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Catalytic oxidations by peroxy, peroxo and oxo metal complexes: an interdisciplinary account with a personal view

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This work is dedicated to Professor Helmut Werner, on the occasion of his retirement, in recognition of his outstanding scientific contributions to organometallic chemistry, and also for his continual support of our work in the SFB 347.

Abstract

In this account, we present a brief overview of our interdisciplinary efforts on the metal-assisted selective oxyfunctionalization of organic substrates in the 'Sonderforschungsbereich (SFB 347): Selektive Reaktionen Metall-aktivierter Moleküle'. The reactivity and selectivity of peroxy-, peroxo-, and oxo-type metal oxidants have been studied to gain insight into the mechanism of the oxygen transfer by such catalytic oxidants. Based on our mechanistic work, effective catalytic oxyfunctionalization methods have been developed by employing Ti, V, Re, Mn or Cr complexes as catalysts for the chemo-, regio-, diastereo- and enantioselective synthesis of hydroxy epoxides (from olefins), sulfoxides (from sulfides), and silanols (from silanes). We show that the stoichiometric dimethyldioxirane (DMD) oxidation of ligands in selected transition-metal complexes provides an useful tool for the synthesis of oxyfunctionalized compounds.

Keywords: Catalysis; Metal complexes; Oxyfunctionalization; Oxygen-transfer mechanism; Reactivity; Selectivity

1. Introduction

The last 2 decades of the 20th century have witnessed major advances in catalytic oxidations, a challenging field of great importance and value since most synthetic sequences incorporate an oxidation step in one form or another. Organometallic chemistry contributed decisively in this success, in particular transition-metal complexes. These spectacular achievements commenced with the asymmetric epoxidation of prochiral allylic alcohols by hydroperoxides, catalyzed by titanium tetraalkoxides. For enantioselectivity, these catalysts were equipped with optically active tartrates as chiral auxiliaries, as jointly discovered in 1980 by Sharpless and Katsuki [1]. This far-reaching breakthrough for synthetic chemistry, appropriately honored with the Nobel Prize in 2001, has kindled intensive research activity in catalytic oxidations. Shortly afterwards, this catalyst system was modified by Kagan, and independently by Modena, for the enantioselective sulfoxidation of prochiral aryl alkyl sulfides [2]. About a decade later (1990), Herrmann's research group reported [3] that methyltrioxorhenium (MTO) serves as highly effective catalyst for the oxidation of organic compounds by hydrogen peroxide. Although this rather reactive oxidant oxidizes unfunctionalized olefins and even electron-rich arenes, asymmetric oxygen transfer has so far not been documented. This advance was achieved in 1990 by Jacobsen [4a], and independently by Katsuki [4b], who employed optically active manganese(salen) complexes as efficacious catalysts for the enantioselective epoxidation of unfunctionalized alkenes; iodosobenzene or sodium hypochlorite was employed as oxygen donors. Unquestionably, these three transition-metal-based catalytic

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systems have established themselves as the most employed 'work horses' in modern oxidation chemistry for preparative purposes.

Of mechanistic relevance is the fact that different oxygen-activated species operate in the oxygen transfer by these catalytic oxidation systems. Similar to vanadium [5], for the titanium catalyst a peroxy-type oxidant applies (Fig. 1), whereas for rhenium the peroxo-type complex acts as oxygen-transfer entity. In contrast, for the manganese catalyst, analogous to chromium [6], an oxo-metal species conducts the oxidation instead of a peroxide functionality. Expectedly, distinct modes of oxygen transfer are displayed by these oxidation system, whose transition structures are exhibited in Fig. 2. In the case of titanium (also vanadium), a template (loaded complex) is formed, in which the substrate (allylic alcohol) and the hydroperoxide (appropriately activated) are bound in form of metal–oxygen bonds to the central titanium atom. Additionally, the tartrate is coordinated to the titanium to provide the chiral environment for asymmetric induction (not shown in the template for sakes of clarity). Contrarily, no template effect applies for the rhenium and the manganese catalysts; thus, steric interactions between the approaching substrate and the oxygen-activated metal complex operate for stereochemical differentiation, particularly in the chiral manganese(salen) oxo complex.

The preparative utility and synthetic value of the three transition-metal-based catalytic oxidants presented above is indisputable, but mechanistic understanding of the complex oxygen-transfer processes is as important, especially for the design of still more effective and generally applicable selective catalytic oxidants. In the context of the 'Sonderforschungsbereich (SFB 347): Selektive Reaktionen Metall-aktivierter Moleküle', the incentive of our work in oxidation chemistry was to scrutinize the mechanistic aspects of the Sharpless–Katsuki, Hermann and Jacobsen–Katsuki catalytic oxidations. In particular, our goal was to understand reactivity and selectivity. Additionally, it should be evident that in metal-catalyzed oxidations the organic ligands are themselves subject to oxidation. This shortcoming of organometallic catalyst severely limits their persistence and thereby depreciates their efficacy in the oxyfunctionalizations of the target substrate. To derive a benefit for synthetic applications from these shortcomings, we have deliberately conducted stoichiometric ligand oxidation in the interest of developing new methodology for selective oxyfunctionalization.

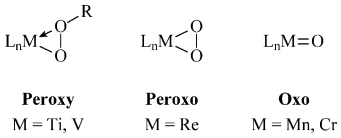


Fig. 1. Metal oxidants for catalytic oxyfunctionalizations.

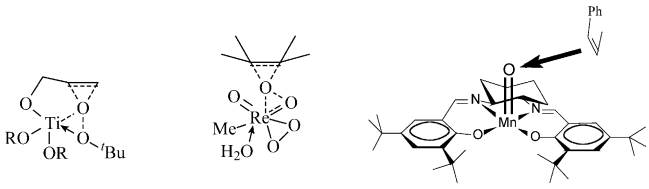


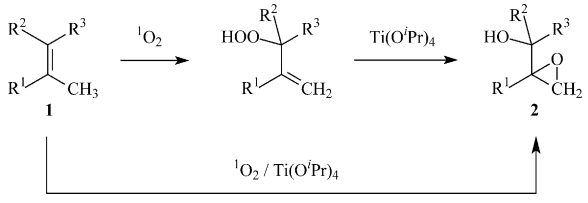
Fig. 2. Transition structures for the Sharpless–Katsuki (left), Herrmann (center) and Jacobsen–Katsuki epoxidations (right).

During the last 12 years of our efforts in the SFB 347, we have regularly reviewed our progress in selective catalytic oxidations [7]. The purpose of the present interdisciplinary account is to feature an overview of our highlights, necessarily focussed with a personal view.

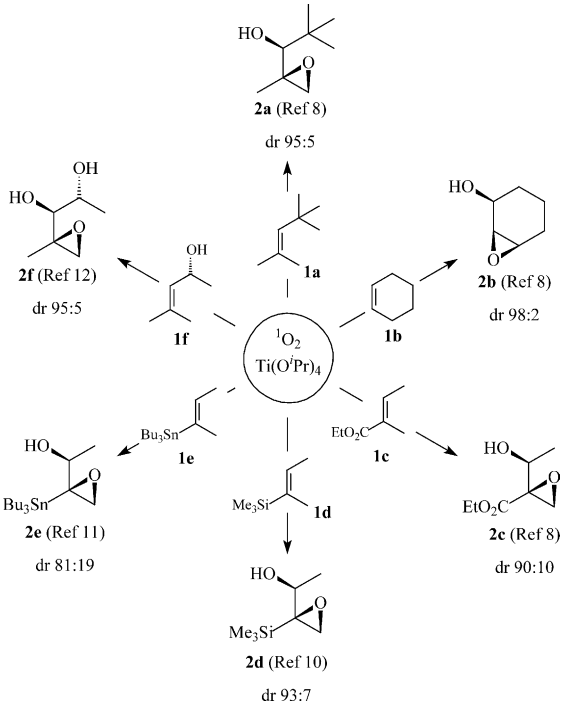
2. Catalytic oxidations by peroxy complexes (Ti, V)

2.1. Epoxidation

As already mentioned in the Introduction, the Ti-catalyzed epoxidation of allylic alcohols with *tert*-butyl hydroperoxide is the most prominent method for the preparation of epoxy alcohols, which constitute valuable building blocks for the synthesis of biologically active compounds. The required allylic alcohols, in turn, may be conveniently prepared by the ene reaction of olefins **1** with singlet oxygen ($^1O_2$) and subsequent reduction of the resulting hydroperoxide. In the conversion of the allylic hydroperoxide to the corresponding epoxy alcohol **2**, at first an oxygen atom is removed by reduction, to be subsequently introduced again through epoxidation with an external oxygen donor. In terms of atom efficiency, a synthetic route would be advantageous, in which both oxygen atoms of the allylic hydroperoxide are used directly for such an oxyfunctionalization. Indeed, for this purpose, titanium tetraisopropoxide [Ti(O^iPr)$_4$] may be used as a catalyst (Scheme 1). A convenient one-pot protocol for this epoxy-hydroxylation of olefins **1** has also been developed, by conducting the photooxygenation in the presence of Ti(O^iPr)$_4$ [7c,8]. Control experiments revealed that the oxygen transfer occurs intermolecularly, i.e. a template structure analogous to that in the Sharpless–Katsuki epoxidation (Fig. 2) [1] is formed, in which the allylic hydroperoxide (oxygen donor) and the corresponding allylic alcohol



Scheme 1. Stepwise vs. one-pot epoxy-hydroxylation of the olefins **1**.

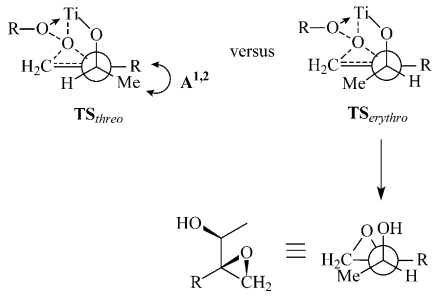


Scheme 2. Substrate scope of the diastereoselective epoxy-hydroxylation method.

(oxygen acceptor) are coordinated to the same titanium center [7c].

As shown in Scheme 2 [8,10–12], the substrate scope is quite general and excellent regio- as well as diastereoselectivities have been observed. Thus, the simple *tert*-butyl-substituted olefin **1a** yields the corresponding epoxy-alcohol **2a** in an *erythro*/*threo* diastereoselectivity of 95:5, whereas the epoxide *cis*-**2b** is the major product (dr 98:2) for cyclohexene (**1b**) [8]. When the tiglic ester **1c** is employed as a substrate, only *twix* abstraction [9] occurs to form almost exclusively (dr 90:10) the *erythro*-**2c** epoxy alcohol [8]. Similarly, for the vinylsilane **1d** and the vinylstannane **1e** also a preference for the *erythro* diastereomer of **2d** and **2e** has been observed in the epoxy-hydroxylation [10,11]. Even functionalized olefins like the allylic alcohol **1f** may be employed, from which the (2*R**,3*R**,4*R**)-configured epoxy-diol **2f** is obtained as the main product [12]. The fact that the highly functionalized olefinic substrate α-ionone (not shown in Scheme 2) was regio- and diastereoselectively oxyfunctionalized to the respective epoxy alcohol [13], emphasizes the synthetic utility of this methodology.

The *erythro* diastereoselectivity, observed for the trisubstituted olefins **1a**,**c**–**f**, may be rationalized in terms of the transition structures proposed for the Ti-catalyzed epoxidation of the intermediary allylic alcohol in Scheme 3, in which the Ti-peroxy species is fixed to the substrate by alcoholate bonding. This loaded complex may adopt the two diastereomeric transition structures TS$_{threo}$ and TS$_{erythro}$, which lead either to

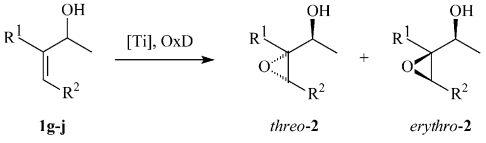


Scheme 3. Diastereomeric transition structures for the Ti-catalyzed epoxidation.

the *threo* (left side) or to the *erythro* epoxy alcohol **2** (right side). Since in TS$_{threo}$ severe steric interactions operate between the methyl group on the stereogenic carbon atom and the R-group. Due to the so-called 1,2-allylic strain (A^{1,2}), this transition structure is disfavored. In contrast, TS$_{erythro}$ is favored because it possesses no allylic strain and, thus, the *erythro*-**2** diastereomer is formed preferentially.

To elucidate the geometry of the transition structure for the epoxidation, the set of allylic alcohols **1g**–**j** has been epoxidized by the homogenous Ti(O^{i}Pr)$_4$–^{t}BuOOH oxidant, as well as by the heterogenous systems Ti-β–H_2O_2 and TS-1–UHP (Table 1) [14]. Evidently, these oxidants fall into two sets in regard to their *threo*/*erythro* diastereoselectivities, which is most apparent for 3-methyl-3-buten-2-ol (**1h**) with only 1,2-allylic strain (entry 2): whereas for the homogeneous Ti(O^{i}Pr)$_4$–^{t}BuOOH oxidant the *erythro*-epoxide **2** is favored *threo*–*erythro* 22:78, for the heterogeneous Ti-β–H_2O_2 and TS-1–UHP oxidants there is essentially no

Table 1
Disstereoselectivities in Ti-catalyzed epoxidation of the allylic alcohols **1g**–**j**



Entry	Substrate	Diastereomeric ratio (*threo*:*erythro*)		
		Ti(O^{i}Pr)^4, ^{t}BuOOH	Ti-β, H_2O_2	TS-1, UHP[a]
1		71:29	62:38	64:36
2		22:78	56:44	55:45
3		91: 9	91: 9	87:13
4		83:17	89:11	81:19

a) Urea / hydrogen peroxide adduct

selectivity *threo*–*erythro* 55:45. Clearly, 1,3-allylic strain dominates for in all three oxidants, as displayed by the stereochemical probe with both 1,2- and 1,3-allylic strain in competition (entry 4). For the Ti(O^iPr)$_4$–^{t}BuOOH oxidant, these results have been confirmed recently by density-functional computations [15]. From these data it may be concluded that distinct transition states are traversed for the homogenous and the heterogenous epoxidations: whereas the main structural motive for ^{t}BuOOH as the oxygen donor is alkoxide bonding of the allylic substrates **1g**–**j** to the Ti-peroxy species, the Ti–H_2O_2 oxidant in zeolite is structurally similar to peracids, e.g. *m*CPBA. For the latter, hydrogen bonding between the allylic alcohol and the Ti-hydroperoxy species has been proposed to account for the observed diastereoselectivities (Fig. 3) [14].

Whereas the simple allylic alcohols **1g**–**j** are readily epoxidized by Ti(O^iPr)$_4$–^{t}BuOOH, alkene diols are quite unreactive towards this oxidation system. This fact is not surprising since the corresponding epoxy-diol product adheres to the titanium center too strongly to be substituted by *tert*-butyl hydroperoxide and, thus, the catalytic turn-over is inhibited [16]. This catalyst poisoning may be overcome by the use of a tridentate oxygen donor instead of the bidentate ^{t}BuOOH. As shown in the epoxy-hydroxylation of 4-methyl-3-penten-2-ol (**1f**), the initially formed allylic hydroperoxy alcohol transfers its peroxidic oxygen atom onto the allylic diol to yield the corresponding epoxy diol **2f** (vide supra). Alternatively, a hydroperoxy alcohol, namely 2,3-dimethyl-3-hydroperoxy-2-butanol (cf. Scheme 4, right column) may be used which is readily prepared by perhydrolysis of tetramethylethylene oxide [17a]. The above-mentioned methodology, combined with the enzymatic kinetic resolution of the hydroperoxide *rac*-**1k** by horseradish peroxidase (HRP), has been successfully employed for the diastereoselective synthesis of both enantiomers of the epoxy diols **2k** (Scheme 4) [17b]. Recently, the Ti(O^iPr)$_4$–2,3-dimethyl-3-hydroperoxy-2-butanol system has also been employed in the selective preparation of optically active 4,6-dideoxyfuranoses [17c].

A special synthetic challenge and the subject of current interest is the enantioselective epoxidation. For allylic alcohols, the Sharpless–Katsuki protocol has

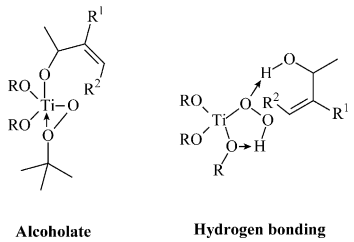
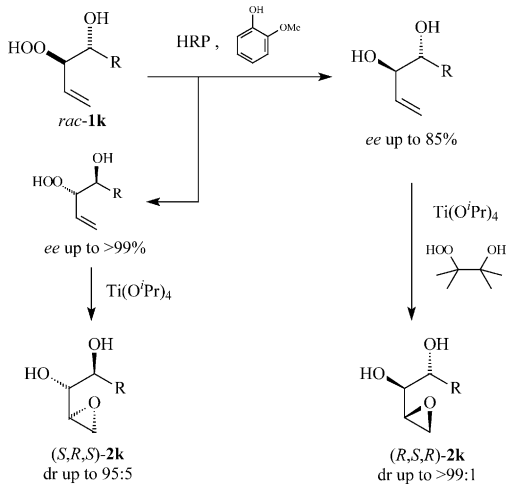


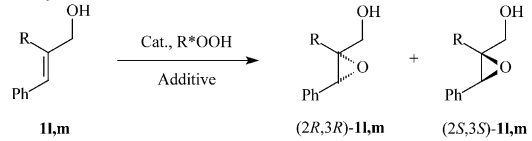
Fig. 3. Alcoholate vs. hydrogen bonding in the Ti-catalyzed epoxidation of the allylic alcohols **1g**–**j** with ^{t}BuOOH and H_2O_2.

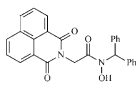
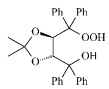
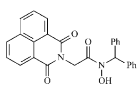


Scheme 4. Synthesis of optically active epoxy diols **2k** by combined enzymatic kinetic resolution and Ti-catalyzed epoxidation.

proven to be most effective, in which the asymmetric induction results from catalytic amounts of optically active tartrate as chiral auxiliary [1]. When optically active hydroperoxides are used, the latter not only serves as the oxygen donor but also as the source of chirality, without the need of tartrate as chiral auxiliary. This concept has been employed in the Ti- and the V-catalyzed asymmetric epoxidation of the substituted cinnamyl alcohols **1l** and **1m** in the presence of achiral additives (Table 2) [18]. With (*S*)-(1-phenyl)ethyl hydroperoxide (entries 1–4), which is readily available by enzymatic kinetic resolution [19], only modest enantioselectivities (up to 34% ee) have been obtained for both substrates and both metals. More successful was the V-catalyzed epoxidation with the TADDOL-derived hydroperoxide (entries 5 and 6), which gave high ee values for the epoxy alcohols (2*R*,3*R*)-**1l** (67% ee) and

Table 2
Catalytic asymmetric epoxidation with optically active hydroperoxides *R**OOH by Ti or V



Entry	Substrate	R	R*OOH	Cat.	Additive	ee (%)
1[a]	**1l**	Me		Ti(O^iPr)$_4$		34 (2*R*,3*R*)
2[a]	**1m**	Ph				4 (2*R*,3*R*)
3[b]	**1l**	Me		VO(O^iPr)$_3$		4 (2*S*,3*S*)
4[b]	**1m**	Ph				34 (2*S*,3*S*)
5[c]	**1l**	Me		VO(O^iPr)$_3$		67 (2*R*,3*R*)
6[c]	**1m**	Ph				71 (2*R*,3*R*)

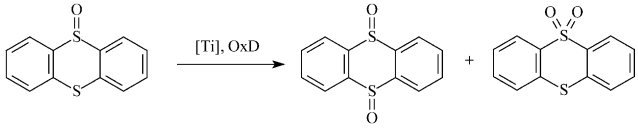
a) Ref 18a; b) Ref 18b; c) Ref 18c.

(2*R*,3*R*)-**1m** (71% ee). The sense of the enantiofacial selection was accounted for in terms of steric interactions in the possible template structures [18].

2.2. Sulfoxidation

The Ti-catalyst–ROOH oxidant has also been used for the transfer of an oxygen atom onto sulfides **3** to yield the corresponding sulfoxides **4**. The sulfoxidation may be accompanied by overoxidation of the initially formed sulfoxide **4** to the sulfone **5**, the extent of which depends on the electrophilicity of the oxidant. To assess the electrophilicity of the oxygen-transfer agent, thianthrene 5-oxide (SSO) has been applied as mechanistic probe [20], in which a sulfide and a sulfoxide functionality are oxidized competitively to form the disulfoxide SOSO and the sulfide–sulfone SSO_2 products (Table 3). From the relative amounts of SOSO and SSO_2, the so-called X_{SO} value may be calculated, which is <0.3 for an electrophilic oxidant, whereas $X_{SO}>0.7$ indicates a nucleophilic oxidant. When SSO was oxidized with the homogeneous Ti(O^iPr)$_4$–^{t}BuOOH system or with several Ti-doped zeolites and ^{t}BuOOH or H_2O_2 as oxygen donors (Table 3), the heterogeneous oxidants (entries 2–6) exhibited definite electrophilic character, since their X_{SO} values range between 0.06 and 0.19. The relatively high X_{SO} value of 0.50 of the homogenous system (entry 1) implies a more nucleophilic oxidant; however, the enhanced formation of SSO_2 was attributed to coordination of the SSO probe at its sulfoxide functionality to the titanium center, such that necessarily oxidation of the Ti-coordinated sulfoxide group to the sulfone SSO_2 is favored. Presumably, this coordination of SSO to the catalyst is hindered for the heterogeneous catalyst due to the steric constraints in the zeolite lattice; thus, SOSO is formed preferentially, which expresses the genuine electrophilic character of the titanium catalyst.

Table 3
Ti-catalyzed oxidation of the mechanistic probe SSO



SSO **SOSO** **SSO_2**

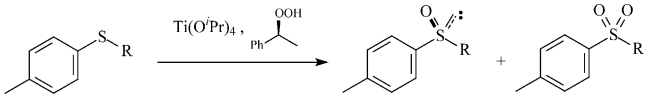
Entry	[Ti]	OxD	X_{SO}[a]
1	Ti(O^iPr)$_4$	^{t}BuOOH	0.50
2	Ti-β	^{t}BuOOH	0.19
3	Ti-MCM-41	^{t}BuOOH	0.17
4	Ti-IQC-2	^{t}BuOOH	0.12
5	Ti-β	H_2O_2	0.14
6	Ti-MCM-41	H_2O_2	0.06

a) Calculated according to $X_{SO}=\frac{SSO_2+SOSO_2}{SSO_2+SOSO+2\times SOSO_2}$; $X_{SO}<0.3$ means an electrophilic oxidant whereas $X_{SO}>0.7$ indicates a nucleophilic oxidant.

As in the case of allylic alcohols, also the Ti-catalyzed asymmetric sulfoxidation with enantiomerically pure hydroperoxides has been examined (Scheme 5) [21]. For (*S*)-(1-phenyl)ethyl hydroperoxide as oxygen donor, ee-values up to 71% have been obtained for the alkyl aryl sulfoxides **4a**–**d**. Detailed mechanistic studies have revealed that the observed enantioselectivity results from a combination of rather low asymmetric induction in the sulfoxidation of the substrates **3a**–**d** and effective subsequent kinetic resolution of the initially formed sulfoxides **4a**–**d** by enantioselective oxidation to the sulfones **5a**–**d**. The kinetic resolution in the asymmetric overoxidation may be explained by means of a template structure, in which one enantiomer of the sulfoxide **4** coordinates preferentially to the chiral Ti-peroxy complex. Thus, high enantioselectivities have been achieved only at the expense of extensive sulfone formation.

2.3. SiH oxidation

Despite the fact that organosilanols are of general synthetic interest in view of their importance in industrial applications [22], only a limited number of convenient and effective methods for their preparation is available. The problem is the tendency of the silanols to dimerize to the corresponding disiloxanes by traces of acid or base. For this reason, there is a need for developing selective as well as catalytic methods for the oxidation of silanes to silanols under neutral conditions (Table 4). When the model substrate dimethylphenylsilane (SiH) was treated with catalytic amounts of Ti(O^iPr)$_4$ and ^{t}BuOOH as the oxygen donor, condensation to the disiloxane Si_2O dominates (SiOH–Si_2O 39:61, entry 1) [23]. Contrarily, the desired silanol SiOH is the sole product when the zeolites Ti-β and TS-1 were employed (entries 2 and 3). Similar results have been achieved for Ti-MCM-41 and Ti-IQC-2, because only a minor amounts of Si_2O were produced (SiOH:Si_2O 90:10 and 95:5, entries 4 and 5) [20b]. Since the oxidation takes place inside the zeolite cavities, there is not enough space for two molecules of SiOH to condense and, thus, the high product selectivity arises from steric constraints in the zeolite lattice. Similar to the allylic-alcohol epoxidation, a peracid-like transition structure has been proposed for this SiH oxidation (cf.



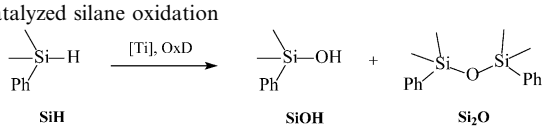
3a-d
R = Me, Et, ^{i}Pr, ^{n}Bu

4a-d
ee 62-71%

5a-d

Scheme 5. Ti-catalyzed asymmetric sulfoxidation with optically active hydroperoxides *R**OOH.

Table 4
Ti-catalyzed silane oxidation



Entry	[Ti]	OxD	SiOH :Si$_2$O
1	Ti(O^{i}Pr)$_4$[a]	^{t}BuOOH	39:61
2	Ti-β	H_2O_2	>99: 1
3	TS-1	H_2O_2	>99: 1
4	Ti-MCM-41	^{t}BuOOH	90:10
5	Ti-IQC-2	^{t}BuOOH	95: 5

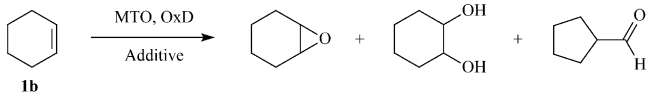
a) In the presence of diethyl *L*-tartrate.

Fig. 3, right), in which the oxygen atom is inserted into the SiH bond with retention of configuration. To confirm this stereochemical course, the enantiomerically pure (*S*)-(α-Np)PhMeSiH silane was treated with Ti(O^{i}Pr)$_4$–^{t}BuOOH and with Ti-β–H_2O_2 [23,24]. Whereas the former yielded the desired (*R*)-(α-Np)PhMeSiOH (change in the Cahn-Ingold-Prelog priority!) with partial racemization (51% ee), for the heterogeneous system no conversion of the silane was observed because (*S*)-(α-Np)PhMeSiH is too bulky to enter the zeolite.

3. Catalytic oxidations by peroxo complexes (Re)

3.1. Epoxidation

MTO, which was discovered in 1989 [3] as a potent oxidation catalyst, effects the epoxidation of olefins by H_2O_2 as oxygen donor. Product selectivity, however, has been a matter of concern, as illustrated in Scheme 6 for the model substrate cyclohexene (**1b**) [25a,25b]. Without an appropriate buffer, little if any epoxide was obtained; the main product (82%) was cyclohexane diol and, additionally, 18% of cyclopentane carboxaldehyde. The Lewis acidity of the perrhenate, which is formed by degradation of the rhenium catalyst, is responsible for the acid-catalyzed opening of the epoxide to the diol, the latter in turn suffers pinacol-type rearrangement and cleavage. To suppress the formation of these undesired side products, the use of additives like the NaY zeolite or urea greatly improved the product selectivity. In this way, the cyclohexane epoxide may be obtained almost exclusively (>95%) in the MTO-catalyzed epoxidation of cyclohexene (**1b**), as shown in Scheme 6 [25a,25b].



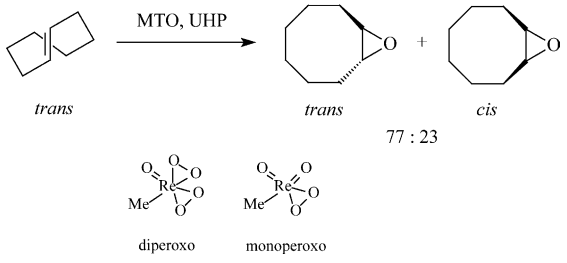
OxD	Additive			
H_2O_2	--	0	82	18
H_2O_2	NaY	> 95	< 5	5
UHP[a]	--	99	1	0

a) Urea / hydrogen peroxide adduct

Scheme 6. Rhenium-catalyzed epoxidation of cyclohexene (**1b**).

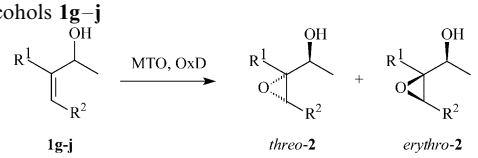
Some puzzling results were found for the MTO-catalyzed epoxidation of *trans*-cyclooctene, which yielded not only the expected *trans* epoxide, but also considerable amounts of the *cis* diastereomer (*trans:cis* 77:23, Scheme 7) [25c]. The monoperoxo complex that is formed from the diperoxo epoxidant after oxygen transfer, was shown to be responsible for the preferential deoxygenation of the *trans* epoxide to a mixture of *cis*- and *trans*-cyclooctenes; in turn, the latter cyclooctenes were reoxidized to the observed mixture of *cis* and *trans* epoxides. This mechanistic rationale was unequivocally proven [25c] by stoichiometric oxidation of the pure *trans*-cyclooctene diastereomer with the authentic peroxo rhenium complex, which led to a mixture (*trans*–*cis* 25:75) of the diastereomeric epoxides, in addition to the isomerized cyclooctenes (*trans*–*cis* 45:55).

As in the case of the Ti-catalyzed epoxidation, the set of acyclic allylic alcohols **1g**–**j** was investigated, to elucidate the transition structure of the MTO-based oxidants MTO–UHP and MTO–H_2O_2–pyridine; the results are summarized in Table 5 [26a]. Since both oxidants show equal diastereoselectivities within the experimental error, the same rhenium diperoxo complex operates as epoxidant. Whereas substrates without allylic strain (entry 1) or only with 1,2-allylic strain (entry 2) are epoxidized unselectively, the allylic alcohols **1i** and **1j** with 1,3-allylic strain display high *threo* selectivities (dr values up to 91:9). Comparison of the observed diastereoselectivities with other oxidants reveals a good correspondence between MTO–H_2O_2 and the peracid *m*CPBA or the perhydrate-type Ti-β–H_2O_2 (Table 1). Further investigations with geraniol and its 1-methyl derivative as regiochemical probes led to the proposed transition structures depicted in Fig. 4, in which hydrogen bonding between the hydroxy function-



Scheme 7. Rhenium-catalyzed epoxidation of *trans*-cyclooctene.

Table 5
Diastereoselectivities in the rhenium-catalyzed epoxidation of the allylic alcohols **1g–j**



1g-j *threo*-**2** *erythro*-**2**

Entry	Substrate	Diastereomeric ratio (*threo:erythro*) UHP[a]	H_2O_2[b]
1		60:40	--
2		50:50	41:59
3		82:18	86:14
4		91: 9	80:20

a) Urea / hydrogen peroxide adduct; b) in the presence of pyridine.

ality and the rhenium catalyst is the mechanistically decisive electronic feature. As is evident from the high *threo*-diastereoselectivity in the epoxidation of the stereochemical probe (*Z*)-3-methyl-3-penten-2-ol (**1j**), with both $A^{1,2}$ and $A^{1,3}$ strain, the latter dominates in the rhenium-catalyzed oxygen transfer. From these stereochemical data, a dihedral angle (C=C–C–O) of ca. 130° was suggested, which was corroborated by the diastereoselectivities observed in the epoxidation of a set of various cyclic allylic alcohols [26b].

3.2. Arene oxidation

Electron-rich arenes **6** may be oxidized by MTO–H_2O_2 in moderate to good yields to the corresponding quinones **7** (Scheme 8), which do not only serve as valuable building blocks in organic synthesis, but some derivatives also show biological activity [27]. In the first step, an arene epoxide is formed, which rearranges by acid catalysis to an intermediary phenol and further oxidation affords the quinone product **7**. The more electron-rich arene leads to better yields in this electrophilic oxidation. Whereas the unsubstituted quinone is

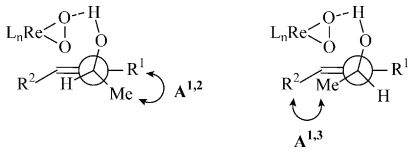
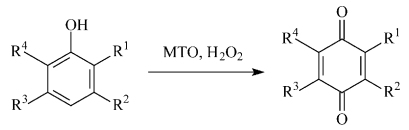


Fig. 4. Transition structures for the rhenium-catalyzed epoxidation to illustrate 1,2- and 1,3-allylic strain ($A^{1,2}$ and $A^{1,3}$).



6 **7**

[37 - 70%]

Scheme 8. Rhenium-catalyzed oxidation of the arenes **6**.

obtained in only 37% yield, trimethylquinone is formed in up to 70% yield and tetramethylquinone essentially quantitatively. An important industrial application of this transformation constitutes the regioselective synthesis of vitamin K_3, a widely used additive for animal feed, from the commercially available and inexpensive β-methylnaphthalene (Scheme 9) [27c,27d].

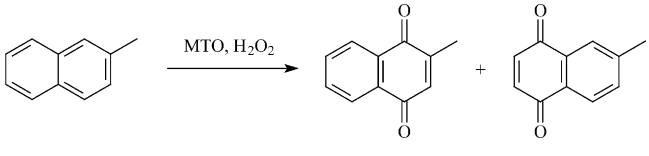
The two regioisomers were obtained in a 86:14 ratio, of which the desired 2-substituted quinone was favored. This catalytic method rivals the industrial synthesis of vitamin K_3, which is conducted with stoichiometric amounts of chromic acid (40–60% yield) [28].

3.3. Sulfoxidation

When sulfides **3** are used as substrates in the Re-catalyzed oxidation, sulfoxides **4** are formed in excellent chemoselectivities (Scheme 10); the extent of overoxidation to the sulfone **5** is in most cases less than 5% [29]. This is in line with the high electrophilic character ($X_{SO} = 0.07$) of the MTO–H_2O_2 oxidant [29b]. Exceptional is dimethyl sulfide, for which substantial amounts (29%) of dimethyl sulfone were obtained, due to the increased reactivity of its sulfoxide. The use of 85% H_2O_2 is crucial for good chemoselectivities, as confirmed for thioanisol as model substrate. When 11% H_2O_2 was employed, the amount of sulfone increased from 3 up to 18% [29]. Possibly, the reactivity of the rhenium peroxo complex is enhanced by hydrogen bonding by water, which would promote sulfone formation.

3.4. SiH oxidation

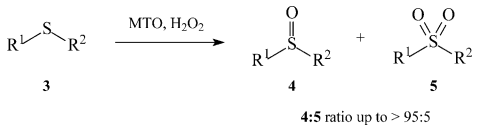
As in the case of the Ti-catalyzed silane oxidation, the unmodified MTO–H_2O_2 oxidant leads to extensive



Vitamin K_3

86 : 14

Scheme 9. Catalytic oxidation of 2-methylnaphthalene by MTO–H_2O_2 to vitamin K_3.

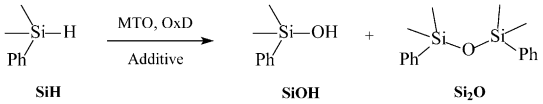


Scheme 10. Rhenium-catalyzed sulfoxidation.

disiloxane formation due to its high Lewis acidity; the yield of the desired silanol SiOH is only 20% (Table 6, entry 1) [24,25b]. By addition of urea or NaY zeolite, excellent product selectivities have been realized, with the silanol SiOH as the sole product ($SiOH–Si_2O$ > 99:1, entries 3 and 4). The use of the urea adduct of hydrogen peroxide (UHP) is even more convenient, without loss in selectivity (entry 2). This oxidation constitutes one of the very few host–guest reactions in UHP channels [24]. For good selectivities in this host–guest chemistry, the order of addition is of crucial importance. The best results are achieved when the urea–H_2O_2 adduct or the zeolite are added to the silane before the MTO catalyst, to ensure that the oxidation occurs only inside the cavities. For the zeolite case, when hydrogen peroxide is administered last, considerable oxidation will take place in solution, which leads to high amounts of disiloxane Si_2O.

To assess the transition structure of the SiH oxygen insertion, the enantiomerically pure α-naphthylphenylmethylsilane (*S*)-(α-Np)PhMeSiH was treated with MTO–H_2O_2 or MTO–UHP [24]. Whereas the former yielded only racemic silanol, the presence of urea proved to be beneficial for the stereoselectivity. The desired (*R*)-(α-Np)PhMeSiOH was obtained with retention of configuration (91% ee). Due to the mechanistic similarity in the oxygen transfer between the catalytically active MTO diperoxo complex and the stoichiometric oxidant dimethyldioxirane (DMD), also a 'butterfly' transition structure was suggested for the oxygen insertion into the SiH bond [7h].

Table 6
Rhenium-catalyzed silane oxidation



Entry	OxD	Additive	SiOH :Si_2O
1	H_2O_2	--	20:80
2	UHP[a]	--	98: 2
3	H_2O_2	Urea	> 99: 1
4	H_2O_2	NaY	> 99: 1

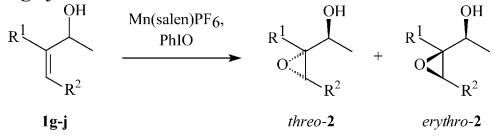
a) Urea / hydrogen peroxide adduct.

4. Catalytic oxidations by oxo complexes (Mn, Cr)

4.1. Epoxidation

It is generally accepted that salen complexes of manganese and chromium catalyze oxidations by means of a metal-oxo species [6], which may react in two different ways with allylic alcohols as substrates: Either the oxygen atom is transferred onto the double bond to form the corresponding epoxide, or the allylic hydrogen atom is abstracted to yield the respective enone. Thus, not only diastereoselectivity but also chemoselectivity, i.e. the ratio between epoxide and enone formation, becomes a useful parameter for mechanistic investigation. When the well established set of allylic alcohols **1g–j** was treated with the achiral Mn(salen)PF_6–PhIO oxidant, epoxidation was the main reaction pathway, whereas only traces (< 5%) of the CH-oxidation product were detected (Table 7) [30a]. For the substrates **1g** and **1h**, a low diastereoselectivity was found (entries 1 and 2); clearly, 1,2-allylic strain does not play a significant role. Contrarily, the epoxidation of the allylic alcohols **1i** and **1j** proceeded with high *threo* selectivity (entries 3 and 4) and, thus, 1,3-allylic strain dominates the stereochemical course of this metal-mediated reaction. As for the structure of the transition state, hydrogen bonding between the hydroxy group of the substrate and the oxygen atom of the intermediary Mn(V)(oxo) species is the decisive structural motive, in which the hydroxy-directing effect [7g] operates. The dihedral angle (C=C–C–O) has been estimated to be 100–115°, by comparison with other oxidation systems and from the diastereoselectivities obtained in the

Table 7
Diastereoselectivities in the Mn-catalyzed epoxidation of the allylic alcohols **1g–j**



Entry	Substrate[a]	Diastereomeric ratio (*threo:erythro*)
1		54:46
2		48:52
3		89:11
4		81:19

a) In the presence of 4-phenylpyridine *N*-oxide (PPNO).

epoxidation of *cis*- and *trans*-5-*tert*-butyl-2-cyclohexenol [30].

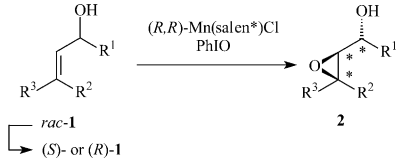
When an optically active Mn(salen*) complex (Jacobsen's catalyst) was used, kinetic resolution of a secondary allylic alcohol took place by means of asymmetric epoxidation (Table 8) [31]. For this purpose, the aryl-substituted allylic alcohols **1n**–**p** were employed, since these give the best enantioselectivity in the Jacobsen–Katsuki epoxidation [4c]. Indeed, the 4-phenyl-3-buten-2-ol (**1n**) (entry 1) was epoxidized in excellent chemo- and diastereoselectivity (>95:5) to afford the corresponding *threo*-configured epoxy alcohol **2n** as a 50:50 mixture of the *cis*- and *trans*-epoxides. At a conversion of 41%, the unreacted (*S*)-configured allylic alcohol **1n** was obtained in 53% ee, whereas the (*R*) enantiomer was epoxidized to the (2*R*,3*S*,4*R*)-*cis*-epoxide **2n** (69% ee) and the (2*R*,3*S*,4*S*)-*trans*-epoxide **2n** (80% ee). Under the same reaction conditions, the allylic alcohols **1o** and **1p** showed selectivity factors of 4.1 and 2.5 (entries 2 and 3). The stereochemical outcome of this asymmetric epoxidation may be explained by a synergistic interplay between the hydroxy-directing effect 7g and the attack of the olefin along the Katsuki trajectory [32].

Optically active Mn(salen*) complexes have also been employed for the preparation of enantiomerically enriched α-hydroxy ketones and esters (ee 22–86%) by asymmetric epoxidation of prochiral silyl enol ethers (Scheme 11, upper equation) [33]. Best results in regard to conversion and enantioselectivity were obtained for bleach as the oxygen source and 4-phenylpyridine *N*-oxide (PPNO) as additive. In this biphasic system, the pH value of the aqueous phase is of crucial importance: whereas at pH 5 the α-hydroxy ketone was formed in only 20% yield, at pH 13 the conversion was almost quantitative; under the latter conditions, also significantly higher ee values were obtained. Isoflavones, which possess an enol–ether functionality have also been successfully epoxidized by chiral Mn-catalysts (Scheme 11, lower equation) [34]. Enantioselectivities up to 92% ee were found, which depended on the substitution pattern. The low yields (22–39%) in this asymmetric epoxidation may be a consequence of incomplete conversion of the starting material due to the electron-poor double bond.

In the absence of an olefinic substrate, the reaction between the Mn(III)(salen) catalyst and an oxygen donor leads to Mn(IV) oxidants (Scheme 12), which have been detected by EPR spectroscopy [35]. Two different Mn(IV) complexes are involved, namely the ClOMn(IV) and the OMn(IV) species, whose formation depends on the counterion and the solvent. The ClOMn(IV) oxidant chlorinates subsequently added olefinic substrates, e.g. 1,2-dihydronaphthalene, through an electrophilic pathway to yield the 1,2-dichloro adduct and the chlorohydrin, whereas OMn (IV) epoxidizes through a radical pathway, as evidenced by the formation of isomerized *trans*-stilbene oxide from *cis*-stilbene. Nevertheless, under the usual Jacobsen–Katsuki conditions (all components present from the start), the OMn (IV)(salen) complexes play a minor role.

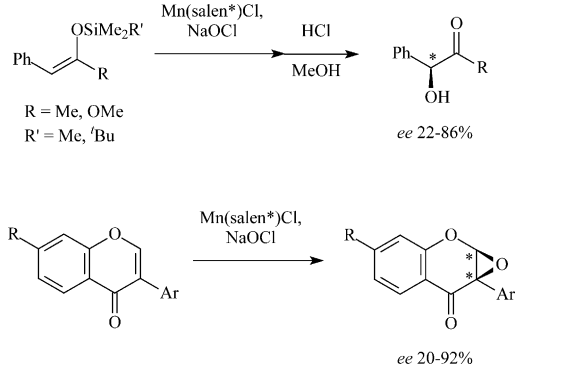
cis-Stilbene was also used as a mechanistic probe to investigate the influence of the oxygen donor O × D and of the counterion X of the Mn(salen)X catalyst on the *cis*–*trans* diastereoselectivity of the Mn-catalyzed epoxidation (Scheme 13); the *cis*–*trans* ratio ranged from 29:71 (extensive isomerization) to 92:8 (almost complete retention) [36]. The counterion effect was attributed to the computationally [37] assessed ligand-dependent reaction profiles and the distinct stereoselectivities of the singlet, triplet, and quintet spin states available to the manganese species. The dependence of the diastereoselectivity on the oxygen source was rationalized in

Table 8
Kinetic resolution of the allylic alcohols **1n**–**p** by Mn-catalyzed asymmetric epoxidation

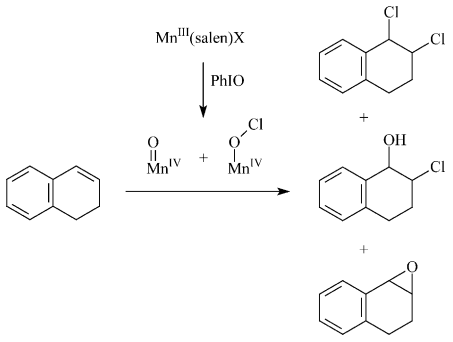


Entry	Substrate[a]	Convn (%)	Selectivities: Diastereo 2	Selectivities: Enantio (% *ee*) 1	Selectivities: Enantio (% *ee*) 2	k_{rel}[b]
1	 **1n**	41	>95: 5	53 (*S*)	69 (2*R*,3*S*,4*R*)[c]	12.5
2	 **1o**	48	93: 7	43 (*S*)	56 (1*S*,2*S*,3*R*)	4.1
3	 **1p**	38	92: 8	21 (*S*)	51 (2*R*,3*S*,4*S*)	2.5

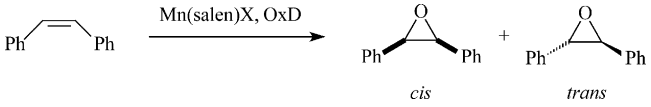
a) In the presence of 4-phenylpyridine *N*-oxide (PPNO); b) Calculated according to $k_{rel} = \frac{\ln(1-convn)[1-ee(2)]}{\ln(1-convn)[1+ee(2)]}$; c) 50:50 mixture of *cis*- and *trans*-epoxides **2n**, *ee* value of *cis*-



Scheme 11. Mn-catalyzed asymmetric epoxidation of enol ethers.



Scheme 12. Reactivity of Mn(IV) species.

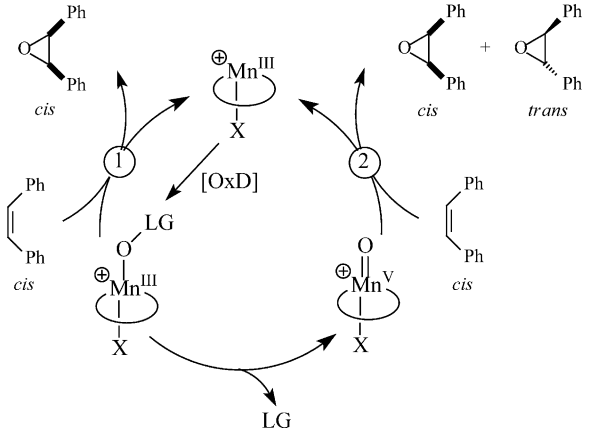


Scheme 13. Counterion and oxygen-donor effects on the *cis*–*trans* ratio in the Mn-catalyzed epoxidation of *cis*-stilbene.

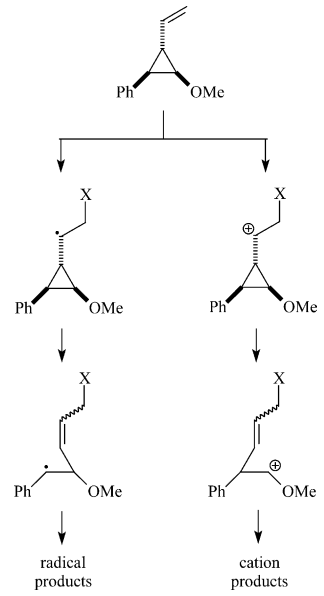
terms of a bifurcation step in the catalytic cycle, in which concerted Lewis-acid-activated oxygen transfer (Scheme 14, path 1) competes with stepwise epoxidation by the established Mn(V)(oxo) species (path 2). The participation of a radical intermediate in the isomerization step was established by the use of (1α,2β,3α)-(2-ethenyl-3-methoxycyclopropyl)benzene (Scheme 15), whose oxidation products allow to differentiate between radical and cationic intermediates [36]. When this mechanistic probe was used as a substrate for the Mn-catalyzed oxidation, no cationic ring-opened products were found and, thus, it was concluded that the isomerized epoxide arises from intermediary radicals.

4.2. CH oxidation

Whereas Mn(salen) complexes catalyze the epoxidation of allylic alcohols (Table 7), allylically activated CH bonds are chemoselectively oxidized by Cr(salen)X–



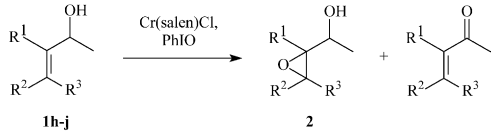
Scheme 14. Catalytic cycle for the Mn(III)-catalyzed epoxidation of *cis*-stilbene by Lewis-acid activation (Path 1) vs. the Mn(V)(oxo) species (Path 2).



Scheme 15. Vinylcyclopropane as mechanistic probe to distinguish between radical and cation intermediates.

PhIO to the corresponding carbonyl compounds (Table 9) [38a]. Thus, the disubstituted allylic alcohols **1h** and **1i** afforded the respective enones exclusively (entries 1 and 2). For allylic alcohols with an increasing number of substituents, the chemoselectivity drops significantly, i.e. the Cr-catalyzed oxidation of the tetrasubstituted substrate **1q** yielded a 52:48 mixture of epoxide **2q** and 3,4-dimethyl-3-penten-2-one (entry 4). Evidently, increased methyl substitution provide a more electron-rich CC double bonds, which promotes epoxidation sufficiently to compete with the usually preferred CH insertion. In

Table 9
Chemoselectivites in the Cr-catalyzed oxidation of the allylic alcohols **1h–j,q**



Entry	Substrate[a]	Epoxide **2** : Enone[b]
1	 **1h**	< 5:95
2	 **1i**	< 5:95 (61:39)
3	 **1j**	30:70 (70:30)
4	 **1q**	52:48

a) In the presence of 4-phenylpyridine *N*-oxide (PPNO).

b) In brackets are given the *cis*/*trans* ratios of enone

the oxidation of the *Z*-configured alcohols **1i** and **1j**, *cis*/*trans* isomerization of the resulting enones was observed (entries 2 and 3). The importance of hydrogen bonding between the substrate and the catalytically active Cr(V)(oxo) species is expressed by the fact that hydroxy-protected derivatives of the allylic substrates were not oxidized under these reaction conditions.

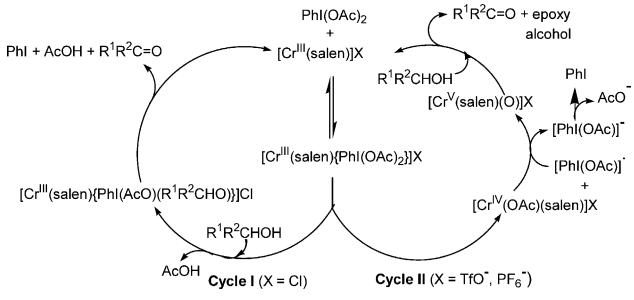
When the readily available iodosobenzene diacetate [PhI(OAc)$_2$] instead of iodosobenzene (PhIO) was used as oxygen donor in the Cr-catalyzed oxidation [38b], even trisubstituted allylic alcohols gave essentially exclusively the corresponding α,β-unsaturated carbonyl products. As could be shown for cinnamyl alcohol as a model substrate, the counterion of the Cr(salen)X catalyst has a marked influence on the chemoselectivity (Scheme 16): for Cl^- as counterion, exclusive CH oxidation was observed, whereas for TfO^- and PF_6^- equal amounts of epoxide **2** and enone were formed. This counterion-dependent oxidation of allylic alcohols by Cr complexes was rationalized in terms of Lewis-acid catalysis by Cr(salen)Cl (cycle I) and redox catalysis for Cr(salen)OTf and Cr(salen)PF$_6$ (cycle II).

5. Ligand-sphere oxidation in metal complexes

Whereas all previous examples dealt with catalytic metal-assisted oxygen-transfer reactions by various oxygen donors, the subject of this section concerns stoichiometric ligand-sphere oxidation by the mild and selective reagent DMD. In particular, we present our efforts on the oxygen transfer to the ligands bound to the metal center, which includes epoxidations, heteroatom oxidations and SiH insertions.

5.1. Epoxidation

Control of regioselectivity is an often encountered difficulty during the oxyfunctionalization of polyenes. Such problems may be overcome by the use of the tricarbonyliron fragment Fe(CO)$_3$ as protecting group, which is illustrated for 5-(4-methyl-3-pentenyl)-1,3-cyclohexadiene as substrate (Scheme 17) [39]. Whereas the diene moiety is coordinated to the metal and, thus, not attacked by DMD, the remote isolated double bond is readily oxidized to the corresponding epoxide. After oxidative removal of the iron fragment by cerium ammonium nitrate (CAN), 3-[2-(2,4-cyclohexadien-1-yl)ethyl]-2,2-dimethyloxirane is obtained as the only regioisomer. Unfortunately, the metal-protecting group is too far away from the reaction center to exercise stereochemical control and, therefore, the product is a 50:50 mixture of both diastereomers.

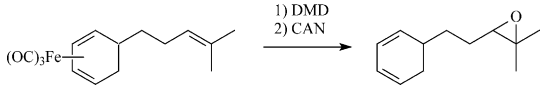


Scheme 16. Counterion-dependent oxidation of allylic alcohols by Cr(salen)X.

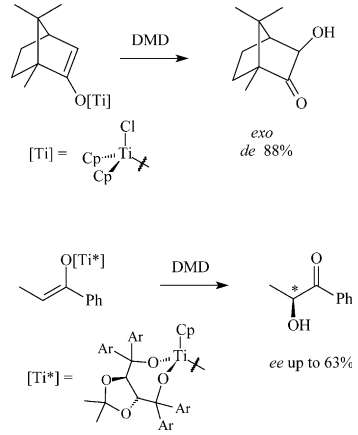
Besides the already mentioned asymmetric epoxidation of prochiral enolates (cf. Section 4.1), the diastereoselective epoxidation of chiral enolates is the method of choice for the preparation of optically active α-hydroxy carbonyl compounds (Scheme 18) [40]. When the camphor enolates were employed (upper equation) [40b], asymmetric induction by the chirality centers in the starting ketone delivered on aqueous workup the *exo*-3-hydroxycamphor as the major product. The diastereoselectivity of this epoxidation depends on the metal to which the enolate is bound: best results have been achieved for the chlorotitanocene enolate depicted in Scheme 18 (88% de), whereas the corresponding lithium enolate exhibits only a moderate devalue (52% de). In the case of α-hydroxy propiophenone (lower equation), the optically active auxiliary derived from TADDOL was employed 40a. In this way, selectivities of up to 63% ee have been obtained in the diastereoselective epoxidation of such a chiral enolate.

5.2. Heteroatom (P, S) oxidation

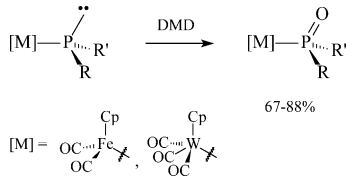
DMD readily oxidizes heteroatoms (phosphorous, sulfur), which are coordinated to a metal center. For



Scheme 17. Regioselective epoxidation of iron-tricarbonyl-protected trienes by DMD.



Scheme 18. Epoxidation of Ti enolates by DMD.

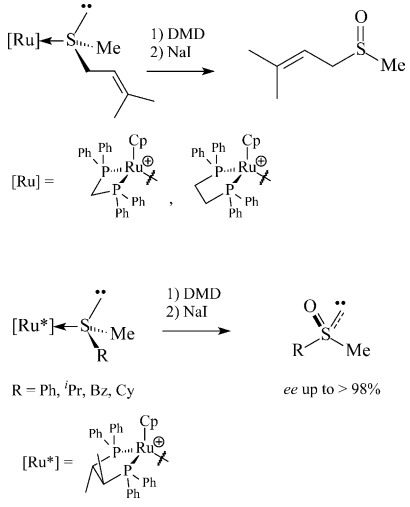


Scheme 19. Oxidation of metallaphosphines by DMD.

instance, metallo phosphines of iron and tungsten are readily converted at −78 °C to the corresponding metallo phosphine oxides in good yields (67–88%, Scheme 19) [41].

This lone-pair oxidation occurs chemoselectively, since insertion of the oxygen atom into the PH bond (cf. SiH oxidation) of the substrate was not observed.

Upon ligation of a sulfide to a metal center, expectedly, the nucleophilicity of its sulfur atom is decreased, but sulfoxidation still takes place in preference to epoxidation. Thus, when the ruthenium complexes of an allyl thioether was treated with DMD (Scheme 20, upper equation), heteroatom oxidation occurred predominantly to afford the corresponding allyl sulfoxides chemoselectively [42a]. However, when a large excess of the oxidant was employed, double oxidation took place and the corresponding epoxy sulfoxide was isolated. For asymmetric sulfoxidation, the sulfide was attached to the optically active CpRu(CHIRAPHOS) metal fragment (Scheme 20, lower equation) [42b,42c]. The subsequent DMD oxidation was highly diastereoselective and yielded the corresponding sulfoxide complexes in almost quantitative yield. Release of the optically active sulfoxide from the metal complexes with sodium iodide in acetone, afforded the product with ee-values up to > 98%.



Scheme 20. Sulfoxidation in ruthenium complexes by DMD.

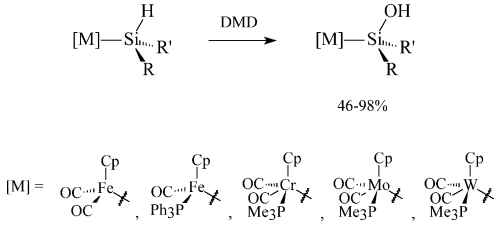
5.3. SiH oxidation

For the synthesis of ferriosilanols from ferriosilanes without the formation of the disiloxane side products, the mild and selective oxidant DMD is the reagent of choice (Scheme 21) [43].

After purification by silica-gel chromatography, the metallo silanols were obtained in moderate to excellent yields (46–98%). The SiH oxidation proceeds stereoselectively with retention of configuration, as was established for the diastereomerically pure ferriosilanol (*R**,*S**)-Cp(OC)(Ph_3P)Fe–SiH(Me)(Ph). This stereochemical course is in accordance with the results achieved for the previously mentioned α-naphthylphenylmethylsilane (*S*)-(α-Np)PhMeSiH (cf. Section 3.4) [43c]. Other metallo silanols with chromium, molybdenum or tungsten fragments have been prepared by the same method; for tungsten silanols, a catalytic pathway has been developed with MTO–UHP as oxidant [44].

6. Conclusion

The present account conveys the importance of metal-catalyzed oxidations for the selective oxyfunctionalization of organic substrates under catalytic conditions. The synthetic value of the three catalytic oxidation systems addressed herein, namely the Sharpless–Katsuki (peroxy type), the Herrmann (peroxo type) and the Jacobsen–Katsuki (oxo type) reactions, is uncontested in regard to convenience, efficiency, and selectivity. A variety of substrates may be oxidized, they include substances with π-bonds, lone pairs and σ-bonds. Therewith, a broad spectrum of differently oxyfunctionalized building blocks are made available for organic synthesis. The choice of the transition metal allows to control chemoselectivity; a case in point is allylic alcohols, for which exclusive epoxidation occurs with manganese versus exclusive allylic oxidation by chromium-oxo complexes. However, the problem of chemoselectivity has as yet not been generally solved for substrates with several functionalities. Many experimental and theoretical efforts will be essential to understand the complexities of the oxygen-transfer process mediated by transition-metal catalysts. In this context, our work has been focussed on gaining mechanistic insight in this



Scheme 21. Oxidation of metallasilanes by DMD.

challenging area of chemistry, in the interest to develop still more efficacious and selective transition-metal-catalyzed oxidation processes.

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