1998) 476.
- [96] J.R. Gregorio, A.E. Gerbase, M. Martinelli, M.A.M. Jacobi, L. de Luca Freitas, M.L.A.v. Holleben, P.D. Marcico, *Macromol. Rapid Commun.* 21 (2000) 401.
- [97] M.S.F.L.K. Jie, C.N.W. Lam, J.C.M. Ho, M.M.L. Lau, *Eur. J. Lip. Sci Tech.* 105 (2003) 391.
- [98] A.E. Gerbase, J.R. Gregorio, M. Martinelli, M.C. Brasil, A.N.F. Mendes, *J. Am. Oil Chem. Soc.* 79 (2002) 179.
- [99] D.W. Marks, R.C. Larock, *J. Am. Oil Chem. Soc.* 79 (2002) 65.
- [100] H.R. Tetzlaff, J.H. Espenson, *Inorg. Chem.* 38 (1999) 881.
- [101] W. Adam, C.M. Mitchell, C.R. Saha-Möller, *Eur. J. Org. Chem.* (1999) 785.
- [102] J. Jacob, J.H. Espenson, J.H. Jensen, M.S. Gordon, *Organometallics* 17 (1998) 1835.
- [103] S. Bellemin-Lapponnaz, J.P. LeNy, Dedieu, A. *Chem. Eur. J.* 5 (1999) 57.
- [104] Z. Zhu, J.H. Espenson, *J. Org. Chem.* 60 (1995) 7728.
- [105] T. Weskamp, Diploma Thesis, Technische Universität München 1996 p. 15.
- [106] S.Y. Jonsson, H. Adolfsson, J.E. Backvall, *Chem. Eur. J.* 9 (2003) 2783.
- [107] W.A. Herrmann, T. Weskamp, J.P. Zoller, R.W. Fischer, *J. Mol. Catal.* 153 (2000) 49.
- [108] S.L. Jain, V.B. Sharma, B. Sain, *Tetrahedron Lett.* 45 (2004) 45.
- [109] M.M. Abu-Omar, J.H. Espenson, *Organometallics* 15 (1996) 3543.
- [110] T.H. Zauche, J.H. Espenson, *Inorg. Chem.* 37 (1998) 6827.
- [111] J.H. Espenson, Z. Zhu, T.H.J. Zauche, *Org. Chem.* 64 (1999) 1191.
- [112] W.A. Herrmann, J.P. Zoller, R.W. Fischer, *J. Organomet. Chem.* 581 (1999) 404.
- [113] J. Finlay, M.A. McKerverey, H.N.Q. Gunaratne, *Tetrahedron Lett.* 39 (1998) 5651.
- [114] S. Stancovic, J.H. Espenson, *J. Org. Chem.* 63 (1998) 4129.
- [115] W. Adam, W.A. Herrmann, J. Lin, C.R. Saha-Möller, R.W. Fischer, J.D.G. Correia, *Angew. Chem. Int. Ed.* 33 (1994) 2475.
- [116] W. Adam, M. Balci, H.J. Kilic, *Org. Chem.* 63 (1998) 8544.
- [117] E.I. Karasevich, A.V. Nikitin, V.L. Rubailo, *Kinet. Katal.* 35 (1994) 810.
- [118] S. Yamazaki, *Chem. Lett.* (1995) 127.
- [119] W. Adam, W.A. Herrmann, J. Lin, C.R. Saha-Möller, *J. Org. Chem.* 59 (1994) 8281.
- [120] W. Adam, W.A. Herrmann, C.R. Saha-Möller, M. Shimizu, *J. Mol. Catal. A* 97 (1995) 15.
- [121] F.E. Kühn, J.J. Haider, E. Herdtweck, W.A. Herrmann, A.D. Lopes, M. Pillinger, C.C. Romão, *Inorg. Chim. Acta* 279 (1998) 44.
- [122] W.A. Herrmann, J.J. Haider, R.W. Fischer, *J. Mol. Catal. A* 138 (1999) 115.
- [123] J. Jacob, J.H. Espenson, *Inorg. Chim. Acta* 270 (1998) 55.
- [124] R. Saladino, V. Neri, E. Mincione, S. Marini, M. Coletta, C. Fiorucci, P. Filippone, *J. Chem. Soc. Perkin Trans. 1* (2000) 581.
- [125] R. Saladino, V. Neri, E. Mincione, P. Filippone, *Tetrahedron* 58 (2002) 8493.
- [126] W. Adam, W. Malisch, K.J. Roschmann, C.R. Saha-Möller, W.A. Schenk, *J. Organomet. Chem.* 661 (2002) 3.
- [127] J.A. Smegal, I.K. Meier, J. Schwartz, *J. Am. Chem. Soc.* 108 (1986) 1322.
- [128] X. Lu, H. Fang, Z. Ni, *J. Organomet. Chem.* 373 (1989) 77.
- [129] A.M. Santos, F.M. Pedro, A.A. Yogalekar, I.S. Lucas, C.C. Romão, F.E. Kühn, *Chem. Eur. J.* (2004) in press.
- [130] W.A. Herrmann, P.W. Roesky, M. Wang, W. Scherer, *Organometallics* 13 (1994) 4531.
- [131] W.A. Herrmann, second ed., in: B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, vol. 3, Wiley-VCH, Weinheim, 2002, pp. 1078–1086.
- [132] S. Cai, D.M. Hoffman, D.A. Wierda, *J. Chem. Soc. Chem. Commun.* (1988) 1489.
- [133] S. Cai, D.M. Hoffman, D.A. Wierda, *Inorg. Chem.* 28 (1989) 3784.
- [134] S. Cai, D.M. Hoffman, D.A. Wierda, *Organometallics* 15 (1996) 1023.
- [135] W.A. Herrmann, K. Öfele, M. Elison, F.E. Kühn, P.W. Roesky, *J. Organomet. Chem.* 480 (1994) C7.
- [136] Z. Zhu, J.H. Espenson, *J. Org. Chem.* 60 (1995) 7090.
- [137] Z. Zhu, J.H. Espenson, *J. Am. Chem. Soc.* 118 (1996) 9901.
- [138] J.H. Espenson, D.T. Yiu, *J. Inorg. Chem.* 39 (2000) 4113.
- [139] A.M. Santos, C.C. Romão, F.E. Kühn, *J. Am. Chem. Soc.* 125 (2003) 2414.
- [140] X. Zhang, P. Chen, *Chem. Eur. J.* 9 (2003) 1852.
- [141] J.K. Felixberger, J.G. Kuchler, E. Herdtweck, R.A. Paciello, W.A. Herrmann, *Angew. Chem. Int. Ed. Engl.* 27 (1988) 946.
- [142] W.A. Herrmann, J.K. Felixberger, J.G. Kuchler, E. Herdtweck, *Z. Naturforsch.* 45b (1990) 876.
- [143] X.P. Chen, X.Y. Zhang, P. Chen, *Angew. Chem. Int. Ed. Engl.* 42 (2003) 3798.
- [144] H.W. Roesky, D. Hesse, M. Noltemeyer, *Eur. J. Solid State Inorg. Chem.* 28 (1991) 809.
- [145] W.A. Herrmann, P.W. Roesky, F.E. Kühn, M. Kleine, W. Scherer, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1714.
- [146] P. Gisdakis, S. Antonczak, N. Rösch, *Organometallics* 18 (1999) 5044.
- [147] S.G. Kukolich, B.J. Drouin, O. Indris, J.J. Dannemiller, J.P. Zoller, W.A. Herrmann, *J. Chem. Phys.* 113 (2000) 7891.
- [148] W.A. Herrmann, P.W. Roesky, W. Scherer, M. Kleine, *Organometallics* 13 (1994) 4536.
- [149] B.E. Ledford, E.M. Carreira, *Tetrahedron Lett.* 38 (1997) 8125.
- [150] W.A. Herrmann, P.W. Roesky, F.E. Kühn, M. Elison, G.R.J. Artus, W. Scherer, C.C. Romão, A.D. Lopes, J.M. Basset, *Inorg. Chem.* 34 (1995) 4701.
- [151] For a recent review on catalytic aldehyde olefination, see: F.E. Kühn, A.M. Santos, *Minirev. Org. Chem.* 1 (2004) 55.
- [152] G.C.N. van den Aardweg, R.H.A. Bosma, J.C. Mol, *J. Chem. Soc. Chem. Commun.* (1983) 262.
- [153] E. Verkuijlen, F. Kapstein, J.C. Mol, C. Boelhouwer, *J. Chem. Soc. Chem. Commun.* (1977) 198.
- [154] J.C. Mol, E.F.G. Woerlee, *J. Chem. Soc. Chem. Commun.* (1979) 330.
- [155] J.C. Mol, *J. Mol. Catal. A* 15 (1982) 35.
- [156] J.H. Espenson, O. Pestovsky, P. Huston, S. Staudt, *J. Am. Chem. Soc.* 116 (1994) 2869.
- [157] P.J. Hansen, J.H. Espenson, *Inorg. Chem.* 34 (1995) 5389.
- [158] R. Buffon, A. Auroux, F. Lefebvre, M. Leconte, A. Choplin, J.M. Basset, W.A. Herrmann, *J. Mol. Catal. A* 76 (1992) 287.
- [159] R. Buffon, A. Choplin, M. Leconte, J.M. Basset, R. Touroude, W.A. Herrmann, *J. Mol. Catal. A* 72 (1992) L7.
- [160] Z. Zhu, J.H. Espenson, *J. Mol. Catal. A* 121 (1997) 139.
- [161] T.M. Mathew, A.J.K. du Plessis, J.J. Prinsloo, *J. Mol. Catal. A* 148 (1999) 157.

- [162] L.J. Morris, A.J. Downs, T.M. Greene, G.S. McGrady, W.A. Herrmann, P. Sirsch, O. Gropen, W. Scherer, *J. Chem. Soc. Chem. Commun.* (2000) 67.
- [163] L.J. Morris, A.J. Downs, T.M. Greene, S.G. McGrady, W.A. Herrmann, P. Sirsch, W. Scherer, O. Gropen, *Organometallics* 20 (2001) 2344.
- [164] A. Borvornwattanought, T. Bein, *J. Phys. Chem.* 96 (1992) 9446.
- [165] C. Huber, G.C. Wu, K. Möller, T. Bein, *Abstr. Pap. Am. Chem. Soc.* 209 (1995) 172.
- [166] A. Malek, G. Ozin, *Adv. Mater.* 7 (1995) 160.
- [167] B. Heyn, R. Hoffmann, *Z. Chem.* 16 (1975) 195.
- [168] G.N. Schrauzer, E.L. Moorehead, J.H. Grate, L. Hughes, *J. Am. Chem. Soc.* 100 (1978) 4760.
- [169] C. Zhang, E.O. Schlemper, G.N. Schrauzer, *Organometallics* 9 (1990) 1016.
- [170] J.W. Faller, Y. Ma, *Organometallics* 7 (1988) 559.
- [171] P. Legzdins, E.C. Phillips, L. Sánchez, *Organometallics* 8 (1989) 940.
- [172] F.E. Kühn, M. Groarke, E. Bencze, E. Herdtweck, A. Prazeres, A.M. Santos, M.J. Calhorda, C.C. Romão, I.S. Gonçalves, A.D. Lopes, M. Pillinger, *Chem. Eur. J.* 8 (2002) 2370.
- [173] F.E. Kühn, W.M. Xue, A. Al-Ajlouni, A.M. Santos, S. Zhang, C.C. Romão, G. Eickerling, E. Herdtweck, *Inorg. Chem.* 41 (2002) 4468.
- [174] M. Abrantes, A.M. Santos, J. Mink, F.E. Kühn, C.C. Romão, *Organometallics* 22 (2003) 2112.
- [175] G. Wahl, D. Kleinhenz, A. Schorm, J. Sundermeyer, R. Stohwasser, C. Rummey, G. Bringmann, C. Fickert, W. Kiefer, *Chem. Eur. J.* 5 (1999) 3237.
- [176] C. Di Valentin, P. Gisdakis, I.V. Yudanov, N. Rösch, *J. Org. Chem.* 65 (2000) 2996.
- [177] D.V. Deubel, J. Sundermeyer, G. Frenking, *J. Am. Chem. Soc.* 122 (2000) 10101.
- [178] Y.D. Wu, J. Sun, *J. Org. Chem.* 63 (1998) 1752.
- [179] D.V. Deubel, G. Frenking, P. Gisdakis, W.A. Herrmann, N. Rösch, J. Sundermeyer, *Acc. Chem. Res.* (in press).
- [180] T. Katsuki, K.B. Sharpless, *J. Am. Chem. Soc.* 102 (1980) 5974.
- [181] I.D. Williams, S.F. Pedersen, K.B. Sharpless, S.J. Lippard, *J. Am. Chem. Soc.* 104 (1984) 6430.
- [182] M. Palucki, P.J. Pospisil, W. Zhang, E.N. Jacobsen, *J. Am. Chem. Soc.* 116 (1994) 9333.
- [183] P. Pietikäinen, *Tetrahedron* 54 (1998) 4319.