Behaviour of dimeric methylrhenium(VI) oxides in the presence of hydrogen peroxide and its consequences for oxidation catalysis

Alexandra M. J. Rost,[a] Andrea Scherbaum,[a] Wolfgang A. Herrmann*[a] and Fritz E. Kühn*[ab]

Received (in Montpellier, France) 9th June 2006, Accepted 20th July 2006
First published as an Advance Article on the web 14th August 2006
DOI: 10.1039/b608219j

Avoiding the use of toxic methyltin precursors to synthesize methyltrioxorhenium (MTO) and its mono- and bis-peroxo derivatives, applicable as oxidation catalysts, dimethyl zinc might be considered a promising alternative alkylating agent. However, the methylrhenium(VI) dimers, formed as reduction products alongside MTO during the reaction of dimethyl zinc with Re_2O_7, are not as straightforwardly transformed into the epoxidation catalysts as MTO itself in the presence of excess H_2O_2. In the case of red (μ-oxo)bis[trimethyloxorhenium(VI)], the main reaction product with H_2O_2 is the catalytically inactive trimethyldioxorhenium(VII). In the case of bis[dimethyl(μ-oxo)oxorhenium(VI)], slow conversion to the monomeric mono- and bis-peroxo congenes of MTO occurs. Furthermore, part of the Re(VI) starting complex is transformed into inactive perrhenate. While bis[dimethyl(μ-oxo)oxorhenium(VI)] might be applied (also in a mixture with MTO) as an oxidation catalyst precursor, (μ-oxo)bis[trimethyloxorhenium(VI)] can be applied as a useful precursor for the synthesis of trimethyldioxorhenium(VII), which was previously only accessible by less convenient synthetic pathways.

Introduction

Industrial transformations of olefins into epoxides involve catalysts that utilize organic peroxides, hydrogen peroxide or oxygen as oxidants. However, for the epoxidation and oxidation of fine chemicals stoichiometric reactions are still commonly used.[1] An important discovery in this field arose with the finding of Herrmann *et al.* that methyltrioxorhenium (**1**, MTO) and some of its derivatives act as efficient catalysts for olefin epoxidation.[2] MTO was first described in 1979 by Beatty and Jones,[3] but its applicability as a catalyst was only detected nearly a decade later, following a much improved synthesis.[4] Due to the broad applicability of MTO in a variety of catalytic reactions,[2,5] several modified synthetic approaches have been reported.[6] Nevertheless, an important drawback of these syntheses that still remains is the use of highly toxic tetramethyltin or the closely related and also toxic methyltributyltin as methylating agents. However, it is known that several derivatives of MTO are available *via* bis(alkyl)zinc precursors.[2,5f,7]

Furthermore, it has been noted that mixtures of MTO and methylrhenium(VI) oxides are available when reacting dimethylzinc with Re_2O_7 at low temperatures.[4,8] The choice of the best alkylation agent in reactions with Re_2O_7 depends largely on the stability of the product and the ease of alkyl transfer. While tetramethyltin only reacts with Re_2O_7 in boiling THF,[4] the reaction with dimethylzinc takes place at dry ice temperature (−78 °C).[8a] At higher temperatures, dimethylzinc reduces Re_2O_7, at least partially, to the oxidation state Re(VI),[4,8a] forming bis[dimethyl(μ-oxo)oxorhenium(VI)] (**2**) and (μ-oxo)bis[trimethyloxorhenium(VI)] (**3**) as the by-products or main products. Since the latter two compounds show some catalytic activity in olefin epoxidation reactions,[9] it might be assumed that they are transformed into the same mono- and bis-peroxo species[10] as is MTO in the presence of excess H_2O_2. However, this would help avoid the necessity of preparing (or even isolating) MTO as a precursor for the active species in oxidation catalysis. Dimethylzinc could be utilized instead of tin precursors in the alkylation of the rhenium species, and the oxidizing agent would oxidize the methylrhenium precursors to a uniform catalyst. It has been observed in olefin epoxidation reactions with organomolybdenum oxides that their organomolybdenum carbonyl precursors can be directly added to the oxidation mixture (in this case *tert*-butyl hydroperoxide acts as oxidizing agent), thus avoiding the necessity of preparing the more sensitive oxides, forming the same catalyst.[11]

In this work we examine the behaviour of the dimeric Re(VI) compounds in the presence of H_2O_2 and their applicability as epoxidation catalysts in comparison to the well established MTO.

Experimental

General

NMR spectra (^1H and ^{13}C) were recorded on a Bruker DPX 400 instrument. Chemical shifts are given in ppm. The spectra are referenced to the residual protons (^1H) or to the ^{13}C signals

---

[a] *Lehrstuhl für Anorganische Chemie der Technischen Universität München, Lichtenbergstraße 4, D-85747 Garching bei München, Germany. E-mail: wolfgang.herrmann@ch.tum.de. E-mail: fritz.kuehn@ch.tum.de; Fax: +49 (0)89 289 13473*
[b] *Department of Chemistry, Instituto Tecnológico e Nuclear (ITN), Estrada Nacional No. 10, 2686-953 Sacavém, Portugal. E-mail: fekuhn@itn.pt; Fax: +351 219946185*

(^{13}C) of the solvent. Elemental analyses were determined at the Microanalytical Laboratory at TU München. CI-MS spectra were measured on a Finnigan MAT 90 mass spectrometer. Thermogravimetric mass spectra (TG-MS) analysis measurements were conducted with a Netzsch TG209 system; typically about 10 mg of each sample was heated from 35 to 1000 °C at 10 K min^{-1}. GC spectra were measured either on a Hewlett-Packard gas chromatograph HP 6890 equipped with a mass selective detector HP or a Hewlett-Packard gas chromatograph HP 5890 using a FID detector. The yields of the products of oxidation catalysis were calculated according to calibrations conducted prior to the measurements. UV-vis spectra were recorded on a Jasco V-550 spectrophotometer. IR spectra were acquired using a Jasco FT/IR-460 Plus spectrometer.

Synthesis

All experiments were carried out under an oxygen- and water-free argon atmosphere using standard Schlenk techniques. All solvents used in the inert atmosphere conditions were purified by standard procedures and distilled under a nitrogen atmosphere directly prior to use. Compounds **1–3** were prepared according to literature procedures.[6a,8a] The observed ^{1}H and ^{13}C NMR data, elemental analyses and mass spectra confirmed that the compounds were pure and identical to previously collected data.[4,6a,8a] All other chemicals were obtained from commercial sources and used without further purification.

Preparation of trimethyldioxorhenium(VII) (4)

To a cooled solution (0 °C) of **3** (100 mg, 0.20 mmol) in 5 mL diethyl ether was added H_2O_2 (35 wt% in water, 41.9 µL, 0.8 mmol). The solution was stirred for 20 min at 0 °C and then warmed to room temperature. The color of the solution changed from deep red to yellow, indicating the completion of the reaction. The solution was washed twice with 2 mL water and then dried over Na_2SO_4. Removal of the solvent *in vacuo* yielded a red oil, which was purified by trap-to-trap fractionation *in vacuo*.

Yield: 84%. IR (in *n*-pentane) ν(Re=O): 1001s, 963vs. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 2.49 (s, 2 H, CH_3), 2.04 (s, 1 H, CH_3). ^{1}H NMR (400.1 MHz, d_8-THF): δ_H 2.41 (s, 2 H, CH_3), 1.99 (s, 1 H, CH_3). ^{13}C NMR (100.1 MHz, $CDCl_3$) δ_C 26.76, 29.69 (CH_3).

Reactions of compounds 1–3 with H_2O_2

^{1}H NMR studies. To a solution of **1–3** (0.063 mmol) in 0.5 mL d_8-THF was added 2 equiv. H_2O_2 (35 wt%) per Re. The reaction was monitored by recording ^{1}H NMR spectra (298 K, 32 scans) at various times. All spectra were referenced to the peak of d_8-THF at $\delta_H = 1.73$.

UV-vis studies. Measurements were carried out in silica cells with a path length of 1 cm and a volume of 1 mL. The data for the kinetic investigations were acquired from freshly prepared solutions comprising 7.3×10^{-5} mol of the rhenium compound in 23.5 mL THF with 7.3×10^{-5} mol of H_2O_2 (35 wt%). To obtain an appropriate concentration, 0.3 mL of the solution was diluted with 0.6 mL THF and transferred immediately to the spectrophotometer. The scanning range was from 500 to 190 nm. The total time of the measurements and the time between the cycles was varied, depending on the compounds.

Oxidation catalysis

Epoxidation of *cis*-cyclooctene. The catalytic activity of compounds **1–3** was tested at room temperature by examining the epoxidation of *cis*-cyclooctene (0.8 g, 7.3 mmol). Mesitylene (1 g, 8.3 mmol) was used as the internal standard and H_2O_2 (35 wt%; 1.41 mL, 14.6 mmol) as the oxidising agent. The oxidation of *cis*-cyclooctene yields quantitatively epoxycyclooctene. A catalyst : oxidant : substrate ratio of 1 : 200 : 100 was used. The samples were first analyzed by GC-MS after 5 min and then every 30 min for 7 h. The reaction was terminated after 23 h.

Oxidation of benzyl alcohol. The catalytic behavior was additionally examined in the oxidation of benzyl alcohol (0.52 mL, 5 mmol) at room temperature. Diethylene glycol dimethyl ether was used as the internal standard, H_2O_2 (35 wt%; 1.5 mL, 15 mmol) as the oxidising agent, LiBr (44 mg, 0.5 mmol) as the co-catalyst and TEMPO (40 mg, 0.25 mmol) as the mediator. The oxidation of benzyl alcohol in this four-component system yields selectively benzyl aldehyde. A catalyst : oxidant : substrate ratio of 1 : 300 : 100 was used. 0.1 equiv. of H_2O_2 was added per minute and the reaction was terminated after 24 h. The reaction product was identified and quantified by GC-MS.

Results and discussion

Synthesis

The preparation of compounds **2** and **3** *via* the processes described in the literature[4,8a] is quite difficult and time consuming, compared to the preparation of **1**. Usually in such preparations, all three compounds **1–3** are formed. However, the nature of the main product depends strongly on the reaction conditions applied. When reacting Re_2O_7 with 1 equivalent of $(CH_3)_2Zn$, **1** is obtained as main product; when applying 3 equivalents of $(CH_3)_2Zn$ below 0 °C, the formation of compound **2** is favoured; with 4 equivalents of $(CH_3)_2Zn$ above 0 °C, compound **3** is obtained as the major product (Scheme 1). The purification of the three products requires several sublimation, extraction and chromatography steps. While compound **2** can be purified by extraction with *n*-hexane and several subsequent sublimation steps, the separation of compound **3** is more difficult due to the pronounced sensitivity of the latter complex to traces of water and oxygen, which convert it easily into compound **2** and other products (see below). Accordingly, the isolation of compound **3** has to be conducted with the rigorous exclusion of moisture and air in extremely dry solvents. Pure (µ-oxo)bis[trimethyloxorhenium(VI)] (**3**) is obtained after extraction with *n*-pentane, sublimation, column chromatography (0 °C, RP_{18} silica gel, *n*-pentane) and if necessary, a further sublimation step.

TG-MS studies

The TG-MS plots of complexes **1–3** are given in Fig. 1. The obtained TG curve of **1** is similar to the published results.[12]

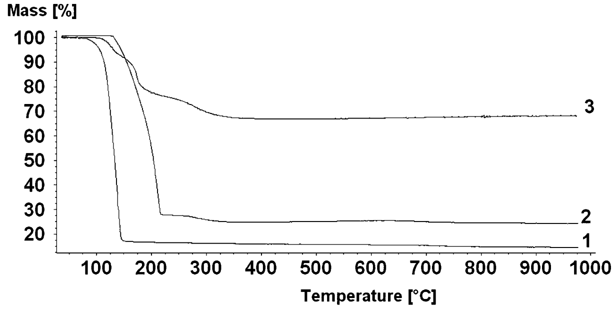


Fig. 1 TG spectra of compounds **1–3**.

Compound **1** starts subliming below 100 °C and the sublimation process is fast. At 150 °C, only 16% of the original mass is left. The sublimation of compound **2** starts at 130 °C and continues until 218 °C. Complex **3** is stable up to 112 °C. In the case of compound **2**, there is only one remarkable weight loss step, with a 73% reduction in the original mass. Compound **3** is the only one of the three examined rhenium complexes that presents visible decomposition steps while being heated to 200 °C. In the first step, until 135 °C, a mass loss of 6% is observed. This is equivalent to the mass of two of its methyl groups. The remaining methyl group is lost before reaching 185 °C. In the last decomposition step, which continues over a larger temperature range, a mass loss of 7% is observed, possibly due to the loss of oxygen ligands.

Additionally, changes can be deduced from the DSC plot (Fig. 2). The observed exothermic reaction of **1**, with a peak at 63 °C, indicates that the sublimation is already starting at 40 °C under the conditions applied. The following endothermic step, with a minimum at 116 °C, is very likely to be associated with the dimerization of **1**.[13] No weight is lost during this process. Compound **2** starts subliming at higher temperatures in an exothermic step and subsequently seems to dimerize at 127 °C, possibly leading to a tetrameric structure.[14] After an exothermic step at 63 °C, compound **3** probably dimerizes. No mass loss is observed during these two steps. The following endothermic steps indicate the beginning of the decomposition of compound **3**. After the loss of two methyl groups, a minimum at 156 °C is reached. Decomposition continues with a significant exothermic step at 177 °C, assigned to the loss of the remaining methyl groups.

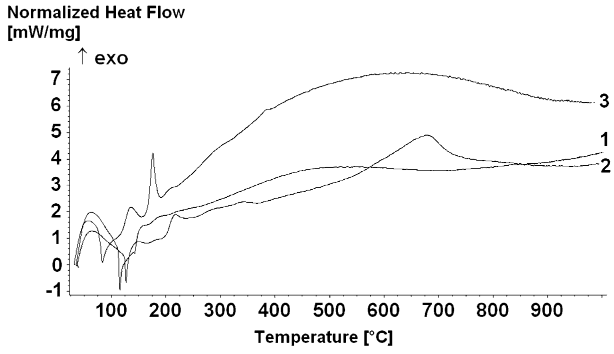
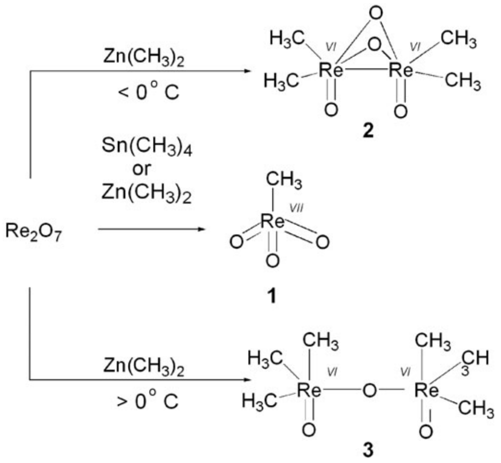


Fig. 2 DSC plots of compounds **1–3**.



Scheme 1 Reaction of Re_2O_7 with dimethylzinc.

Reactions of compounds 1–3 with H_2O_2

Kinetic ^{1}H NMR studies. The reaction of compound **1** with H_2O_2 (**1** : H_2O_2 = 1 : 2; 2 equiv. H_2O_2 per Re) in d_8-THF affords four CH_3 signals in the ^{1}H NMR spectrum (see Fig. 3), ascribable to MTO (δ = 2.1), $CH_3Re(O_2)O_2$ (**5**) (δ = 2.3), $CH_3Re(O_2)_2O \cdot H_2O$ (**6**) (δ = 2.6) and the decomposition product CH_3OH (δ = 3.2). In correspondence with published results, the reaction reached equilibrium after 1 h under the applied conditions.[15] As expected, during this time, the peaks originating from **1** (MTO) and, after a while, **5** decreased, while the signals originating from **6** and methanol increased (see Scheme 2). This behavior is in full accordance with the well documented literature data.[15] Adding a large excess of H_2O_2 lead to the fast formation of **6** and only a small amount of methanol, as also reported in the literature.[15]

The reaction of **2** with H_2O_2 (**2** : H_2O_2 = 1 : 4; 2 equiv. H_2O_2 per Re) was also monitored by ^{1}H NMR spectroscopy (see Fig. 4). During the reaction, four CH_3 signals are observed (see Fig. 4): $\delta_H(CH_3)$ = 2.3 (**5**), 2.6 (**6**), 2.7 (**2**) and 3.2 (CH_3OH from partial decomposition). About 1 h after the addition of H_2O_2, the very slowly emerging peaks of **5** (at 2.3 ppm) and **6**

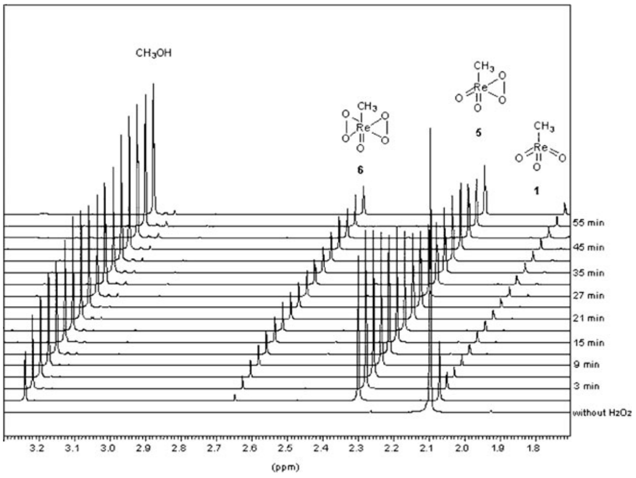
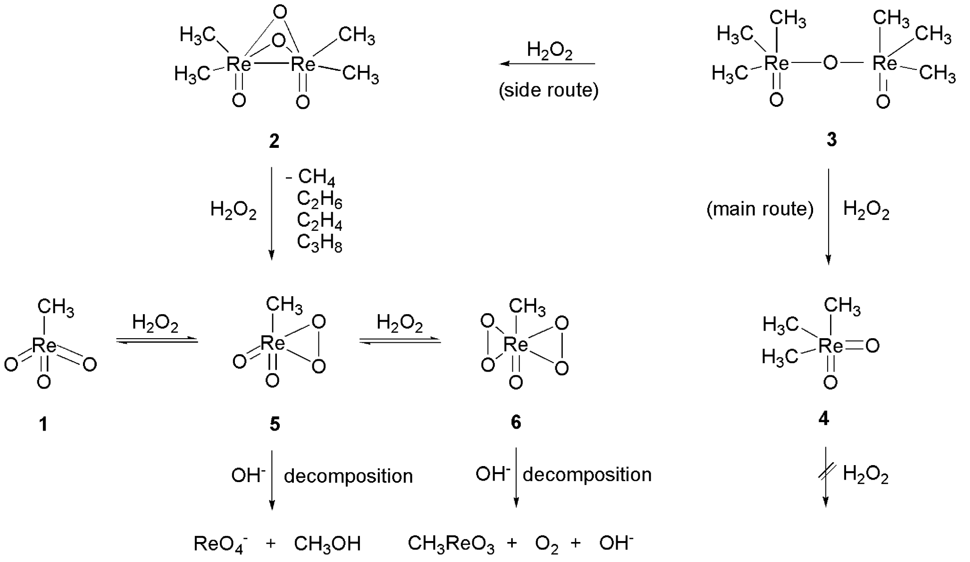


Fig. 3 ^{1}H NMR kinetic study of the reaction of compound **1** with H_2O_2.



Scheme 2 Reaction of compounds **1–3** with H_2O_2.

(at 2.6 ppm) become visible. The peak of methanol at 3.2 ppm increases steadily during the 20 h reaction time. The peak due to compound **2** (at 2.7 ppm) decreases insignificantly during the first 8 h of the reaction. Only after this time do the peaks of compounds **5**, **6** and concomitantly formed methanol become more pronounced. After an 18 h reaction time, the peaks of **5** and **6** begin to decrease slowly. These experimental results are indicative of the cleavage of the Re–Re bond, the loss of two methyl groups per molecule of **2**, and the formation of **5** and **6** (see Scheme 2). Methane, ethane, ethene and propane are detected by GC-MS during the reaction in the gas phase. Traces of these also appear in the NMR spectrum but these peaks are not depicted in Fig. 4. The formation of these hydrocarbons probably results from the radical cleavage of the Re–C bonds.[16] Only one methyl group remains at the Re center. The oxidative degradation of **2** also leads to a change in the oxidation state of Re (from Re(VI) to Re(VII)), resulting in the formation of **5** and **6**, analogously to the reaction observed for compound **1** with H_2O_2. Due to the slow oxidative degradation of **2**, the partial decomposition of **5**, yielding methanol, is more pronounced than in the case of compound **1**. Only part of the applied quantity of **2** is converted into **5** and **6** because some H_2O_2 is decomposed by the radicals created during the cleavage of the Re–methyl bonds. Adding a large excess of H_2O_2 leads to a faster formation of **6** and a smaller amount of methanol. However, when compared to the reaction of MTO, the latter reaction is still significantly slower and a more pronounced formation of methanol from partial decomposition is observed. In presence of an alkene, *e.g.*, *cis*-cyclooctene, the resulting amount of methanol formed is only one-third of that found in the reaction in the absence of an alkene (as shown in Fig. 4). Thus, the addition of an alkene significantly suppresses the formation of methanol. This behavior suggests that methanol formation results from the decomposition of **5** and **6**, and not from other processes, *e.g.*, the cleavage of two methyl groups per molecule of **2** during the reaction of the dimeric methylrhenium(VI) oxide with H_2O_2.

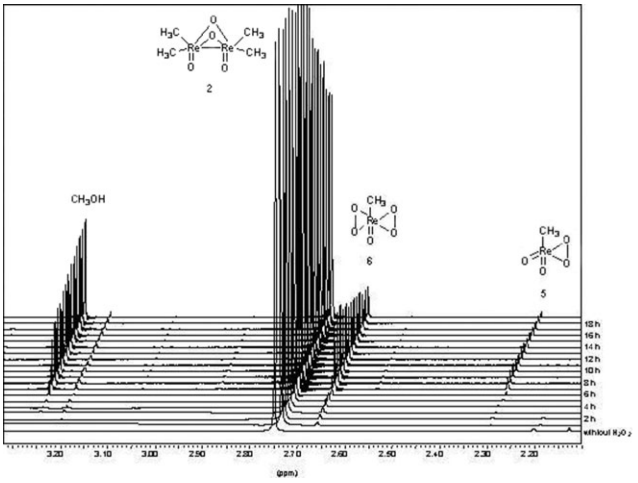


Fig. 4 ^1H NMR kinetic study of the reaction of compound **2** with H_2O_2.

During the reaction of compound **3** with H_2O_2 (see Fig. 5), signals at δ = 2.44 and 2.46 (originating from compound **3**), at δ = 2.7 (originating from compound **2**), and at δ = 2.0 and 2.41 are apparent. Immediately after the addition of H_2O_2, pronounced signals at δ = 2.0 and 2.41, and a minor peak for compound **2** emerge. As for the peaks observed for compound **3**, displaying a 2 : 1 (δ 2.44 : δ 2.46) ratio, the new peaks display a 2 : 1 ratio (δ 2.41 : δ 2.0). The deep red color of the reaction mixture turns quickly to yellow. Within minutes, the signals of **3** disappear entirely. However, in contrast to MTO, where a fast epoxidation reaction takes place when cyclooctene is provided, in case of **3**, the reaction is quite sluggish. A newly formed compound, responsible for the peaks at δ = 2.0 and 2.41, can be isolated from the cyclooctene-free reaction mixture. The application of several spectroscopic methods (see experimental section) leads to its identification as trimethyldioxorhenium (**4**). This compound can be synthesized from **3** in good yields by the

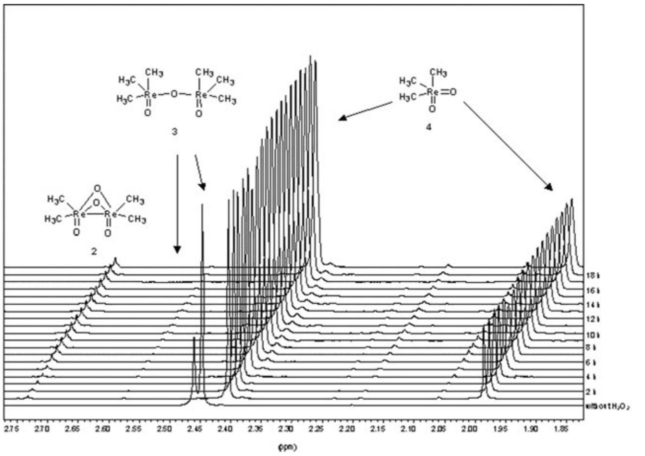


Fig. 5 ^{1}H NMR kinetic study of the reaction of compound **3** with H_2O_2.

addition of H_2O_2. Prior to this work, the only known synthesis of compound **4** was the oxidation of **3** with trimethyl amine *N*-oxide.[8a,17] The synthetic pathway found during this work seems to be easier than the one described previously in the literature. While, in the presence of H_2O_2, the tiny amounts of compound **2**, formed during the fast reaction of compound **3** with H_2O_2, behave as described above, compound **4** does not react with H_2O_2, even when the latter is present in a large excess. Neither **5** or **6** are formed starting from isolated compound **4**. However, this observation sheds new light on the applicability of compound **3** as an oxidation catalyst. Obviously, the main product from the oxidation of **3** with H_2O_2 is compound **4**, not being transformable into **5** or **6** by the reaction of **4** with H_2O_2. Moreover, compound **4** seems to be virtually inert to H_2O_2, even when exposed to it for many hours. Due to the formation of only tiny amounts of **2** during the reaction of **3** with H_2O_2, which forms very slowly the active species **5** and **6**, no methanol originating from the deactivation could be detected by NMR, but traces of the latter were detected by GC-MS.

UV-vis studies. The reaction kinetics of the rhenium compounds with H_2O_2 in water in the absence of olefin was additionally examined by UV-vis spectroscopy.

The complexes were combined in a 1 : 100 ratio with respect to the oxidant to more closely mimic catalytic conditions.

Compound **1** forms the active species fastest among the examined rhenium complexes. After 1 h, the characteristic and very pronounced maximum for compound **6** was observed at 350 nm.[9] It remained unchanged for 2 h, before **6** started slowly decomposing in the absence of olefin.

During the reaction of compound **2** with H_2O_2, the visible yellow color seemed to remain unchanged. However, in reference to pure compound **2**, the changes were easily detectable in the UV-vis spectrum (see Fig. 6), indicating the formation of yellow compound **6** from the yellow compound **2**, as observed in the ^{1}H NMR spectra (see above). A minimum at 350 nm was established during the reaction time.

Treating compound **3** with H_2O_2 leads to visible changes in the UV-vis spectrum (see Fig. 7). The maximum at λ = 275 nm decreased during the reaction time of 10 h, indicating the disappearance of the red-coloured **3**. Additionally, a maximum at λ = 350 nm increases.

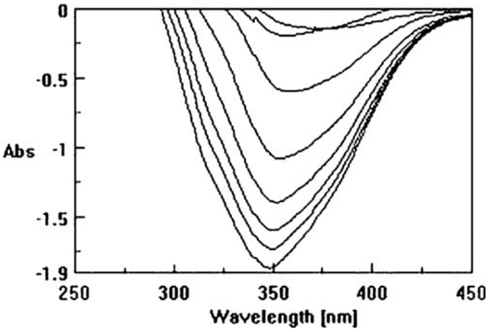


Fig. 6 The formation of compound **6** from the reaction of **2** with H_2O_2 (difference spectrum to emphasize the changes); see text for more details.

Oxidation catalysis

Epoxidation of *cis*-cyclooctene. The catalytic activities of **1–3** were tested on the epoxidation of *cis*-cyclooctene (see Fig. 8). In comparison to compounds **2** and **3**, MTO showed 100% olefin conversion after a reaction time of 150 min. After the same time, **2** (as a catalyst precursor) achieved only a conversion of 37%. However, after 420 min, it also reached complete conversion. Compound **3** lead to an olefin conversion of only 10% after 270 min. In the case of **1**, the quickest conversion rate was obtained during the first hour, while **2** and **3** did not increase the conversion rate during the first 4 h of the reaction. Only 12% conversion was obtained after 24 h with compound **3**. The notably higher catalytic activity of **1** in olefin epoxidation reactions can be explained by the formation of the bisperoxocomplex **6**, which represents the catalytically active species. Due to its smaller steric bulk and higher oxidation state in comparison to **2** and **3**, the catalyst precursor **1** forms the active species much faster in presence of H_2O_2. This phenomenon is supported by kinetic UV-vis and ^{1}H NMR studies. After 250 min, **2** has been converted mainly into the catalytically active species, the formation reaction accelerating significantly and finally reaching 100% conversion. Nevertheless, the formation of the catalytically active species **6** takes much longer than in the case of compound **1**.

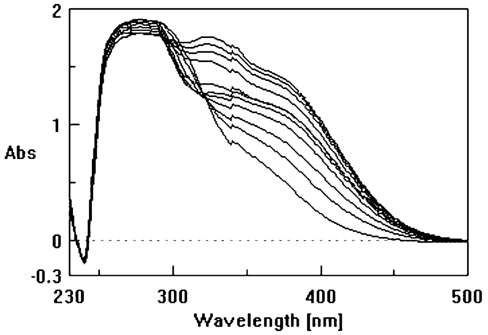


Fig. 7 UV-vis spectra of compound **3**, treated with hydrogen peroxide (see text).

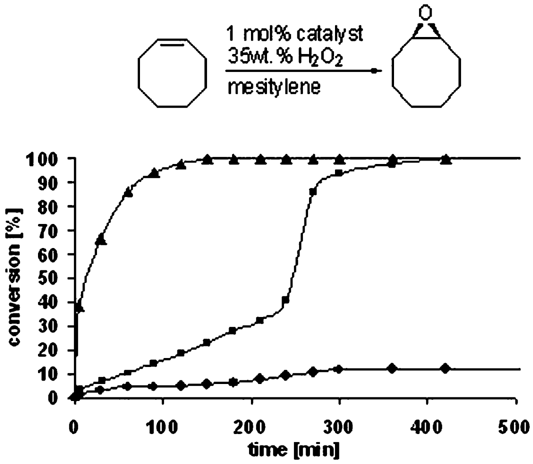


Fig. 8 Time–conversion diagram of the epoxidation of *cis*-cyclooctene with **1** (▲), **2** (■) and **3** (●) as catalyst precursor.

Oxidation of benzyl alcohol. The catalytic behavior of **1–3** was additionally examined in the oxidation of benzyl alcohol (see Fig. 9). Compared to the alkylrhenium(VI) oxides **2** and **3**, MTO (**1**) showed excellent performance. Complete conversion was already achieved after 120 min with catalyst **1**. After the same reaction time, compound **2** reached only a conversion of 50% and compound **3** reached a conversion of merely 8%. With compound **2** as catalyst precursor, the conversion was complete after 48 h. Compound **3** reached only 10% conversion after the same time, and during the following 24 h no additional conversion increase was observed. In order to test whether all the oxidant had been reacted or whether deactivation took place, again 300 mol% of H_2O_2 was added in a second step. No further conversion could be observed in the case of compound **3**. The results of the ^{1}H NMR and UV-vis kinetic studies of the reaction of **3** with H_2O_2 showed that trimethyldioxorhenium(VII) (**4**) was mainly formed and about 5% of **2** was also obtained. The ^{1}H NMR spectra also proved that **4** does not react with excess H_2O_2 and does not form peroxo species. In this case, the catalytic activity originates—as mentioned above—from the conversion of by-product **2** into **5** and **6**. Due to the very low concentration of compound **2**, the conversion increased only slowly until a 10% aldehyde yield was reached. The stagnation of the conversion at this value after 240 min is a consequence of the partial decomposition of the Re precursor to methanol and perrhenate during the slow formation of the active catalyst species **5** and **6**.

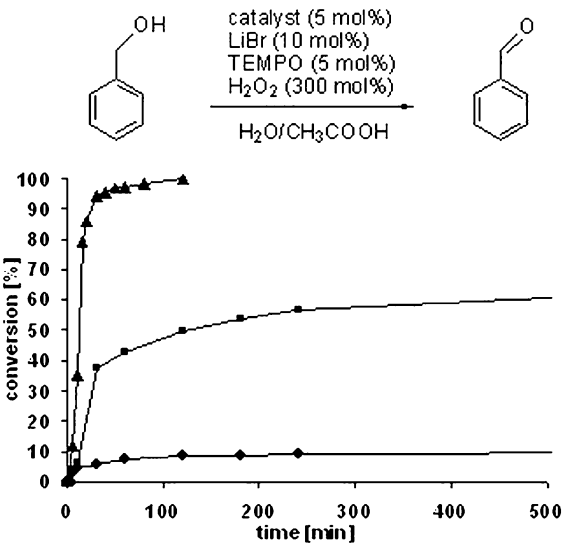


Fig. 9 Time–conversion diagram of the oxidation of benzyl alcohol with **1** (▲), **2** (■) and **3** (●) as catalyst precursor.

The oxidation of benzyl alcohol with compound **2** as the catalyst precursor reached completeness after 48 h. Compared to compound **1**, the reaction rate of **2** was much lower. This is a consequence of the significantly slower formation of the catalytic active species **5** and **6** from **2** due to the higher steric bulk of the latter, the necessary cleavage of the dirhenium complex and the change in oxidation state having already been mentioned above. When, after one catalytic cycle with complete conversion of benzyl alcohol, new substrate and oxidant are added, total conversion was again reached after 240 min. Due to the fact that the catalytically active species **5** and **6** have already been formed in the first cycle, the reaction in the second cycle is significantly faster than in the first, but not as fast as in the case of compound **1**. During the formation of the catalytically active species from precursor **2** in the first cycle, part of the monoperoxo complex **5** is deactivated to methanol and perrhenate, leaving less catalytically active species for the second cycle and therefore reducing the reaction rate in comparison to catalyst precursor **1**.

Conclusions

MTO is transformed much faster into the catalytically active species of olefin epoxidation than the dimeric Re(VI) derivatives **2** and **3**. While compound **2** is slowly reacting to give the same active species as MTO itself, compound **3** mainly reacts to form the catalytically inactive trimethyldioxorhenium(VII). This complex does not react with hydrogen peroxide at all. Only a small proportion of compound **3** reacts to yield the catalytically active mono- and bis-peroxo species **5** and **6** *via* compound **2**. Both compounds **2** and **3** are also partially transformed into methanol and perrhenate in the presence of H_2O_2, additionally reducing their catalytic applicability.

These results demonstrate that the Re(VI) compounds **2** and particularly **3** are not suitable replacements for MTO as catalyst precursors in oxidation reactions. Despite being only available *via* toxic tin precursors, MTO seems currently to be the only easily accessible, high oxidation state methylrhenium oxide applicable to oxidation reactions. However, the synthesis of trimethyldioxorhenium is straightforwardly achieved starting from compound **3**, thus presenting a good alternative to the known literature preparation of this compound.

Acknowledgements

The authors are grateful to the Margarethe-Ammon-Stiftung (PhD grant for A. R.) and the Bayerische Forschungsstiftung (PhD grant for A. S.) for financial support.

References

1 R. A. Sheldon, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, 2nd edn, 2002, vol. **1**, pp. 412–427.

2 (*a*) W. A. Herrmann and F. E. Kühn, *Acc. Chem. Res.*, 1997, **30**, 169; (*b*) C. C. Romão, F. E. Kühn and W. A. Herrmann, *Chem. Rev.*, 1997, **97**, 3197.

3 R. Beatty and J. P. Jones, *Inorg. Chem.*, 1979, **18**, 2318.

4 W. A. Herrmann, J. G. Kuchler, J. K. Felixberger, E. Herdtweck and W. Wagner, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 394.

5 (*a*) A. M. J. Rost, H. Schneider, J. P. Zoller, W. A. Herrmann and F. E. Kühn, *J. Organomet. Chem.*, 2005, **690**, 4712; (*b*) F. E. Kühn and A. M. Santos, *Mini-Rev. Org. Chem.*, 2004, **1**, 55; (*c*) A. M. Santos, F. M. Pedro, A. A. Yogalekar, I. S. Lucas, C. C. Romão and F. E. Kühn, *Chem.–Eur. J.*, 2004, **10**, 6313; (*d*) F. M. Pedro, S. Hirner and F. E. Kühn, *Tetrahedron Lett.*, 2005, **46**, 7777; (*e*) F. E. Kühn, J. Zhao and W. A. Herrmann, *Tetrahedron: Asymmetry*, 2005, **16**, 3469; (*f*) F. E. Kühn, A. Scherbaum and W. A. Herrmann, *J. Organomet. Chem.*, 2004, **689**, 4149.

6 (*a*) W. A. Herrmann, F. E. Kühn, R. W. Fischer, W. R. Thiel and C. C. Romão, *Inorg. Chem.*, 1992, **31**, 4431; (*b*) W. A. Herrmann, W. R. Thiel, F. E. Kühn, R. W. Fischer, M. Kleine, E. Herdtweck and W. Scherer, *Inorg. Chem.*, 1993, **32**, 5188; (*c*) W. A. Herrmann, R. M. Kratzer and R. W. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2652; (*d*) W. A. Herrmann and R. M. Kratzer, *Inorg. Synth.*, 2002, **33**, 110.

7 (*a*) W. A. Herrmann, C. C. Romão, R. W. Fischer, P. Kiprof and C. Méric de Bellefon, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 185; (*b*) W. A. Herrmann, F. E. Kühn, C. C. Romão, H. Tran Huy, M. Wang, R. W. Fischer, W. Scherer and P. Kiprof, *Chem. Ber.*, 1993, **126**, 45.

8 (*a*) W. A. Herrmann, C. C. Romão, P. Kiprof, J. Behm, M. R. Cock and M. Taillefer, *J. Organomet. Chem.*, 1991, **413**, 11; (*b*) F. E. Kühn, J. Mink and W. A. Herrmann, *Chem. Ber./Recl.*, 1997, **130**, 295; (*c*) J. M. Huggins, D. R. Randolph and L. Lebioda, *J. Organomet. Chem.*, 1986, **312**, C15.

9 W. A. Herrmann, R. W. Fischer, M. U. Rauch and W. Scherer, *J. Mol. Catal.*, 1994, **86**, 243.

10 (*a*) W. A. Herrmann, R. W. Fischer, W. Scherer and M. U. Rauch, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1157; (*b*) A. M. Al-Ajlouni and J. H. Espenson, *J. Am. Chem. Soc.*, 1995, **117**, 9243; (*c*) J. H. Espenson, *Chem. Commun.*, 1999, 479; (*d*) W. Adam, C. R. Saha-Möller and O. Weichold, *J. Org. Chem.*, 2000, **65**, 5001; (*e*) P. Gisdakis and N. Rösch, *Eur. J. Org. Chem.*, 2001, **4**, 719; (*f*) P. Gisdakis, I. V. Yudanov and N. Rösch, *Inorg. Chem.*, 2001, **40**, 3755; (*g*) C. Valentin, R. Randolfi, P. Gisdakis and N. Rösch, *J. Am. Chem. Soc.*, 2001, **123**, 2365.

11 (*a*) M. Abrantes, A. M. Santos, J. Mink, F. E. Kühn and C. C. Romão, *Organometallics*, 2003, **22**, 2112; (*b*) J. Zhao, A. M. Santos, E. Hertweck and F. E. Kühn, *J. Mol. Catal. A: Chem.*, 2004, **222**, 265; (*c*) F. E. Kühn, J. Zhao, M. Abrantes, W. Sun, C. A. M. Afonso, L. C. Branco, I. S. Gonçalves, M. Pillinger and C. C. Romão, *Tetrahedron Lett.*, 2005, **46**, 47; (*d*) F. E. Kühn, A. M. Santos and W. A. Herrmann, *Dalton Trans.*, 2005, 2483; (*e*) F. E. Kühn, A. M. Santos and M. Abrantes, *Chem. Rev.*, 2006, **106**, 2455.

12 W. A. Herrmann, W. M. Wachter, F. E. Kühn and R. W. Fischer, *J. Organomet. Chem.*, 1998, **553**, 443.

13 P. Gisdakis, N. Rösch, É. Bencze, J. Mink, I. S. Gonçalves and F. E. Kühn, *Eur. J. Inorg. Chem.*, 2001, **981**.

14 S. Köstlmeier, G. Pacchioni, W. A. Herrmann and N. Rösch, *J. Organomet. Chem.*, 1996, **514**, 111.

15 (*a*) M. M. Abu-Omar, P. J. Hansen and J. H. Espenson, *J. Am. Chem. Soc.*, 1996, **118**, 4966; (*b*) S. Yamazaki, J. H. Espenson and P. Huston, *Inorg. Chem.*, 1993, **32**, 4683; (*c*) P. J. Hansen and J. H. Espenson, *Inorg. Chem.*, 1995, **34**, 5839; (*d*) J. H. Espenson, O. Pestovski, P. Huston and S. Staudt, *J. Am. Chem. Soc.*, 1994, **116**, 2869.

16 R. W. Fischer, PhD Thesis, TU München, 1994.

17 A. Haaland, W. Scherer, H. V. Volden, H. P. Verne, O. Gropen, G. S. McGrady, A. J. Deuns, G. Dierker, W. A. Herrmann, P. W. Roesky and M. R. Geisberger, *Organometallics*, 2000, **19**, 22.