

Chemical Reviews

Volume 89, Number 3

May 1989

Transition-Metal-Catalyzed Epoxidations

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Received March 21, 1988 (Revised Manuscript Received August 2, 1988)

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"Not every collision,
not every punctilious trajectory
by which billiard-ball complexes
arrive at their calculable meeting places
leads to reaction.

Most encounters end in
a harmless sideways swipe.
An exchange of momentum,
a mere deflection"¹

I. Introduction

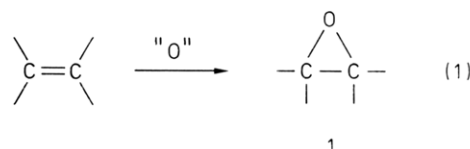
The direct oxidation of hydrocarbons is a field of both academic and industrial importance and challenge.



Karl Anker Jørgensen was born in Aarhus, Denmark, 1955, and is a graduate of Aarhus University (1984). He did his postdoctoral work with Roald Hoffmann, Cornell University (1985), and is now adjunct at Aarhus University. His research interests are mainly in the area of organic and organometallic chemistry.

Catalysis by metal complexes plays a central role in the selective, partial oxidation of both saturated and unsaturated hydrocarbons to useful products.

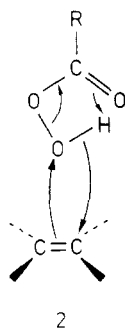
Epoxidation reaction 1 is an important reaction in



organic synthesis because the formed epoxides **1** are intermediates that can be converted to a variety of products. Reaction 1 is also attractive in asymmetric cases since it can lead to two chiral carbons in one step.

Epoxidation by peracids has been known for almost 80 years and has found great use.²⁻⁴ The rate of epoxidation by peracids is not very sensitive to steric hindrance, but is sensitive to electronic changes; increasing the electron density of the alkene or decreasing that of the peracid increases the reaction rate.⁵ These observations indicate that the oxygen transferred in **2** is of electrophilic character. Based on both experimental and theoretical investigations, a mechanism in

which the peroxygen distal to the carbonyl group of the peracid interacts with the alkene is most likely to be involved (2), but other mechanisms have also been suggested.⁵



The use of transition-metal complexes as catalysts for (1) has received increased attention during the past 2 decades. There are many reasons for this increased interest: e.g., the requirement for functionalization of lower alkenes formed as byproducts in the manufacture of gasoline by gas oil cracking, the interest in understanding reactions of biological importance, the need for partial selective oxidation, and the preparation of compounds with a specific spatial structure.

The transition-metal complexes seem to fulfill some of these requirements, and today many different systems are available that can utilize a variety of oxygen sources for the epoxidation reaction.

The present review will try to cover transition-metal-catalyzed epoxidations starting with the group IV transition metals (Ti, Zr, Hf) and ending with group I transition metals (Cu, Ag, Au). The following topics pertaining to catalysts are discussed: (a) transition-metal ions, (b) transition-metal-oxo and -peroxo complexes, (c) organotransition-metal complexes (including clusters), and (d) transition-metal surfaces.

The application of the different systems a-d as catalysts for alkene epoxidation from both a practical and mechanistic point of view is presented. The mechanisms suggested for the oxygen-transfer step are discussed, and attempts to present a more coherent picture, hopefully leading to a better understanding of these reactions, are made.

II. Ti, Zr, and Hf

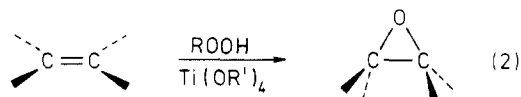
1. Ti

Although the reaction of titanium(IV) with an oxidation reagent (hydrogen peroxide) has been known for more than 100 years,⁶ the use of titanium(IV) as catalyst for epoxidation is not more than about 20 years old. Titanium(IV) alkoxides, while not the most effective epoxidation catalysts, promote the reaction of alkenes with alkyl peroxides in high yield and with high selectivity. The titanium(IV) catalysts catalyze reactions with a variety of different alkenes ranging from low molecular weight alkenes to large molecules including alkenes of biological interest.

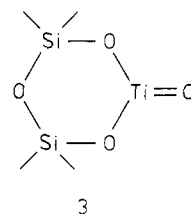
Titanium(IV) catalysts, like other good epoxidation catalysts such as vanadium(V), molybdenum(VI), and tungsten(VI), are characterized as being Lewis acids in their highest oxidation state -d⁰. These Lewis acids have a low redox potential^{7,8} and are labile with respect to ligand substitution.⁹⁻¹¹ Transition-metal complexes

in a high oxidation state, such as those of titanium(IV), vanadium(V), molybdenum(VI), and tungsten(VI), can facilitate the heterolysis of alkyl peroxides and of hydrogen peroxide by forming complexes analogous to the inorganic peracids formed with hydrogen peroxide. For synthetic purposes, these transition metal-alkyl hydroperoxide reagents are of more utility than the analogous transition metal-hydrogen peroxide reagents by virtue of their solubility in nonpolar solvents.^{7,8}

Titanium(IV) alkoxides catalyze the epoxidation of a variety of alkenes with an alkyl hydroperoxide as the oxygen donor:^{7,8,12-15}



The reaction is relatively slow and byproducts formed by addition of *tert*-butyl peroxide radicals to the substrate are often observed.¹³ These problems have been overcome by the development of a heterogeneous titanium(IV)-silicon dioxide catalyst.^{14,16} The catalyst is prepared by impregnating silica with TiCl₄ or an organotitanium compound, followed by calcination. The titanium(IV)-silicon dioxide catalyst is unique in that it is highly active, and its action is truly heterogeneous.^{14,17} It has been claimed that propylene is oxidized to propylene oxide in 93-94% yield at 96% ethyl hydroperoxide conversion.¹⁶ The combination of titanium(IV) with silicon dioxide seems to provide the right stereochemical and electronic environment for coordination of the hydroperoxide and subsequent oxygen transfer to the alkene.^{13,14} The structure of the active site has been suggested to be^{8,13,14}

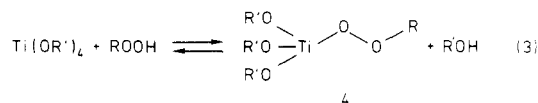


The function of the silicate ligands is to increase the Lewis acidity of titanium(IV), and they may also stabilize the titanil (Ti=O) group by retarding polymerization, which is characteristic of titanil complexes.⁸

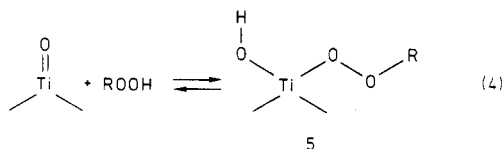
Investigations of substituent effects indicate that the active epoxidation reagent is an electrophilic species.

In the case of titanium(IV)-catalyzed epoxidations with alkyl or hydrogen peroxide as the oxygen donor very little information is available about the reaction mechanism, and it might here be useful to use the results from other d⁰ transition-metal-catalyzed epoxidations.¹⁸

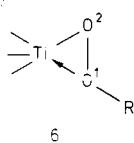
The first step in the titanium(IV)-catalyzed epoxidation using, e.g., titanium(IV) alkoxides or the titanium(IV)-silicon dioxide catalyst 3 with peroxides is the conversion of the peroxide to a peroxo-metal intermediate. For titanium(IV) alkoxides this reaction leads to an exchange of one of the alkoxide ligands by the peroxide, giving 4:^{8,18}



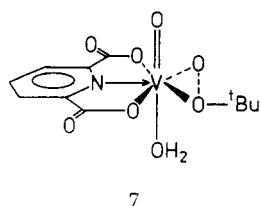
However, the titanyl complex **3** might react by the following pathway:⁸



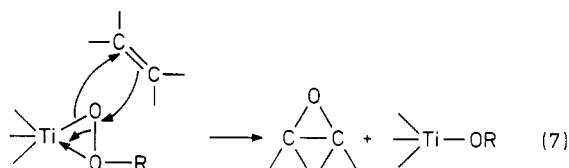
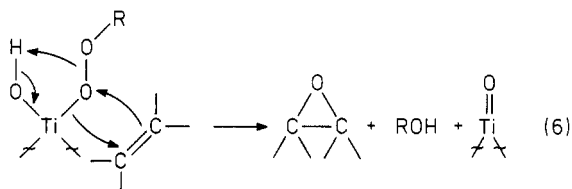
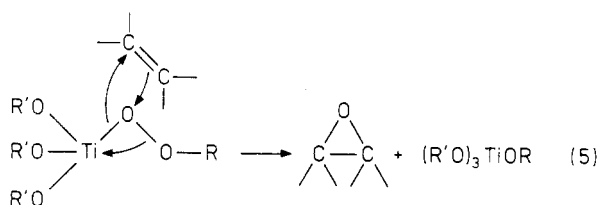
The exact structures of **4** and **5** are unknown, but from vanadium- and molybdenum-catalyzed epoxidations evidence has been provided through ¹⁸O-labeling studies that the alkyl peroxide remains intact during the reaction,¹⁸ and it might be expected that the alkyl peroxide behaves in a similar way with titanium(IV). The binding of the alkyl or hydrogen peroxide to titanium(IV) in **4** and **5** takes place via the terminal oxygen, but the other oxygen might also be involved in the coordination to titanium, leading to a bidentate coordinated titanium peroxide complex, **6**. An O-O-



bound d⁰ peroxy complex such as **6** has recently been found in a (dipic)VO(OO-*t*-Bu)H₂O complex, **7**.¹⁹ (We will return to **7** later.)



The coordination of the peroxide to titanium(IV) as depicted in **4**–**6** leads thus to an activation of the peroxide for oxygen transfer, and the following three mechanisms have been suggested:^{8,13,14,18}



A fourth type of mechanism involving an intramolecular nucleophilic attack of a transition metal-alkylperoxy ligand on a coordinated alkene **8** has also been suggested;²⁰ this mechanism proceeds via a qua-

SCHEME 1

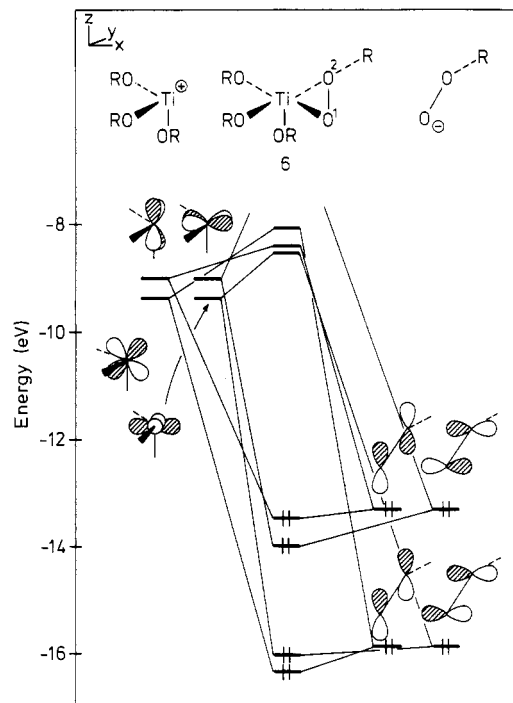
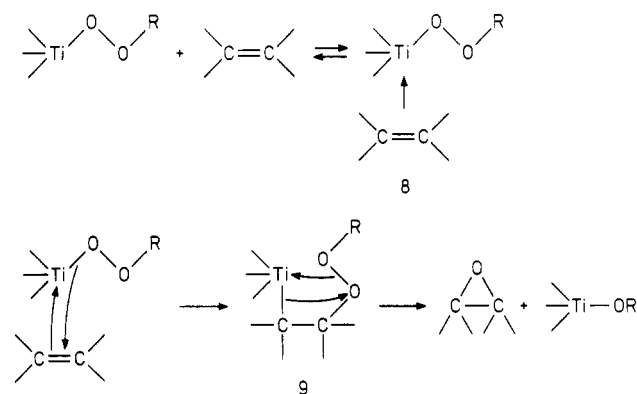


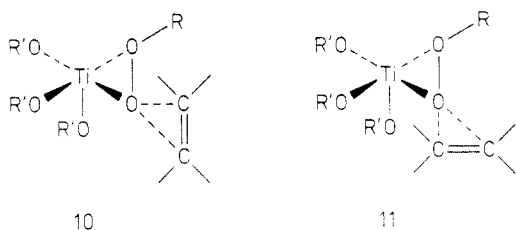
Figure 1. Interaction diagram for the formation of a bidentate coordinated alkyl peroxide ligand to titanium trialkoxide (**6**) from titanium trialkoxide and alkyl peroxide.

si-peroxometallacyclic intermediate **9** as outlined in Scheme 1 (a more general discussion of peroxometallacycles as intermediates in transition-metal-catalyzed epoxidations is presented later).

The interaction of a d⁰ transition metal with a peroxide has been described from a theoretical point of view in an attempt to understand the oxygen transfer from the transition metal-peroxy complex to an alkene.^{21–24} A schematic representation of the interaction of the frontier orbitals of an alkyl peroxide ligand with titanium(IV) trialkoxide, leading to the active catalyst shown as **6**, is depicted in Figure 1.²⁵

To the right in Figure 1 are the frontier orbitals of the alkyl peroxide fragment, and to the left those of the titanium(IV) trialkoxide fragment. In the middle is the titanium(IV)-alkyl peroxide complex, **6**. The alkyl peroxide orbitals of p_x character, antibonding and bonding between the two peroxygens, respectively, interact with the titanium d_{xy} and d_{x²-y²} orbitals, respectively, and the alkylperoxy p_z orbitals of similar symmetry interact with d_{yz} and d_{xz}.^{21–25} The HOMO of **6** is mainly p_z at the peroxygens and antibonding between the two peroxygens; the second HOMO is mainly of p_x

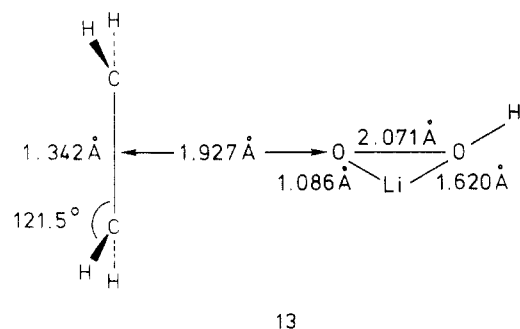
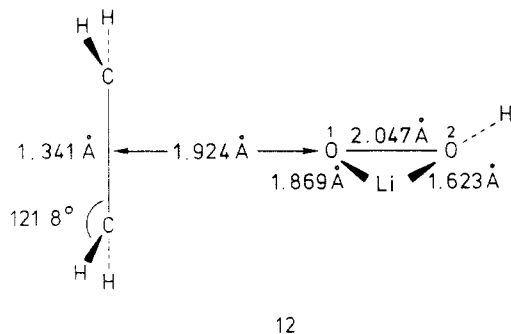
character at the peroxygens and also antibonding between two peroxygens. The LUMO of **6** is mainly of p_y character at the peroxygens and antibonding (not shown in Figure 1) with the largest amplitude at peroxygen 1, making this oxygen electrophilic. The frontier orbitals of **6** lead to the following interaction possibilities with an alkene:²¹⁻²⁵



The orientation of the alkene in **10** corresponds to a spiro orientation relative to the titanium-peroxide plane whereas the orientation in **11** is planar.

The interaction in **10** takes place mainly between the π orbital of the alkene and the LUMO of **6** and between the π^* orbital of the alkene and the HOMO of **6**. In the case of **11**, the π orbital of the alkene interacts in a similar way as in **9**, but the π^* orbital of the alkene interacts here with the second HOMO of **6**.

Detailed ab initio calculations have been performed in an attempt to understand the mechanism for the oxygen transfer from LiOOH, which was used as a model for **6**, to ethylene.²² The calculated (basis set 4-31G) activation energies for oxygen transfer from LiOOH to ethylene for a spiro (**12**) and planar (**13**) orientation were 22.8 and 23.6 kcal·mol⁻¹, respectively. The two transition states are shown in **12** and **13**:²²

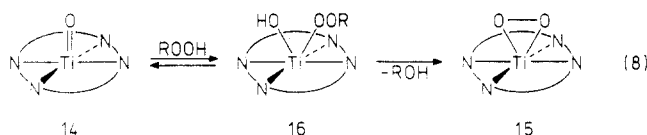


The two transition states **12** and **13** are very similar; the only difference is the orientation of the alkene.²² The alkene performs a nucleophilic attack on the "electrophilic oxygen", 0.22 electron having been transferred from ethylene to the peroxide fragment.²² As the alkene attacks the peroxygen the flow of electron density into the region between O-2 and the metal leads to a decrease in bond length between these two atoms, whereas the increase of the electron density at O-1 leads

to an increase in the bond length between the transition metal and O-1.²² In the transition states **12** and **13** the peroxy bond has been elongated by about 30% relative to the peroxygen bond in the lithium-peroxy species.²²

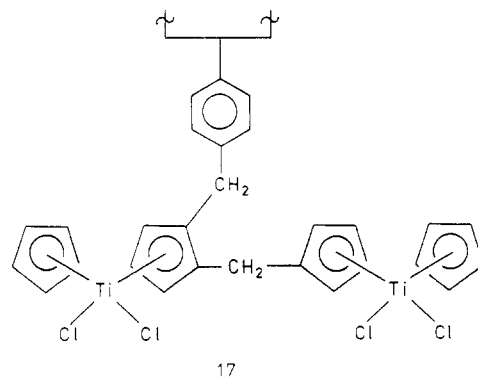
A nearly similar picture emerges for the oxygen transfer from titanium(IV)-alkylperoxy complexes to alkenes using extended-Hückel calculations.^{24,25} The theoretical calculations seem then to support a mechanism for the oxygen transfer from titanium(IV)-peroxy complexes to alkenes as suggested experimentally and shown in (7).

Titanium dioxide,¹³ oxotitanium diacetylacetonate,¹³ and oxotitanium porphyrin²⁶ have also been used as catalysts for epoxidations with TBHP as oxygen donor, but the catalytic properties of these complexes are not as good as those of the silicon dioxide supported titanil derivatives.¹²⁻¹⁴ When oxotitanium porphyrin (**14**) was used as catalyst, the peroxotitanium porphyrin (**15**) was formed during the epoxidation (8).^{26,27} The peroxy-



titanium porphyrin **15** was, on the other hand, found to be unreactive toward alkenes.^{26,28} The reason for the unreactive peroxotitanium porphyrin **15** might be that it is not possible for the alkene to interact with one of the peroxygens, as outlined in **12** or **13**, because of steric repulsion between the porphyrin ring and the alkene. It has been suggested that it is the *cis*-hydroxy(alkylperoxy)titanium porphyrin **16** that is most likely to be involved in the reaction of **14** and that it is **16** which is acting as the active catalyst.^{26,28} However, photochemical irradiation of **15** in the presence of cyclohexene produced a mixture of oxidized products, one of which was cyclohexene oxide.²⁹

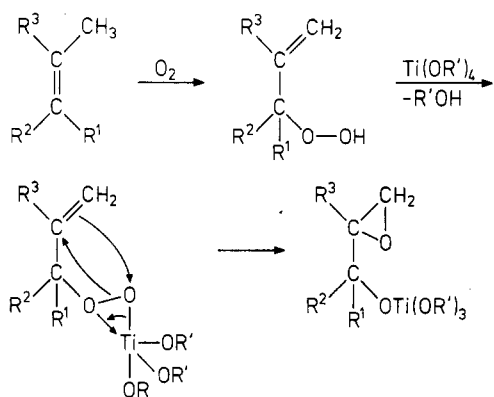
Polymer-supported TiCp₂Cl₂ (**17**) and TiCpCl₃ can also be used as catalysts for epoxidations.³⁰ TBHP



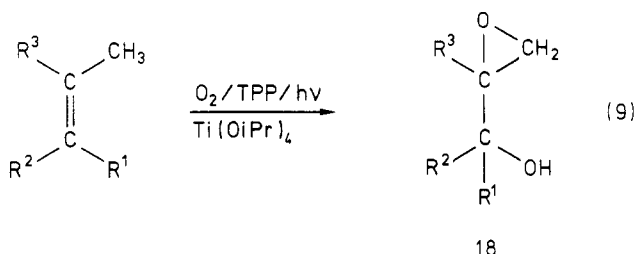
reacts with alkenes in the presence of **17** or polymer-supported TiCpCl₃ to give the corresponding epoxides. Polymer-supported TiCpCl₃ was found to act as a better catalyst than polymer-supported TiCp₂Cl₂, and yields of epoxides up to 88% have been reported.³⁰

Molecular oxygen can also be used as an oxygen source for titanium(IV)-catalyzed epoxidations of alkenes:^{31,32} The ene reaction of singlet oxygen with alkenes in the presence of titanium(IV) alkoxides has

SCHEME 2



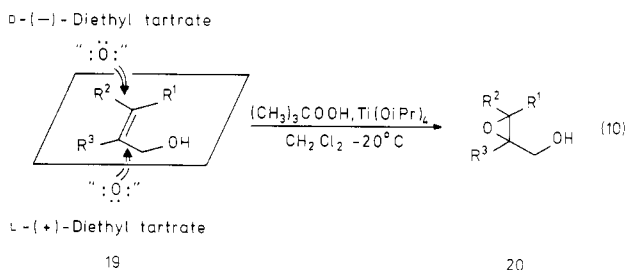
been used to prepare epoxy alcohols **18** with high diastereoselectivity:



The mechanism for (9) might be as shown in Scheme 2.³²

The epoxidation of allylic alcohols with TBHP mediated by titanium(IV) tetraisopropoxide leads to the *syn*-epoxy alcohols, whereas epoxidation of the same allylic alcohols with MCPBA affords largely the *anti*-epoxy alcohols.³³

Probably the best known group IV transition-metal-catalyzed reaction is the treatment of a mixture of commercially available titanium(IV) tetraisopropoxide, TBHP, and (+)- or (-)-diethyl tartrate with allylic alcohols under formation of the epoxy alcohols **20** with high ee (reaction 10).³⁴⁻⁴³ This asymmetric ep-



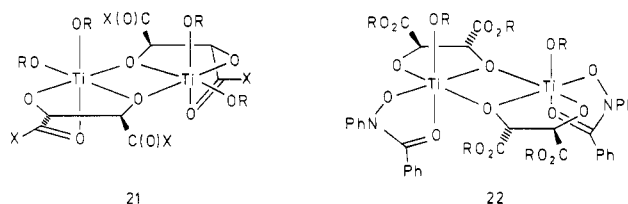
oxidation, now known as the Sharpless epoxidation, has already shown its power in the synthesis of, e.g., natural products.⁴⁴ With (-)-diethyl tartrate the oxidant approaches the allylic alcohol from the top plane shown in **19** whereas the bottom side is accessible to the (+)-diethyl tartrate reagent, giving rise to the corresponding optically active epoxy alcohols **20**.

Hydroperoxides other than TBHP can also be used in the asymmetric epoxidation reaction.⁴¹ It has been found that tartrate esters and amides are the most effective ligands for the asymmetric epoxidation of allylic alcohols.^{41,45} A variety of allylic alcohols have been oxidized successfully under asymmetric conditions to the corresponding asymmetric epoxy alcohols.³⁴⁻⁴⁴ The allylic alcohols that react slowly and with poor ee are, e.g., some *cis*-allylic alcohols and a few severely hindered

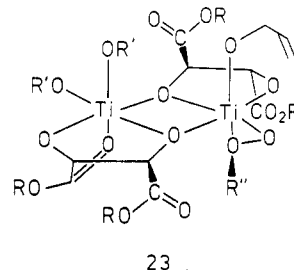
molecules of other substitution types; other poor substrates are those that are epoxidized at a rapid rate and with high selectivity, but yield epoxy alcohols that are unstable under the reaction conditions.⁴¹ It has been found that electron-withdrawing groups attached to the alkene decrease the rate of epoxidation while electron-donating groups increase the rate³⁵—these substrate reactivities are similar to those mentioned earlier for other titanium(IV)-catalyzed epoxidations. The asymmetric epoxidation of allylic alcohols depicted in (10) is a relatively slow reaction, but the reaction time can be reduced by the presence of metal hydride and silica gel.⁴⁶ The presence of 3–4-Å molecular sieves under the asymmetric epoxidation conditions has been found to increase the enantioselectivity of the reaction.^{42,43}

Tartrate esters have been attached to a polymeric support to provide a heterogeneous titanium–tartrate catalyst.⁴⁷ The enantioselectivity of the heterogeneous system is lower than that of the homogeneous system, but the polymer seems to be reusable several times before it loses its activity.

The structures of several catalytically active titanium–tartrate complexes have been determined by X-ray crystallographic investigations.^{41,48} The titanium–tartrate complexes are at least dimeric,^{41,48} and the structures of two of those are shown in **21** and **22**.



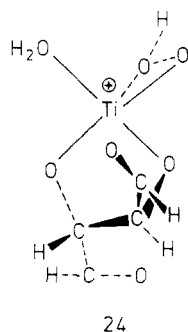
With these structures in hand attempts have been made to explain the mechanism of these asymmetric epoxidations from both an experimental⁴¹ and a theoretical point^{22,24} of view. It has been suggested that the axial and equatorial ligands in **21** undergo exchange with a bidentate coordinated peroxide and that the axially coordinated carbonyl is released from the titanium center and substituted by the allylic alcohol.⁴¹ A model in which the peroxide bond is nearly perpendicular to the equatorial plane appears to be the least crowded one, resulting in a linear alignment of allylic alkoxide and peroxide oxygen atoms and a roughly octahedral titanium coordination geometry as shown in **23**.⁴¹ Based on **23** a transition state has been suggested that explains the reaction course.⁴¹



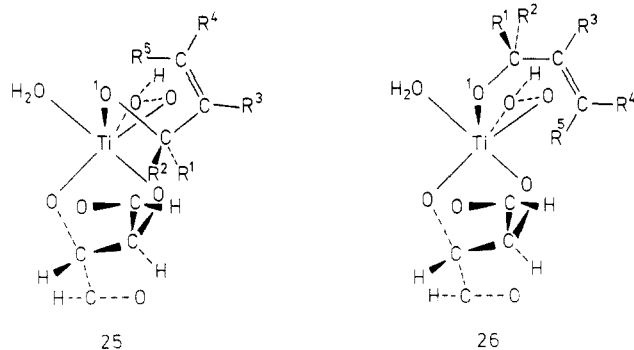
The theoretical approach to the mechanism for the titanium–tartrate catalyzed asymmetric epoxidation of allylic alcohols (reaction 10) has involved both *ab initio*²² and extended-Hückel calculations.²⁴ In the *ab initio* study LiOOH was used as a model for the titanium–tartrate system without taking the tartrate moiety into account.²² When the orientation of the allylic alcohol

around the peroxygens was varied, no electronic origin for the high enantioselectivity observed in the reaction was found. It was then concluded that steric effects associated with the three-dimensional chiral nature of the catalyst are largely responsible for the transfer of the oxygen to a specific enantioface of the allylic alcohol.²²

In the extended-Hückel investigation of (10) the electronic structure of the titanium-tartrate catalysts was studied.²⁴ It was found that the coordination of one tartrate carbonyl moiety to the axial position of the titanium atom leads to a preference of the other tartrate group to coordinate trans to the titanium-coordinated carbonyl group, leaving two vacant sites for a bidentate coordination of the peroxide.²⁴ The most stable bidentate coordination of the peroxide to this complex is shown in **24** (H_2O is used as model for the other tartrate moiety). The interaction of the peroxy group



with titanium-tartrate generates a set of orbitals of the peroxide fragments like those discussed in relation to Figure 1. The frontier orbitals of the titanium-tartrate-peroxide-allylic alcohol complex lead to the following transition states for the epoxidation.²⁴

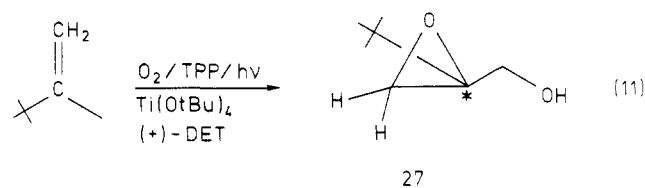


The interaction of the alkene part of the allylic alcohol and the peroxide part of **25** and **26** is very similar to the interaction outlined earlier for the epoxidation of alkenes with titanium(IV) peroxides. For both steric and electronic reasons **26** was found to be the most probable transition state, and the reaction mechanism outlined on the basis of extended-Hückel calculations was in good agreement with the one suggested on the basis of the experimental results.²⁴

Homoallylic alcohols can also undergo asymmetric epoxidation by TBHP using the titanium-tartrate complex as catalyst,⁴⁹ but the homoallylic alcohols react more sluggishly and with poorer yield and enantioselectivity than the corresponding allylic alcohols. The enantiofacial selection rule for homoallylic alcohols is opposite to that for allylic alcohols.⁴⁹

In the presence of diethyl tartrate (DET) as chiral auxiliary under the reaction shown in (9) an ee of the

epoxy alcohol is also obtained:³¹



Using (10) for the preparation of **27** gave a lower yield of the epoxy alcohol than the photochemical procedure (11), but the ee for the latter was found to be less (72%) than with TBHP as the oxygen donor (85%).³¹

Titanium carbide and boride (TiC and TiB_2) can catalyze the epoxidation of styrene with molecular oxygen as the oxygen donor.⁵⁰ Titanium dioxide was found to be inert in this reaction.⁵⁰

2. Zr and Hf

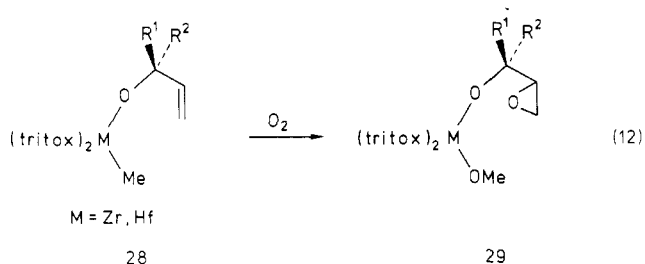
Much of the work done in the field of zirconium(IV)- and hafnium(IV)-catalyzed epoxidations is parallel to work done with titanium(IV) as catalyst, but when TBHP is used as oxygen donor, the general trend is that lower yields of the epoxides are obtained.

Zirconium(IV) alkoxides catalyze the epoxidation of, e.g., cyclohexene with TBHP, but the yield of cyclohexene oxide is <10%, compared with the 66% yield when the corresponding titanium(IV) alkoxide is used as catalyst.¹³ The major product in this reaction is (*tert*-butylperoxy)cyclohexene (60%). Similar results are obtained with other zirconium(IV) complexes.¹³

Polymer-attached zirconocene and hafnocene chlorides, which are similar to the polymer-supported titanocene chlorides **17** have also been tested as catalysts for epoxidation, but their activities are lower than those of the attached titanocene chlorides.⁵¹

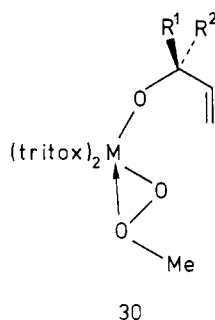
Zirconium(IV) and hafnium(V) alkoxides, dicyclohexyltartramide, and TBHP have also been used for the asymmetric epoxidation of homoallylic alcohols.⁵² The reason for choosing zirconium and hafnium as catalysts was the desire to reduce the steric repulsion in the homoallylic alcohol in the transition state because the metal-oxygen bonds in these systems are longer than in the similar titanium systems, and thus less steric interaction could be anticipated.⁵² The zirconium catalysts were the most effective, but showed the same sense of asymmetric induction as titanium.⁵² One hafnium and tantalum catalyst exhibited, under similar conditions, poor asymmetric induction.⁵²

Both zirconium and hafnium complexes are able to use molecular oxygen as the oxygen donor for epoxidation.^{53,54} Treatment of the (*tritox*)₂M(Me)(allylic alcohol) ($\text{M} = \text{Zr}, \text{Hf}$) complex **28** with molecular oxygen leads to epoxidation.⁵⁴ It has been suggested that



molecular oxygen is activated by the metal and inserted

into the transition metal–methyl bond, leading to a bidentate coordinated methyl peroxide complex **30**,



which then epoxidizes the attached alkene in a similar way as, e.g., TBHP coordinated to a d^0 transition metal.⁵⁴ The link between molecular oxygen activation and insertion into the transition metal–methyl bond in **28** and the epoxidation was established by the observation that $(\text{triox})_2\text{ZrCl}(\text{OCMe}_2\text{CH}=\text{CH}_2)$ reacts with sodium *tert*-butyl peroxide, which leads to the epoxidation of the attached alkene.⁵⁴

III. V, Nb, and Ta

1. V

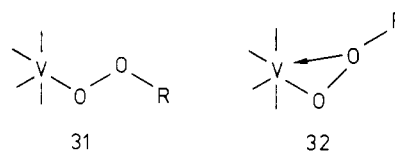
Vanadium pentoxide was probably one of the first transition-metal complexes used for catalytic epoxidation with TBHP as oxidant.⁵⁵ But now both vanadium pentoxide and several oxovanadium–ligand complexes have been studied as catalysts for alkene epoxidation.^{7,8,12–15,55–60} Vanadium(V) has been found to be a relatively poor catalyst for alkene epoxidation compared with molybdenum catalysts.^{7,8,13,14,57} The molybdenum(VI)-catalyzed epoxidations are about 10^2 times faster than those catalyzed by vanadium(V),^{8,13,14,57} whereas with allylic alcohols vanadium(V) gives higher rates and better yields than molybdenum(VI).⁶¹ The catalytic order of reactivity of vanadium(V) is similar to the activity of titanium(IV). The stereochemistry of epoxidation reactions catalyzed by the oxovanadium–ligand complexes is dependent on the ligand present in the complex.^{19,58,59} If 2,6-pyridinedicarboxylate is present as ligand, **7**, *cis*-2-butene gives an approximately 3:1 mixture of the corresponding *cis*- and *trans*-epoxides,⁹ whereas with *N*-(2-hydroxyphenyl)salicylideneamine, a tridentate Schiff base, present as ligand, the epoxidation of *cis*-2-butene affords only *cis*-2,3-epoxybutane.⁵⁸

The oxovanadium ion has been incorporated into polymer resins.^{61–68} Among the complexes studied are insoluble polystyrene polymers containing oxovanadium attached to acetylacetone, ethylenediamine, pyridine, dithiocarbamate, aminodiacetic acid, and phosphonate methyl and hydroxymethyl ligands.^{61,64,67} The vanadyl ion has also been immobilized on sulfonated ion-exchange resins.⁶³ The catalytic activity of heterogeneous oxovanadium catalysts for alkene epoxidation using TBHP as oxygen donor is better than that of the homogeneous oxovanadium complexes. $\text{VO}(\text{acac})_2$, a homogeneous catalyst, promoted yields of cyclohexene oxide in the 10–12% range (based on the oxidant consumed), whereas vanadyl ion, bound to a polystyrene support through acetylacetonate or ethylenediamine ligands, gave yields of cyclohexene oxide up to 26%,

which is about a twofold increase compared with the homogeneous system.⁶² But with the vanadyl ion immobilized on the sulfonate ion-exchange resin, yields up to 74% of cyclohexene oxide were obtained.⁶³ Another major advantage of the heterogenized catalyst over the homogeneous counterpart is in the ease of recovery and reuse of the catalyst.⁶³ The incorporation of the oxovanadium ion into cross-linked polystyrene resins functionalized with iminodiacetic acid or diethylenetriamine derivatives affords a heterogeneous catalyst that can promote epoxidation of allylic alcohols in a highly stereoselective manner.^{66,67} A $(\mu_3\text{-oxo})\text{tri-vanadium hexacarboxylate complex } [\text{V}_3\text{O}(\text{O}_2\text{CR})_6(\text{H}_2\text{O})_3]^{n+}$ has also been attached to a polymer and has been found to have catalytic activity for the epoxidation of cyclohexene using TBHP as oxidant.⁶⁹

When TBHP is used as oxygen donor in connection with oxovanadium(V)-catalyzed epoxidations, ^{18}O -labeling studies reveal the existence of a peroxometal intermediate and favor a vanadium(V)–alkylperoxo complex as the reactive species.^{18,70}

There is until now one example of an oxovanadium(V)–alkyl peroxide complex, **7**, which possesses a triangularly bound *tert*-butyl peroxide group and has both equatorial adjacent positions occupied by the tridentate dipicolinate ligand.¹⁹ But oxovanadium(V)–alkylperoxo complexes have been suggested to be the active species in epoxidation reactions, with the alkyl peroxide ligand coordinated in a mono- (**31**) or in a bidentate fashion (**32**).^{13–15,18–21,56–60,70} The chemistry of the active catalyst

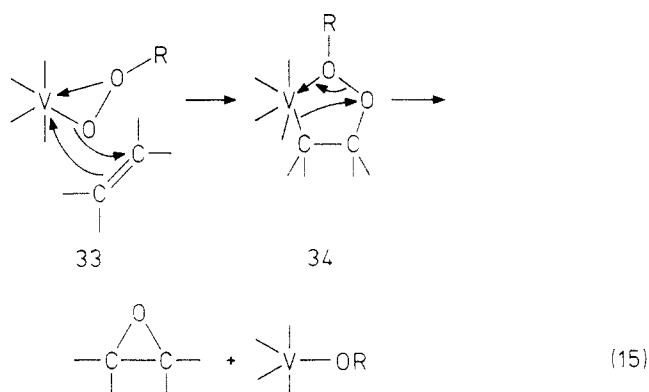
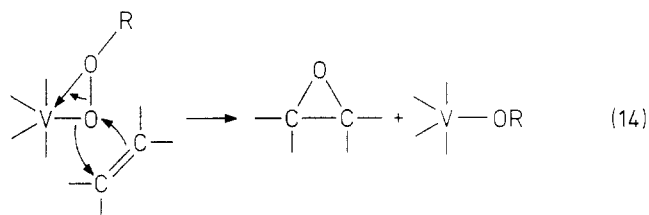
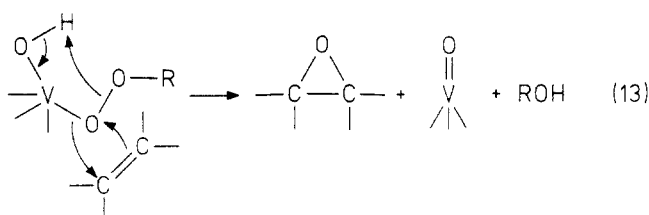


in the heterogeneous resin-bound vanadyl ion shows some similarities with the oxidation of the vanadyl ion by hydrogen peroxide,⁶³ but no conclusive results are available.

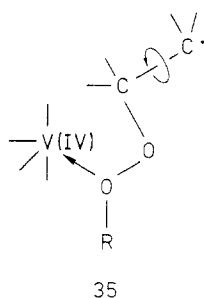
The transfer of the oxygen atom from vanadium alkyl peroxides as well as from other transition metal d^0 alkyl peroxides and peroxides has been the subject of debate.^{8,13,14,18–20,41,58–60,70,71} Three mechanisms are outlined in Scheme 3.

The two first mechanisms depicted in Scheme 3 (reactions 13 and 14) are similar to the mechanisms shown to operate in the titanium(IV)–alkyl peroxide catalyzed epoxidations outlined in reactions 5–7. The third mechanism in Scheme 3 (reaction 15) takes place via a five-membered peroxometallacyclic intermediate, **34**.^{20,58,59,70,71} The first step in this mechanism is coordination of the alkene to vanadium, **33**, followed by insertion of the coordinated alkene into the vanadium–peroxy oxygen bond, giving **34**, from which the epoxide is formed by decomposition.^{20,58,59,70,71} The peroxometallacycle **34** has been characterized from reactions of platinum- and rhodium-peroxo complexes with cyano-substituted alkenes,^{41,72} but no examples with vanadium are known. A similar mechanism has been proposed for alkene oxidation by molybdenum–peroxo complexes (see later).

SCHEME 3

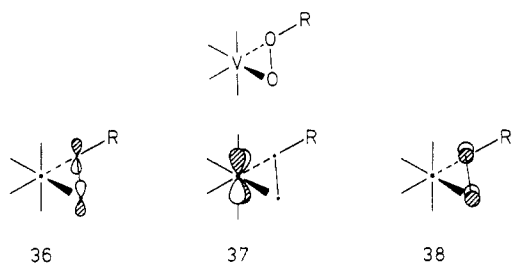


A diradical $\text{V(IV)}\leftarrow\text{O(R)}\text{-O-alkene}$, **35**, has also been suggested as an intermediate to account for the isomerization of *cis*-alkenes in the following manner:⁵⁹



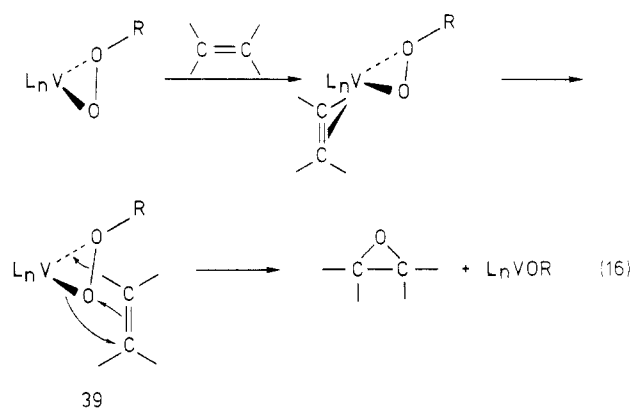
The electronic structure of **32** has been investigated by using extended-Hückel calculations,²¹ and a picture very similar to that obtained for the titanium(IV)-alkylperoxy complex shown in Figure 1 emerges.

The HOMO in **32** is mainly p_z at the peroxygens and antibonding between them; the LUMO is mainly vanadium d_{yz} -peroxy π^* , and right above the LUMO is located mainly the peroxygen σ^* orbital.²¹ These orbitals are shown in **36-38**. It should also be noted



that the vanadium d_{xy} is also located among the LU-

SCHEME 4

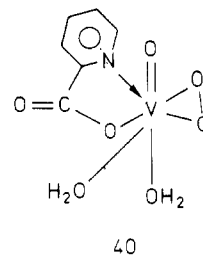


MOs of **32**. The frontier orbitals of the vanadium(V)-alkylperoxy complex seem to support mechanisms similar to those outlined as (13) or (14) in Scheme 3. For a further discussion of the oxygen transfer from the vanadium(V)-alkylperoxy complex **32** to the alkene, cf. the similar discussion in the titanium section.

Given the empty acceptor d orbitals at vanadium, a coordination of donors as, e.g., of an alkene to vanadium might be possible, and kinetic studies have revealed that the alkene coordinates to vanadium prior to the decomposition of the vanadium-alkene complex in the rate-determining step, which has been suggested to be the first step in (15) (Scheme 3).⁵⁸ The next step leading to **34** is then the migratory insertion of the alkene into the vanadium-peroxy bond, which results from the nucleophilic attack of the peroxygen on the alkene. This step should be well suited for electron-deficient alkenes, but these have not been observed to react in these transition-metal-catalyzed epoxidations.⁴¹ To account for the kinetic results indicating a coordination of the alkene to vanadium as the first step in this type of epoxidation, (16) (Scheme 4) is proposed as an alternative mechanism to (13) and (14) in Scheme 3.⁷³

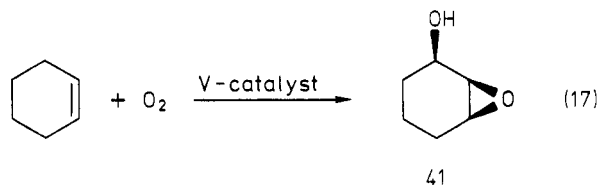
The first step in (16) is the coordination of the alkene to vanadium, followed by a slipping motion of the alkene toward the peroxygen, leading to **39**, which produces the epoxide in a similar way as shown in (13) and (14) in Scheme 3.

Several vanadium-peroxy complexes are known in the form of both anionic monoperoxo complexes as, e.g., $[\text{VO}(\text{O}_2)(\text{dipic})]\text{NH}_4$,^{74,75} $[\text{VO}(\text{O}_2)(\text{pic})_2]\text{H}$, or PPH_4 ⁷⁶ or neutral as $\text{VO}(\text{O}_2)(\text{pic})$ (**40**).⁷⁶ Some of the monoperoxo



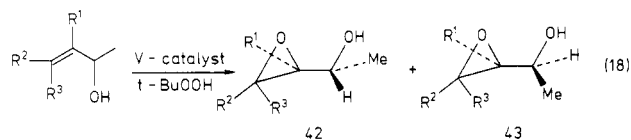
complexes epoxidize in a nonstereoselective manner and relatively low yields of epoxides are obtained.⁷⁶ The epoxide is mainly formed at the beginning of the reaction course, but under the reaction conditions further oxidation takes place.⁷⁶ It has been suggested that it is a radical species $\text{V(IV)}\text{-O-O}$ that adds to the double bond.⁷⁶

Molecular oxygen has also been applied as oxidant in vanadium-catalyzed epoxidations:⁷⁷⁻⁸⁰ $\text{CpV}(\text{CO})_4$, $\text{VO}(\text{acac})_2$, and V_2O_5 have been found to be able to catalyze the stereoselective oxidation of cyclohexene to *cis*-1,2-epoxycyclohexan-3-ol (41) as the major product^{78,79} (reaction 17). Cyclohexene oxide, 2-cyclo-



hexen-1-ol, and 2-cyclohexenone were also found as products in these reactions.⁷⁹ It has been found that addition of azobis(isobutyronitrile), a radical initiator for $\text{VO}(\text{acac})_2$, is necessary for this complex to act as a catalyst.⁷⁹ $\text{V}(\text{acac})_3$, in combination with $\text{RhCl}(\text{PPh}_3)_3$ or $\text{Co}(\text{acac})_3$, also catalyzes the oxidation of cyclohexene to cyclohexene oxide with molecular oxygen as oxidant.⁸⁰ Especially vanadium–chromium, but also other vanadium–metal complexes, act as heterogeneous catalysts for the epoxidation of cyclohexene with molecular oxygen.^{81,82} It has been suggested that cyclohexene oxide is formed by two successive catalytic processes, first the formation of cyclohexenyl hydroperoxide by autoxidation and then the selective oxidation of cyclohexene with the hydroperoxide.^{81,82}

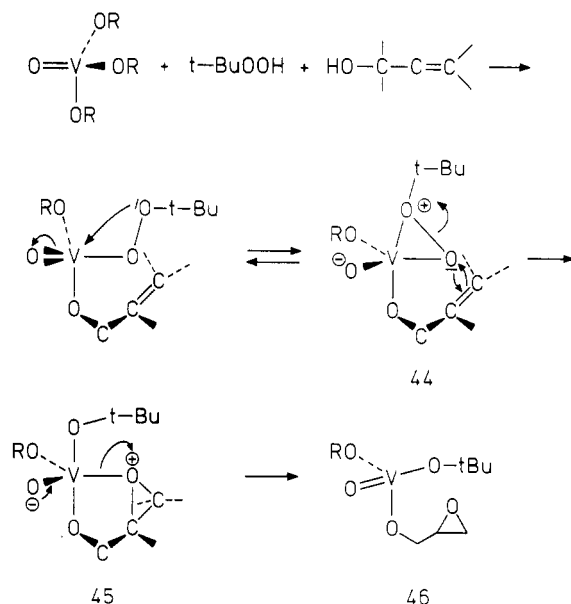
As mentioned earlier it has been found that vanadium is a very efficient catalyst for allylic epoxidations with TBHP as oxidant.^{15,61,66,67,83-90} The epoxidation of allylic alcohols is on the order of 10^3 times faster than that of the parent alkene.^{8,15} The vanadium-catalyzed epoxidation of allylic alcohols has often been utilized in complex synthetic sequences.^{8,15} The epoxidation of allylic alcohols with vanadium as catalyst favors formation of the *erythro*-epoxy alcohols, 43. The stereoselectivity of reaction 18 is opposite to that obtained with MCPBA as oxidant.



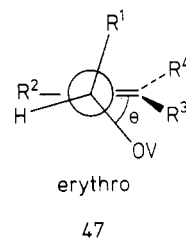
The proposed mechanism for the vanadium-catalyzed epoxidation of allylic alcohols is shown in Scheme 5.¹⁵

The exceptional reactivity of the allylic alcohols toward vanadium–alkyl hydroperoxides can be attributed to the fast and strong coordination of alcohol ligands to vanadium,⁹¹ followed by an intramolecular oxygen transfer from the coordinated alkyl peroxide to the double bond of the allylic alcohol (Scheme 5). The first step is the exchange of two alkoxy groups by the peroxide and the allylic alcohol; the next step, leading to 44, is a bidentate coordination of the peroxide moiety. The alkene part of the allylic alcohol in 44 is lined up perpendicularly to the vanadium–alkylperoxy plane, making an interaction between the alkene and the peroxygen possible. This interaction is, from a frontier orbital point of view, similar to the interactions between alkenes and other d^0 transition metal–peroxy complexes. The step 44 \rightarrow 45 is the step in which the stereoselectivity is determined. With the mechanism outlined in Scheme 5 for the epoxidation of allylic alcohols, the stereoselectivity for the formation of the

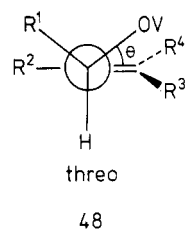
SCHEME 5



erythro-epoxy alcohol can be explained from the conformation of the intermediate, 47. The $\text{O}-\text{C}-\text{C}=\text{C}$



dihedral angle θ in 47 is about 50° , whereas a rotation of the $\text{O}-\text{C}-\text{C}=\text{C}$ dihedral angle about 50° above the $\text{R}^2\text{R}^3\text{R}^4$ plane, shown in 48, will lead to the *threo* product. The substitution pattern supports the sug-

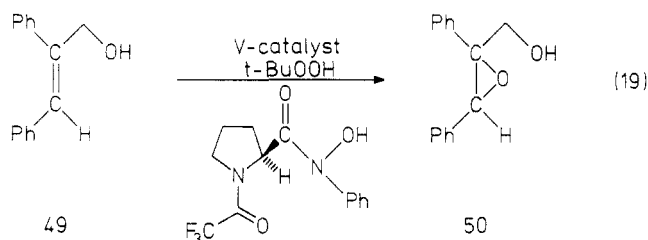


gested conformations since alkyl substitution in R^1 and R^2 will cause steric repulsion in 48, whereas this is not the case in 47.

The preferred orientation of the alkene part of the allylic alcohol perpendicular to the vanadium–alkylperoxy plane is very similar to the orientation of the allylic alcohol in titanium–tartrate catalyzed epoxidations, which has gained theoretical support as discussed earlier in the section on group IV catalyzed epoxidations.^{22,23} Ab initio calculations indicate a small ($\sim 1 \text{ kcal}\cdot\text{mol}^{-1}$) preference for a planar orientation in the transition state; for these allylic alcohols an increase in the anionic character of the metal–oxygen bond, with its associated effect on the energy of the π bond, should enhance the rate of epoxidation.²²

Vanadium(V) in the presence of hydroxamate ligands as chiral auxiliaries induces asymmetric epoxidations of allylic alcohols.^{15,41,92} The most effective chiral hydroxamate ligand is shown in (19), and up to 80% ee has been obtained for the epoxidation of (*E*)- α -

phenylcinnamyl alcohol (49).^{15,92}

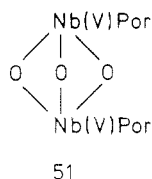


Vanadium(V) also achieves reasonable selectivities with some homoallylic and bihomoallylic alcohols.⁹³⁻¹⁰⁰

2. Nb and Ta

Both Nb(V) and Ta(V) alkoxides catalyze the epoxidation of cyclohexene with TBHP as oxidant, but the reaction times are long and the yield of the epoxide is relatively low; epoxidation of cyclohexene afforded (*tert*-butylperoxy)cyclohexene as the major product.¹³ Nb(acac)₄ shows properties similar to those of Nb(V) alkoxides.⁶⁰ Free and polymer-supported Cp₂NbCl₂ show low and no catalytic activity, respectively.^{101,102}

The tri- μ -oxo dimer of Nb^V(*p*-CH₃-TPP) (51) epoxidizes alkenes under photochemical conditions with molecular oxygen as oxygen donor.¹⁰³



IV. Cr, Mo, and W

In the transition-metal-catalyzed epoxidations using group IV and V metals, the active catalytic oxidant has been described as a mono- or bidentate coordinated alkyl hydroperoxide (hydrogen peroxide) or a bidentate coordinated peroxy group. For group VI transition-metal-catalyzed epoxidations a new type of active catalytic oxidant appears—the oxotransition-metal complexes.

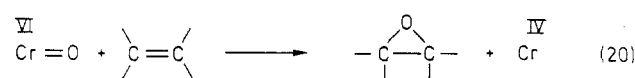
The oxidation reagents used to generate the active catalytic oxidant for group IV and V transition metals are alkyl hydroperoxides, hydrogen peroxide, or molecular oxygen. For the generation of the active catalytic oxidant in group VI, as well as some of the later groups, iodosyl compounds, *N*-oxides, and hypochlorite have also found use.

1. Cr

Chromium complexes such as Cr(acac)₃ are relatively poor catalysts for the epoxidation of cyclohexene with TBHP.¹³ The main reaction of TBHP in the presence of Cr(acac)₃ is its decomposition with formation of molecular oxygen.¹³ Cr(VI), which is a strong Lewis acid, should be expected to be a good catalyst, but this is not the case and must be ascribed to the fact that Cr(VI) is a strong oxidant and promotes the decomposition of TBHP.¹³

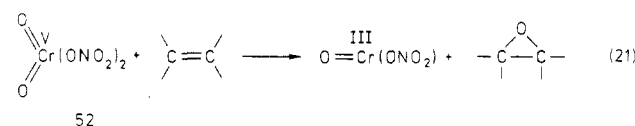
The oxochromium bond, O=Cr, is present in chromyl complexes and is the most common feature in such high-valent complexes. The oxidative properties of the oxochromium complexes are due to the fact that these complexes can effect a direct transfer of the oxygen

atom to an alkene (reaction 20):

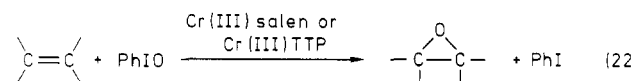


Several chromyl complexes are able to epoxidize alkenes, but the generated epoxides are often intermediates from which ketones, aldehydes, glycerols, etc. are formed. Chromic acid, usually formed in the dissolution of chromium trioxide in aqueous acetic acid, is generally not a useful reagent for epoxidation.^{104,105} Sodium chromate has been found to be effective for the epoxidation of *seco*-dodecahedrene, which contains a strained and highly reactive double bond.¹⁰⁶ Chromium oxide complexes can oxidize allylic alcohols to various epoxy derivatives,^{107,108} but epoxides are not known to be the major products from nonfunctionalized alkenes.¹⁰⁹⁻¹¹² Chromyl acetate is, compared to chromic acid, a better epoxidation reagent, and epoxides are formed in isolable amounts, especially from highly substituted alkenes, but the yields are generally poor.¹¹³⁻¹¹⁷ Chromyl chloride reacts with most alkenes, but complex mixtures of products are often found; stereochemical and deuterium labeling studies have indicated that epoxides are formed in large amounts, but undergo further oxidation.¹¹⁸⁻¹²¹

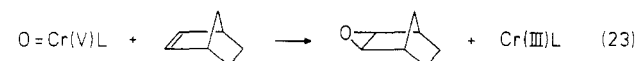
Chromyl nitrate has been found to be the best epoxidation reagent among these chromyl complexes and epoxidizes a variety of alkenes.¹²² The epoxidation properties of chromyl nitrate are solvent dependent; thus a high yield of styrene oxide is obtained in DMF, whereas only traces are formed in CH₂Cl₂.¹²² ESR investigations of chromyl nitrate in solution have demonstrated that chromium(V) is formed in significant amounts by one-electron oxidation of the solvent.¹²² The epoxidation of alkenes by chromyl nitrate has thus been described as involving a chromium(V) species, 52, rather than chromium(VI) as shown in (21).¹²²



Oxochromium(V) complexes formed from chromium(III)-salen or -TTP complexes with iodosylbenzene also achieve the conversion of an alkene to its epoxide.¹²³⁻¹²⁵ The oxygen atom is successively transferred from the terminal oxidant, e.g., iodosylbenzene, to the chromium(III)-ligand complex acting as a catalyst and hence to the alkene (reaction 22):

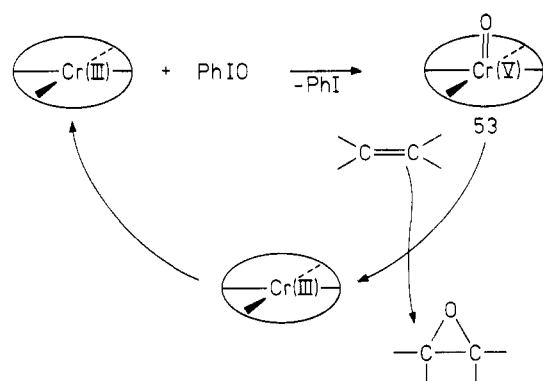


The crystal structure of some oxochromium(V)-salen and -TTP adducts has been determined by X-ray crystallographic investigations.¹²⁶⁻¹²⁸ The oxochromium(V)-salen complexes can effect the direct epoxidation of norbornene (reaction 23), and the addition of donor ligands can increase the rate of epoxidation as well as increase the yield of epoxide.¹²⁵

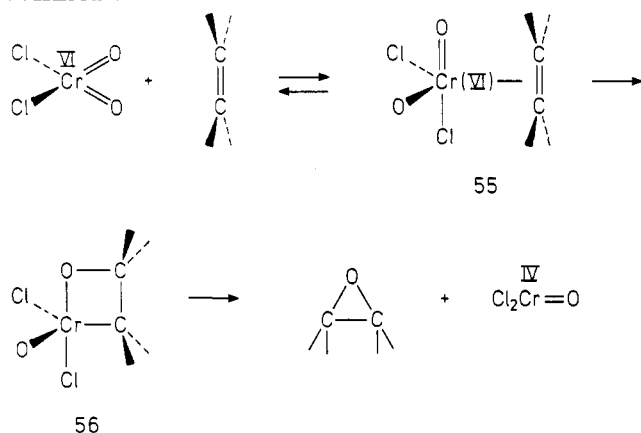


The catalytic cycle of the chromium(III)-catalyzed epoxidation of alkenes with the oxochromium(V) (53)

SCHEME 6



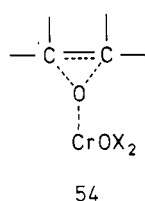
SCHEME 7



intermediate is shown in Scheme 6.

The oxochromium(V)-TPP complex can also be generated electrochemically by oxidation of the corresponding oxochromium(IV)-porphyrin.¹²⁹

Several mechanisms have been suggested for the epoxidation of alkenes by chromyl complexes. Until recently, a symmetric three-membered cyclic activated complex, **54**, had been considered as the transition state.¹³⁰

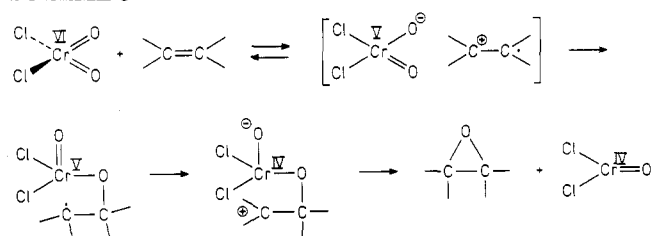


This satisfies the mechanistic criteria and accounts as well for the electrophilic character of the chromyl complexes, but a positively charged product-determining species could also be involved to explain the different products formed.¹³⁰ However, a novel mechanism based on low-temperature oxidations with chromyl chloride has been invoked.¹²¹ The mechanism is outlined in Scheme 7.¹²¹

The first step is an attack of the alkene on the chromium atom, producing an organometallic intermediate **55**, followed by a [2 + 2] cycloaddition of the alkene to the oxochromium bond, giving a chromoxetane **56**, which decomposes as shown.

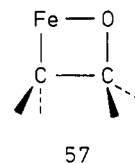
Theoretical investigations using ab initio generalized valence bond calculations have concentrated on the thermochemistry of the cycloaddition of ethylene to chromyl chloride.^{131,132} The formation of **56** is exothermic by 14 kcal·mol⁻¹ if a singlet state of the system

SCHEME 8



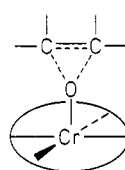
is considered whereas a direct addition of ethylene to the oxo ligands in chromyl chloride, **54**, is endothermic by 56 kcal·mol⁻¹.¹³¹ Theoretical calculations of the activation energy for the formation of the three-membered cyclic activated complex, **54**, and activation energies for the different steps in Scheme 7 would shed some light on the mechanism.

Support for **56** as an intermediate in the reaction of oxochromium complexes with alkenes comes also from reaction of ClCrO₂⁺ with ethylene in a selected-ion flow tube where a product originating from a carbon-chromium-bonded intermediate is found.¹³³ It should also be noted that a ferraioxetane **57** has been observed at low temperature in a matrix after reaction of atomic iron with ethylene oxide.¹³⁴

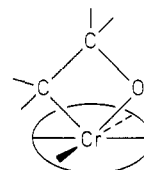


It has also been suggested that the formation of epoxides from alkenes and chromyl chloride could take place by an initial one-electron transfer from the alkene to chromyl chloride followed by a solvent cage combination of the cation radical with the oxo anion as shown in Scheme 8.⁸

Two types of intermediates, **58** and **59**, have been suggested for the chromium(III)-catalyzed epoxidation of alkenes with an oxochromium(V) complex as reactive intermediate.¹²⁵ Species **58** is a three-membered cyclic



58

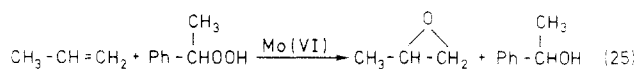
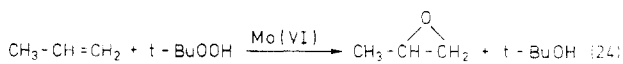


59

activated complex similar to one of the transition states suggested for the oxidation of alkenes with chromyl complexes,¹³⁰ whereas **59** is a chromoxetane complex, the other type of transition state discussed for the chromyl complex oxidation of alkenes.^{121,131,133} Based on the concept of least motion for the rate-limiting step **58** is a close relative to the activated complex.¹²⁵ Epoxidation of both *cis*- and *trans*-stilbene is achieved quite well with both chromium(III)-salen and chromium(III)-TTP as catalyst; it could be expected that significant steric repulsion between the phenyl groups in the alkene and the ligands in the chromium complexes would be possible in **59** whereas this repulsion is diminished in **58**, which might indicate that **58** represents the transition state.

2. Mo

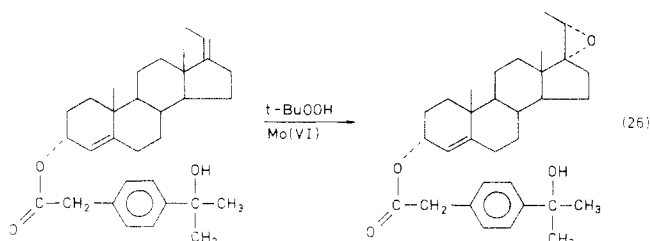
Molybdenum(VI) complexes are probably the best catalysts for epoxidation with alkyl hydroperoxides as oxidants, and an enormous amount of literature is available about molybdenum-catalyzed epoxidations.^{7,8,12-15,17,60} Propylene oxide is currently manufactured on a large scale by molybdenum-catalyzed epoxidation of propylene with TBHP (reaction 24) or 1-phenylethyl hydroperoxide (reaction 25) (the Halcon process).¹³⁵ The *tert*-butyl alcohol coproduct



in (24) can be recycled by dehydration followed by hydrogenation or converted to methyl *tert*-butyl ether, a high-octane component for gasoline.⁸ The coproduct in (25), 1-phenylethanol, can be dehydrated to styrene or recycled.⁸

The molybdenum complexes, ranging from monomeric molybdenum compounds such as $\text{Mo}(\text{CO})_6$ and $\text{MoO}_2(\text{acac})_2$ ¹³ to molybdenum clusters such as $[\text{MoO}(\text{O}_2\text{CR})_6(\text{H}_2\text{O})_3]^{n+}$,⁶⁹ $[\text{C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3]_3\text{-}[\text{PMo}_{12}\text{O}_{40}]^{3-}$,^{136,137} and ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ ¹³⁸ to metallic molybdenum,⁴ catalyze the epoxidation of many different alkenes with different peroxides as oxygen donors. A variety of molybdenum-ligand complexes have been synthesized and tested for catalytic activity.¹³⁹⁻¹⁴⁷ Among the most frequently used and tested monomeric complexes are probably $\text{Mo}(\text{CO})_6$ and $\text{MoO}_2(\text{acac})_2$, which catalyze the epoxidation of alkenes in high yield and with low yields of byproducts (e.g., alkylperoxy compounds).^{8,17} The catalytic properties of molybdenum complexes are to a certain extent dependent on the ligands attached to molybdenum.^{14,147} It has been observed that a higher epoxidation rate can be achieved by using relatively stable complexes of molybdenum, e.g., $\text{MoO}_2(\text{oxinate})_2$.¹⁴⁷ In contrast to the oxochromium-salen and -porphyrin complexes, which can epoxidize an alkene directly, oxomolybdenum-porphyrin needs TBHP for achieving epoxidation.¹⁴¹

Molybdenum-catalyzed epoxidations have been used with alkenes ranging from the simplest, ethylene, to large molecules of, e.g., biological interest. For the epoxidation of ethylene with TBHP a high yield of ethylene oxide (69% based on TBHP) was obtained with $\text{MoO}_2(\text{oxinate})_2$.^{148,149} Molybdenum-catalyzed epoxidations have been reported in the template-directed remote epoxidation of double bonds (reaction 26).¹⁵⁰ The use of molybdenum(VI) as epoxidation catalyst has also been reported for other systems of similar type.¹⁵¹

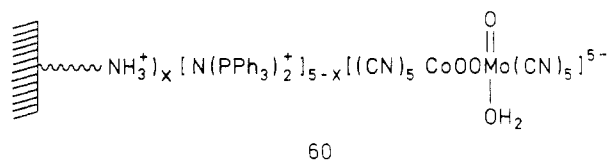


Some molybdenum(V) complexes can also achieve catalytic epoxidation of alkenes with alkyl peroxides as

oxidant,¹⁵²⁻¹⁵⁵ but the yields of the epoxides are often lower compared with those with, e.g., $\text{MoO}_2(\text{acac})_2$.

Many different types of heterogeneous molybdenum catalysts have been prepared: e.g., molybdenum trioxide deposited on silica,^{156,157} modification of an Amberlite cation exchanger with molybdenum hexacarbonyl,^{158,159} polymer-immobilized molybdenum peroxide,¹⁶⁰ molybdenum oxide-tin complexes on charcoal,^{161,162} molybdenum zeolites,¹⁶³⁻¹⁶⁵ molybdenum heterobimetallic complexes,¹⁶⁶ molybdenum complexes on Wofatit-AD-41,¹⁶⁷ and molybdenum(VI) on phosphate cellulose.¹⁶⁸ The yields of epoxides vary widely for the different heterogeneous catalysts studied, but, e.g., MoHY_u zeolites with different Mo loadings give up to 100% selective epoxidation.¹⁶⁵ Some of the heterogeneous molybdenum catalysts are able to use molecular oxygen as an oxygen source.¹⁶³

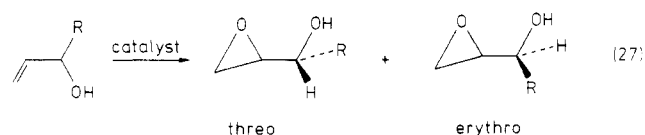
A cobalt-molybdenum heterogenized complex 60 activates molecular oxygen and epoxidizes cyclo-



hexene.^{169,170} It has been suggested that a surface Mo(VI)-Co(III) μ -peroxy compound is formed which is responsible for the selective oxidation.¹⁶⁹

Epoxidations catalyzed by $\text{MoO}_2(\text{acac})_2$ proceed approximately 10^2 times as rapidly as those catalyzed by active vanadium complexes under corresponding conditions.⁵⁷ The mechanistic investigations of Mo(VI) -catalyzed epoxidations with peroxides as oxidant show that the mechanism is similar to those discussed earlier for both titanium(IV)- and vanadium(V)-catalyzed epoxidations.

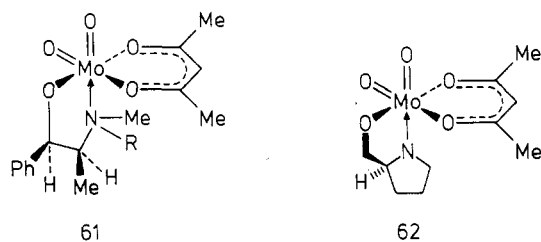
Molybdenum(VI) is an effective catalyst for the epoxidation of allylic alcohols.^{8,15} A comparison of the stereoselectivities attained in the epoxidation of 2-cyclohexenol revealed that $\text{Mo}(\text{CO})_6$ and $\text{VO}(\text{acac})_2$ with TBHP were identical, but that the latter reacted about 50 times faster than the former.⁸³ In the epoxidation of 3-cyclohexenol, a homoallylic alcohol, a similarly high stereoselectivity was observed, and the reaction rates for the $\text{Mo}(\text{CO})_6$ and $\text{VO}(\text{acac})_2$ catalysts were of similar magnitude.⁸³ In a comparative investigation it was found that the $\text{VO}(\text{acac})_2$ -TBHP system gave a higher yield of the *erythro*-epoxide compared with $\text{Mo}(\text{CO})_6$ -TBHP as catalyst.⁸⁹



| R | system | % threo | % erythro |
|---|---|---------|-----------|
| CH ₃ | $\text{VO}(\text{acac})_2/t\text{-BuOOH}$ | 20 | 80 |
| | $\text{Mo}(\text{CO})_6/t\text{-BuOOH}$ | 44 | 56 |
| C ₂ H ₅ | $\text{VO}(\text{acac})_2/t\text{-BuOOH}$ | 20 | 80 |
| | $\text{Mo}(\text{CO})_6/t\text{-BuOOH}$ | 42 | 58 |
| <i>i</i> -C ₃ H ₇ | $\text{VO}(\text{acac})_2/t\text{-BuOOH}$ | 15 | 85 |
| | $\text{Mo}(\text{CO})_6/t\text{-BuOOH}$ | 35 | 65 |

The mechanism for the stereospecific epoxidation of allylic alcohols catalyzed by molybdenum(VI) is probably similar to the one outlined above for the catalysis by vanadium(V).

Chiral molybdenum catalysts have been applied in the asymmetric epoxidation of allylic alcohols. Oxidation with cumene hydroperoxide and the dioxo-molybdenum complex of *N*-ethylphedrine (**61**) afforded up to 33% ee.¹⁷¹ Exchanging the *N*-ethylphedrine



ligand of **61** for *L*-*N*-methylprolinol to form **62** gives nearly similar results.¹⁷² Use of $\text{MoO}_2(\text{acac})_2$ -TBHP in the presence of optically active sugar derivatives and tartrate esters as catalysts for asymmetric epoxidation of isolated alkenes gave up to 14% ee.¹⁷³ None of these methods seems to compete with the titanium-tartrate procedure.

Several monoperoxo-molybdenum complexes, $\text{MoO}(\text{O}_2)\text{L}_n$ (**63**), and diperoxo-molybdenum complexes, $\text{MoO}(\text{O}_2)_2\text{L}_1\text{L}_2$ (**64**), have been prepared and found to epoxidize many different types of alkenes.¹⁷⁴

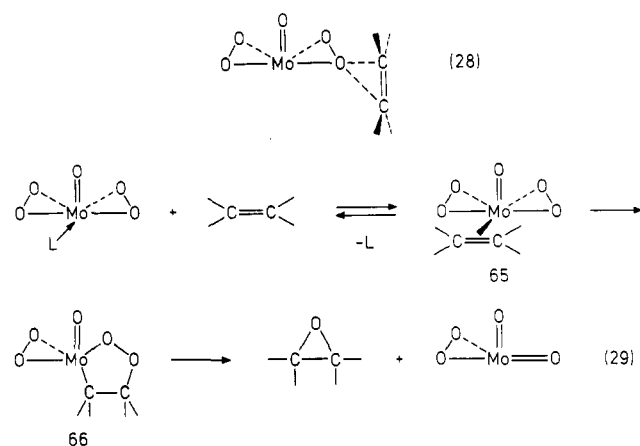


Among the monoperoxo-molybdenum complexes synthesized are $\text{MoO}(\text{O}_2)(\text{dipic})\cdot\text{H}_2\text{O}$,^{175,176} $\text{MoO}(\text{O}_2)-[\text{PhCON}(\text{Ph})\text{O}]_2$,¹⁷⁷ $\text{MoO}(\text{O}_2)\text{X}_2\text{L}_2$, and $\text{MoO}(\text{O}_2)\text{Cl}(\text{pic})$.⁷⁰ $\text{MoO}(\text{O}_2)\text{Cl}_2\cdot\text{HMPA}$ epoxidizes unactivated alkenes, but the epoxide is mainly formed at the beginning of the reaction and progressively disappears to be replaced by products of oxidative cleavage.⁷⁰ The bis(hydroxamato) monoperoxo complex $\text{MoO}(\text{O}_2)-[\text{PhCON}(\text{Ph})\text{O}]_2$ only epoxidizes allylic alcohols that can displace one hydroxamate ligand on molybdenum.¹⁷⁷ The peroxo-molybdenum complex derived from $[\text{C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3]_3[\text{PMo}_{12}\text{O}_{40}]^{3-}$ can also oxidize alkenes to epoxides.¹⁷⁸

The diperoxo-molybdenum complexes **64** have been prepared with a great variety of basic ligands.¹⁷⁴ These complexes are easily prepared from addition of the ligands to a solution of molybdenum trioxide in hydrogen peroxide.¹⁷⁹ An X-ray structure determination of $\text{MoO}(\text{O}_2)_2\cdot\text{HMPA}\cdot\text{H}_2\text{O}$ reveals a bipyramidal-pentagonal structure, with HMPA occupying the equatorial position in the same plane as the two peroxo triangles and H_2O trans to the oxo group, L_1 and L_2 , respectively, in **64**.¹⁸⁰ The complex is easily dehydrated, producing $\text{MoO}(\text{O}_2)_2\cdot\text{HMPA}$, which is very soluble in organic solvents. $\text{MoO}(\text{O}_2)_2\cdot\text{HMPA}$ and other diperoxo-molybdenum-ligand complexes have been found to stoichiometrically oxidize alkenes to epoxides in good yields at room temperature in aprotic solvents.^{167,179,181-185} The epoxidation of alkenes is stereoselective; i.e., *cis*-alkenes are transformed into *cis*-epoxides and *trans*-alkenes into *trans*-epoxides.^{174,181}

The coordination of a chiral bidentate ligand such as (*S*)-*N,N*-dimethylacetamide to $\text{MoO}(\text{O}_2)_2$ leads to a

SCHEME 9



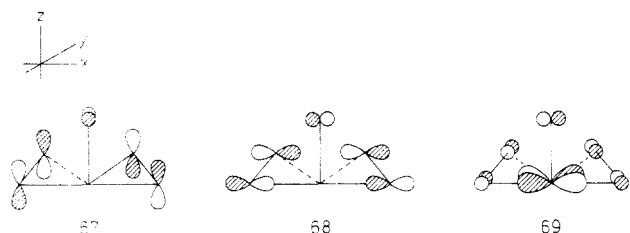
complex that can induce asymmetric epoxidation of low-molecular-weight alkenes in up to 35% ee.^{186,188}

The mechanism for the transfer of an oxygen atom from **64** to an alkene has been the subject of many discussions. Spectroscopic and kinetic studies reveal that the first step in the epoxidation of an alkene by $\text{MoO}(\text{O}_2)_2\cdot\text{HMPA}$ is a reversible displacement of the ligand (probably the equatorial) by the alkene, followed by irreversible oxygen transfer to the alkene.^{71,181,182} It has been observed that the rate of epoxidation is reduced by the presence of σ -donor ligands, and furthermore, complexes with the equatorial positions adjacent to the peroxo moiety occupied by anionic ligands or strongly complexing bidentate or tridentate ligands are unreactive.²⁰ ^{18}O -Labeling studies demonstrate that it is the peroxygen that is transferred to the alkene.¹⁸⁵ The reactivity of the alkenes increases with their nucleophilicity.¹⁸¹ The two mechanisms suggested for the oxygen transfer from $\text{MoO}(\text{O}_2)_2$ to an alkene are outlined in Scheme 9.^{181,185}

The first mechanism (Scheme 9, (28)) involves interaction of the alkene with one of the peroxygens; this mechanism is similar to those suggested from both an experimental and a theoretical point of view for epoxidation with group IV and V transition metals and peroxides as well as epoxidation of alkenes with peracids. The second mechanism (Scheme 9, (29)) starts with the coordination of the alkene to molybdenum by which the alkene loses its nucleophilic character, **65**. The next step consists then of an intramolecular 1,3-dipolar cycloaddition of the peroxo group to the coordinated electrophilic alkene, yielding a five-membered peroxometallacycle, **66**, which decomposes by a 1,3-dipolar cycloreversion mechanism to the epoxide and the $\text{MoO}_2(\text{O}_2)$ complex.

The peroxometallacycle **66** has been isolated from reactions of group VIII (Pt and Rh) peroxo complexes with cyano-substituted alkenes, but not in the case of group IV-VI complexes. Extended-Hückel calculations have been performed to shed some light on the mechanism.^{23,189,190} One investigation takes its starting point in the electronic structure of $\text{MoO}(\text{O}_2)_2$ and analyzes how an oxygen atom can be transferred from this complex to an alkene,²³ while the others studied the decomposition of **66** and compared it with the corresponding rhodium complex.^{189,190}

The two HOMOs of **64** are mainly of p_z and p_x character at the peroxygens and antibonding, schematically shown in **67** and **68**, whereas among the LU-

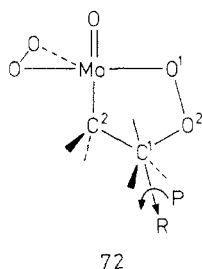


MOs an orbital with p_y character, σ antibonding between the two peroxygens, is found, **69**.²³

The empty orbitals of **64** are mainly d orbitals at molybdenum and thus able to interact with ligands. The orbitals depicted in **67**–**69** are thus of similar symmetry to those in the titanium(IV)– and vanadium(V)–alkylperoxo complexes discussed previously. The two mechanisms in Scheme 10 for the epoxidation of alkenes have been suggested on the basis of the frontier orbitals of $\text{MoO}(\text{O}_2)_2$.²³

The first step in the two mechanisms is the coordination of the alkene to molybdenum in a parallel (Scheme 10, route a) or perpendicular (Scheme 10, route b) orientation relative to the molybdenum–peroxo plane. By a slipping motion of the alkene from the two orientations at the molybdenum atom toward one of the peroxygens favorable interactions between the π and π^* orbitals of the alkene and **69** and **68** (or **67**) become possible. The similarities of the transition states **70** and **71** and of those discussed in relation to oxygen transfer from the other d^0 transition metal–alkylperoxo complexes outlined above are thus obvious. It was not possible on the basis of the extended-Hückel calculations to distinguish energetically between **70** and **71**.²³ The total energy for **66** was found to be higher than those of the transition states in the mechanisms in Scheme 10.²³

The stability of two different types of the **66** has been investigated by extended-Hückel calculations; the most stable was alkene coordination and peroxometallacycle formation trans to the oxo ligand, **72**.¹⁸⁹ The formation



of the epoxide from **72** has been studied along two reaction paths, R and P, shown in **72**.^{189,190} R is a movement of C-1 in the direction of the arrow and a simultaneous movement of C-2 and O-2 toward each other, leading to an antarafacial interaction of the two atoms (see **72**). P is the dihedral angle defined by rotating the $\text{C}^1\text{C}^2\text{O}^2$ plane. The potential surface for the change in energy as a function of P and R has been calculated. The minimum of the surface is found for $P = 180^\circ$, which corresponds to the isomerized five-membered ring in which the original O–O and Mo–C bonds are replaced by O–C and Mo–O bonds—a 1,2-ethanediolate coordination to molybdenum.¹⁹⁰ The potential surface shows also that an adiabatic cycloreversion to form an epoxide is possible, but the surface for the Mo(VI) complex compared with the surface for

the Rh(III) complex gives no clue as to why the former produces epoxide while the latter fails to do so, producing instead a carbonyl oxidation product.¹⁹⁰

3. W

Tungsten(VI) complexes are probably the best transition-metal catalysts for epoxidation reactions of alkenes with hydrogen peroxide, but they do not have the same broad synthetic utility as the transition metal–alkyl hydroperoxide system.^{7,8,191} When hydrogen peroxide is used as oxidant, the presence of water or a polar solvent can retard the reaction. It has also been observed that the epoxides formed often hydrolyze to the corresponding glycols, but good yields of epoxides can be obtained when the water is removed from the reaction medium.^{8,14} The combination $\text{WO}_4^{2-}/\text{H}_2\text{O}_2$ is used in industry for the preparation of epichlorohydrin.⁸

The catalytic properties of tungsten complexes are not comparable with those of molybdenum(VI) when alkyl hydroperoxides are applied as oxidant;¹³ tungsten hexacarbonyl is an exception.¹³

The combination of tungsten(VI) complexes with hydrogen peroxide for epoxidation of alkenes goes back to the late 1940s.¹⁹² Pertungstic acid and perstungstates are known to give highly stable aqueous solutions, and the tungstate ion has been shown to be quite superior to molybdate and vanadate, since the transition metal ion induced decomposition of hydrogen peroxide is much slower and allows the use of a broader pH range, up to 6–7.^{193,194}

The pertungstate–hydrogen peroxide mixture has been used for a variety of alkenes such as isolated double bonds,^{195–198} allylic and homoallylic alcohols,^{199–201} and α,β -unsaturated acids.^{202,203}

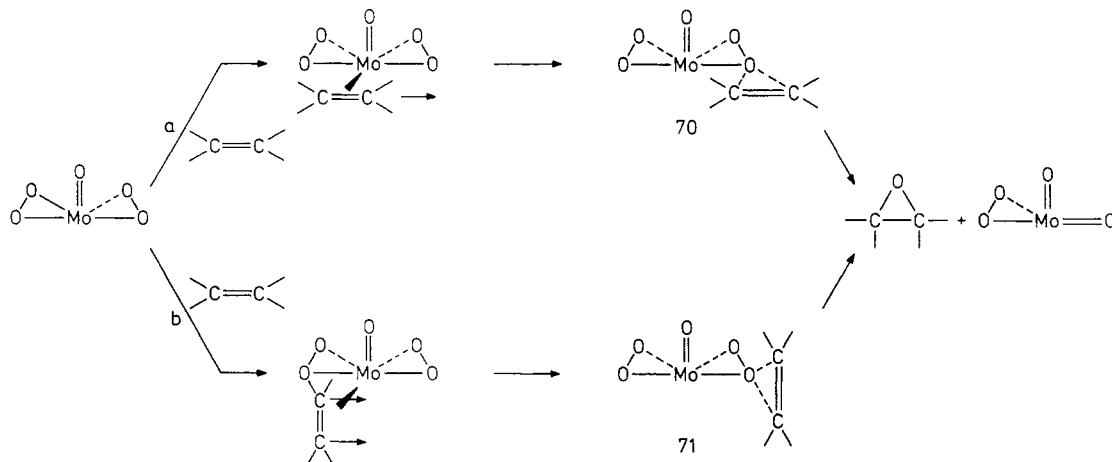
The experimental results for the epoxidation reactions indicate that the oxidizing species also here is electrophilic; i.e., increased nucleophilicity of the double bond increases the reaction rate.^{203,204} The reaction is stereospecific and occurs with retention of configuration of both *cis*- and *trans*-alkenes, and the stereoselectivity for the epoxidation of allylic alcohols compares well with that of the vanadium-catalyzed TBHP system.²⁰¹

The reactive intermediate in the tungsten–hydrogen peroxide catalyzed epoxidations is then probably also a mono- or bidentate peroxide–tungsten complex that achieves the oxygen-transfer step in a similar way to the other transition metal d^0 -peroxide complexes. But the tungsten-catalyzed epoxidations show some abnormalities which might be related to the fact that tungstates can be polymeric in acidic, neutral, and mildly basic solutions and that one has to deal with a complex mixture of tungstate species that exhibit different catalytic activities.²⁰³

Tungstate attached to a resin²⁰⁵ and tungstic acid–tributyltin chloride on charcoal²⁰⁶ are more effective as catalysts for epoxidation of some alkenes, with hydrogen peroxide as terminal oxidant, than the tungstate salts.

The tungsten–peroxo complexes behave in many ways very similarly to molybdenum complexes,¹⁷⁴ and both monoperoxo species¹⁸⁷ and diperoxo species are known.¹⁷⁹ Because of the low solubility of the tungsten complexes their reactivity has not been studied much.¹⁷⁴ $\text{WO}(\text{O}_2)_2\cdot\text{HMPA}$ epoxidizes alkenes,^{174,207} and it has been observed that it is a more effective oxidant than $\text{MoO}(\text{O}_2)_2\cdot\text{HMPA}$ (their structures are similar¹⁸⁰); how-

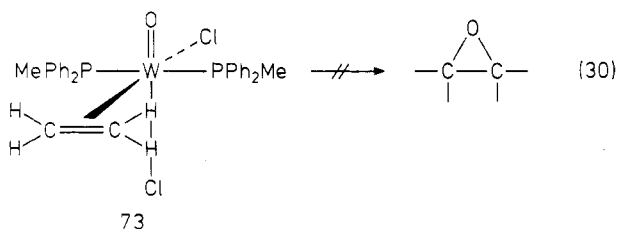
SCHEME 10



ever, the former behaves mainly as a monooxygenating species.²⁰⁷ The experimental results indicate that the mechanism for the oxygen-transfer step from the tungsten-peroxo complex to the alkene involves attack of the alkene on one of the peroxygens of the complex,²⁰⁷ a mechanism similar to one of those suggested to operate for the molybdenum-peroxo system.^{23,185}

A polytungstate-peroxo complex $[(C_6H_{13})_4N^+]_3\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ is found to be an effective epoxidation reagent for nonactivated alkenes in nonprotic solvents as well as an effective catalyst for epoxidations with hydrogen peroxide under phase-transfer conditions.²⁰⁸

The metallacycle has also been discussed in relation to oxygen transfer from some tungsten complexes. A tungsten complex 73, the first example of a transition-metal complex containing both a terminal oxo ligand and an alkene, has been characterized.²⁰⁹ This type of



complex could be involved in alkene epoxidations via metallacycles,^{121,209} but the complex does not rearrange to an epoxide (see (30)).^{210,211} However, the reverse reaction, an oxidative addition leading to 73, takes place when epoxides react with $WCl_2(PMePh_2)_4$.²¹⁰

V. Mn, Tc, and Re

The catalytic properties of the transition metals from groups IV–VI (except Cr) with peroxides as oxidant are mainly attributed to the coordinative properties of the transition metal by which the peroxide is activated toward nucleophilic attack by the alkene. The catalytic properties of the transition metal to be discussed in the following are mainly due to the fact that they can undergo an oxygen-rebound reaction in which the transition metal serves as a relay for the oxygen atom transfer from the terminal oxidant to the alkene via an oxotransition-metal reactive intermediate.

The transition-metal complexes in these reactions are capable of readily undergoing one-electron changes (e.g., $Mn(II) \rightleftharpoons Mn(III)$, $Fe(II) \rightleftharpoons Fe(III)$, and $Co(II) \rightleftharpoons$

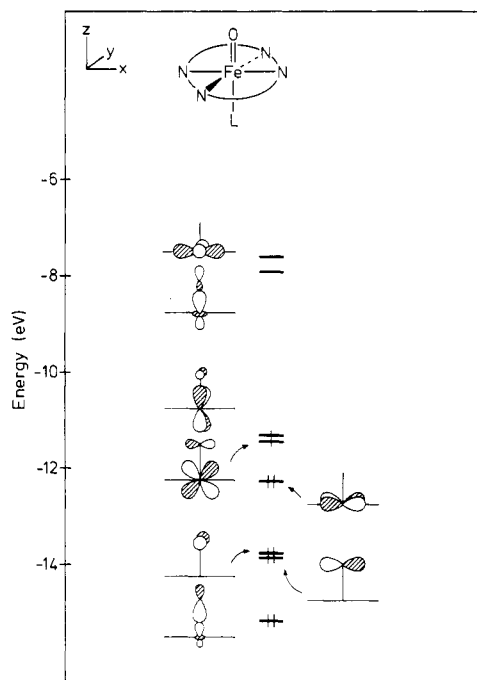


Figure 2. Frontier orbitals of an oxo-iron complex.

$Co(III)$). However, a formal two-electron oxidation state change of the catalyst has also been proposed for these systems by the reaction with an oxygen donor, e.g., $Mn(III) \rightleftharpoons O=Mn(V)$. With these facile changes in oxidation state of the transition metals of the oxotransition-metal systems the possibility for several electronic states located around the ground state of the oxotransition-metal complex appears. Therefore, changes in the electronic environment of the transition-metal center might have an influence on the reaction course. In the case of the d^0 transition metal-peroxo complexes one might expect from the electronic structure of these types of systems that the main reaction path originates from a singlet state of the system. But from consideration of frontier orbitals of an oxometal complex, shown for the oxoiron(II) case in Figure 2,^{212,213} it appears that several spin states are possible for this system. The frontier orbital picture for the oxotransition-metal complex in Figure 2 indicates a triplet ground state, but removal of an electron can lead to a doublet ground state. The change from a triplet to a singlet ground state might also be possible by changing the electronic environment around the tran-

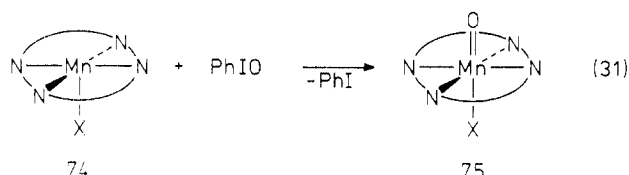
sition metal. Thus the electronic structure at the transition metal in these oxotransition-metal complexes might have an influence on the bonding between the transition metal and oxygen, which might affect the reactivity of these intermediates.

1. Mn

The interest in manganese complexes as catalysts for alkene epoxidations comes mainly from the relationship of these catalytic systems to the biologically relevant manganese porphyrins. In the case of manganese porphyrins as epoxidation catalysts different oxygen sources have been used: iodosylbenzene, sodium hypochlorite, molecular oxygen in the presence of an electron source, alkyl peroxides and hydroperoxides, *N*-oxides, potassium hydrogen persulfate, and oxaziridines.^{214,215}

The presence of porphyrin or salen ligands around the manganese is not necessary to achieve the catalytic properties of manganese since even a soluble manganese salt such as manganese(II) triflate in acetonitrile catalyzes the epoxidation of alkenes with iodosylbenzene as oxygen donor.²¹⁶ The reaction is nonstereospecific since epoxidation of *cis*-stilbene gives a mixture of *cis*- and *trans*-stilbene oxide and also benzaldehyde.²¹⁶

The major part of the work done with manganese complexes as catalysts for alkene epoxidation has been done with manganese porphyrins, because of their relation to the biological oxidation systems. Mn(TPP)Cl catalyzes epoxidation of alkenes with iodosylbenzene as oxygen donor. The first step in the reaction between Mn(TPP)Cl (74) and iodosylbenzene is the formation of an unstable and reactive oxo-Mn(TPP)Cl complex (75), which then epoxidizes the alkene.²¹⁷

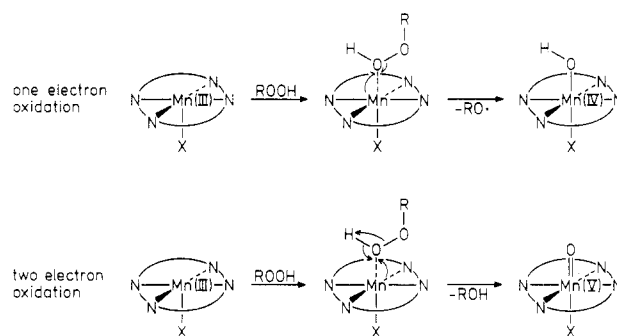


The oxygen-transfer process from 75 to an alkene takes place, as in the case of manganese(II) triflate, in a nonstereospecific fashion since epoxidation of *cis*-stilbene gives both *cis*- and *trans*-stilbene oxide in the ratio 35:65.²¹⁷

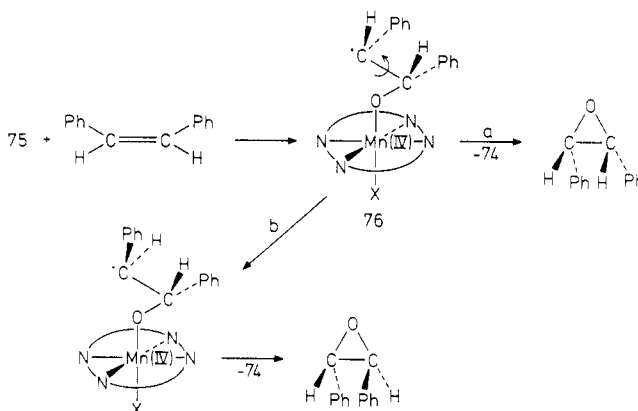
Hypochlorite is a convenient oxygen source for manganese porphyrin catalyzed epoxidations. The catalytic system NaOCl/Mn(Por)X is a relatively poor epoxidation system, but considerable improvement of the catalytic system can be obtained when small quantities of nitrogen bases, e.g., pyridine or *N*-methylimidazole, are added.²¹⁸⁻²²⁸ These nitrogen bases act as axial ligands of the catalyst and increase the reaction rate, the selectivity for epoxide formation, and the stereoselectivity. In the absence of pyridine the *cis*:*trans* ratio for epoxidation of *cis*-stilbene is 35:65, whereas with pyridine a ratio up to 94:6 has been found.²²¹ This influence of nitrogen bases applies also to some other oxygen donors, e.g., iodosylbenzene.

Molecular oxygen in the presence of a reductant, e.g., H₂/Pt, Zn, or ascorbate, and manganese porphyrins constitute also an epoxidation system, and the catalytic properties can also be improved by addition of imidazole.²²⁹⁻²³⁴ The reactivity of alkenes with Mn(TPP)-

SCHEME 11



SCHEME 12



Cl/O₂-Pt as catalyst is similar to that observed for Mn(TPP)Cl/PhIO, indicating that an oxomanganese species of a similar nature could be involved. The Mn(TTP)OAc/O₂-H₂/Pt system epoxidizes the double bond in geraniol acetate remote from the acetate group as opposed to the TBHP/VO(acac)₂ system.²³⁰

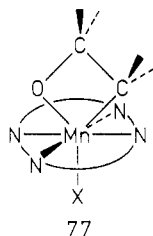
Alkyl and hydrogen peroxides can also be applied as oxidants catalyzed by manganese porphyrins,²³⁵⁻²³⁷ but the major problem is to diminish the homolytic cleavage of the peroxide bond, which leads to the formation of a radical. The homolytic oxidation, corresponding to a one-electron transfer, and the heterolytic oxidation, corresponding to a two-electron transfer, of manganese porphyrins by a peroxide are shown in Scheme 11. In the absence of imidazole only traces of epoxide are observed when alkyl peroxides are used as terminal oxidant, whereas in the presence of imidazole epoxidation occurs with yields comparable to those obtained with iodosylbenzene as terminal oxidant.²³⁵

Amine *N*-oxides as terminal oxidants are also useful in catalytic oxygenation reactions. The attention has here mainly been focused on the kinetics of the reactions, and it has been observed that the slow step is the formation of the high-valent oxomanganese complex with the amine *N*-oxide.²³⁸

The reactivity of the alkenes found in these manganese porphyrin catalyzed epoxidations is mainly such that electron-rich alkenes react faster than electron-poor alkenes.^{214,239}

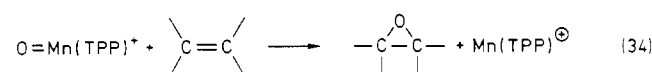
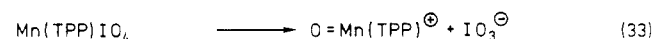
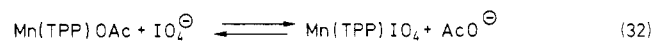
The loss of stereochemistry in the epoxidation of alkenes catalyzed by manganese porphyrins can be explained by the formation of a radical intermediate 76 with a long enough lifetime to allow isomerization by rotation around the carbon-carbon bond (Scheme 12).

A metallacyclic intermediate 77 has also been suggested.²²⁴



Arguments have been presented against the presence of a radical species in the dominant reaction pathway and against the oxomanganese porphyrin alkene having radicaloid character.^{224,240}

Mn(TTP)⁺ with ClO₄⁻ and IO₄⁻ as oxidants is able to epoxidize alkenes photocatalytically.²⁴¹ It has been suggested that the reactive intermediate is an oxomanganese-porphyrin complex, and the following mechanism has been suggested:²⁴¹



Photolysis of Cr(TPP)ClO₄ produces the stable species O=Cr(TPP), which supports the involvement of an oxomanganese-porphyrin intermediate.²⁴¹

Cationic manganese(III)-salen complexes are also effective catalysts for the epoxidation of various alkenes with iodosylbenzene as the terminal oxidant.²⁴² The presence of electron-withdrawing groups in the salen ligand enhances the catalytic activity.²⁴² Epoxidations of *cis*-alkenes catalyzed by manganese(III)-salen complexes produce high yields of *cis*-epoxides with only minor amounts of the corresponding *trans* isomer. The addition of donor ligands such as pyridine or pyridine *N*-oxide increases the yield of epoxide when especially electron-poor alkenes are epoxidized by the manganese(III)-salen-iodosylbenzene system.²⁴² The stereochemistry of the oxygen transfer from the oxomanganese-salen complex to the alkene depends on the electronic environment around the oxomanganese function. The stereoselectivity is best with electron-withdrawing substituents in the salen ligand, which is compatible with a radical intermediate (like 76) if the rate of ring closure (Scheme 12, path a) relative to that of bond rotation (Scheme 12, path b) is controlled by the electron-deficient manganese center. The corresponding manganese(II)-salen complex also shows catalytic activity, but is less soluble in acetonitrile than the manganese(III)-salen complexes.²⁴²

Two pathways have been observed for the epoxidation of alkenes using alkyl hydroperoxides or iodosylbenzene as oxidants catalyzed by manganese(III)-salen complexes.²⁴³ With TBHP as terminal oxidant and cyclohexene as substrate both (*tert*-butylperoxy)cyclohexene and cyclohexene oxide have been identified.²⁴³ The pathway leading to (*tert*-butylperoxy)cyclohexene involves a free radical chain mechanism, which is completely inhibited by a radical scavenger (ionol). The presence of ionol during the reaction does not affect the epoxidation when alkenes are treated with TBHP-pyridine and a catalytic amount of Mn(III)-salen. The epoxide is formed via an oxo-

manganese(V) complex, and there is no distinction between iodosylbenzene and TBHP-pyridine as terminal oxidants.²⁴³

A few other manganese-ligand complexes have also been prepared and show catalytic properties. Manganese(III)-amide complexes have been found to catalyze the epoxidation of alkenes in the presence of iodosylbenzene,²⁴⁴ and manganese(II)-salicylidene-amino acid complexes containing different amino acids have also been shown to be effective catalysts for alkene epoxidation.²⁴⁵ The manganese(II)-salicylidene-amino acid complex containing L-phenylalanine as amino acid has been found to be able to epoxidize styrene to styrene oxide with about 5% ee.²⁴⁵ A manganese polyoxotungstate, (*n*-Bu₄N)₄H(Mn)PW₁₁O₃₉, a member of a soluble class of inorganic complexes is also a catalyst for oxygen transfer from oxygen donors such as iodosylbenzene or aniline *N*-oxide to alkenes.²⁴⁶ The catalytically active site in the manganese polyoxotungstate resides in a completely inorganic ligand environment containing only oxidatively stable oxide and d⁰ tungsten ions.²⁴⁶

The permanganate ion, MnO₄⁻, can, in isolated cases, convert alkenes to epoxides,²⁴⁷⁻²⁴⁹ but further oxidation is usually observed.

2. Tc and Re

Several complexes of the long-lived ⁹⁹Tc isotope, formed by fission of ²³⁵U, have been prepared and tested for catalytic activity in epoxidation reactions.^{250,251} The technetium complexes are poor epoxidation catalysts with TBHP as oxidant. The catalytic activity of technetium seems to be comparable to that of rhenium, which also has been tested, and both seem to be low.²⁵⁰

VI. Fe, Ru, and Os

1. Fe

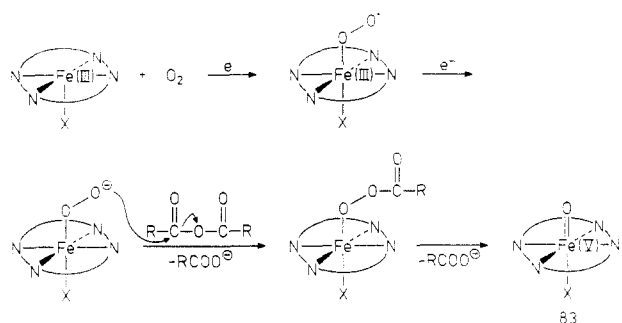
The interest in iron complexes as catalysts for alkene epoxidations is in many respects parallel to that for the manganese complexes, and many similarities between iron and manganese complex catalyzed epoxidations are observed. But the iron porphyrin catalyzed epoxidations show some properties that are not observed when manganese porphyrins are used as catalyst.²¹⁴ The same oxygen sources useful in the case of manganese complexes can also be applied as terminal oxidants when iron complexes are used for alkene epoxidation.

Fe(acac)₃ with hydrogen peroxide as oxygen donor catalyzes the epoxidation of alkenes, but *trans*-epoxides are obtained as the major product when *cis*-alkenes are used as substrates.²⁵² However, the iron(III) chloride-hydrogen peroxide system for epoxidation of a *cis*-alkene gave mainly the corresponding *cis*-epoxide.²⁵³ Using iodosylbenzene as terminal oxidant affords mainly *cis*-epoxides from *cis*-alkenes when iron(III) triflate²¹⁶ and iron(III) acac²⁵⁴ are catalysts, whereas with iron(III) chloride, *trans*-epoxides are obtained.²⁵⁴

Molecular oxygen in the presence of Fe(acac)₃ and egg lecithin gave a small yield of epoxide when cholesterol was used as substrate.²⁵⁵

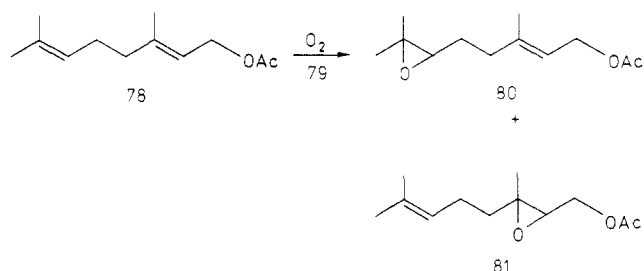
The binuclear iron complexes (Me₄N)[Fe₂L(OAc)₂] catalyze the epoxidation of alkenes along with the formation of byproducts due to autoxidation when hydrogen peroxide is used as oxygen donor.²⁵⁶ The ep-

SCHEME 13



oxidation of *cis*-stilbene by the binuclear complex results in a *trans*:*cis* ratio of the epoxide similar to the results found for $\text{Fe}(\text{acac})_3/\text{H}_2\text{O}_2$.²⁵²

The (μ_3 -oxo)triiron cluster complexes $[\text{Fe}_3\text{O}(\text{OCOR})_6\text{L}_3]^+$ catalyze the epoxidation of alkenes by molecular oxygen.²⁵⁷ Treatment of geranyl acetate (78) with $[\text{Fe}_3\text{O}(\text{piv})_6(\text{MeOH})_3]\text{Cl}$ (79) under molecular ox-



xygen produced only 6,7-epoxygeranyl acetate (80), and no isomeric 2,3-epoxide 81 could be detected.²⁵⁷ These results are thus very similar to the results obtained in the epoxidation of 78 by the $\text{Mn}(\text{TTP})\text{OAc}/\text{O}_2\text{-H}_2/\text{Pt}$ system.²³⁰ Other (μ_3 -oxo)triiron complexes such as $[\text{Fe}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{OAc}$ and $[\text{Fe}_3\text{O}(\text{OAc})_6\text{Py}_3]\text{Cl}$ are also efficient catalysts for epoxidation.²⁵⁷

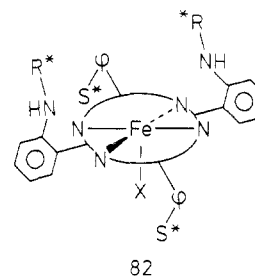
A series of iron(III) amino acid linked bipyridines have also been prepared and tested for catalytic activity in alkene epoxidation.²⁵⁸ They were found to catalyze alkenes with iodosylbenzene as terminal oxidant.²⁵⁸ Analysis of the stereoselectivity of styrene oxide formation revealed an essentially racemic product.²⁵⁸

The iron porphyrin catalysts for alkene epoxidation have attracted much interest due to their relationship to oxidation reactions in biological systems. Many types of iron porphyrins have been prepared and tested for catalytic activity under a variety of conditions.²¹⁴ Relatively high yields of epoxides can be obtained, but in the case of oxidations with iodosylbenzene, most yields of oxidation products are expressed with respect to the terminal oxidant, which often hides a low conversion of the organic substrate.²¹⁴

The epoxidation of alkenes catalyzed by $\text{Fe}(\text{TTP})\text{Cl}$ and iodosylbenzene as oxygen donor is performed in a stereospecific way; *cis*-alkenes give only the corresponding *cis*-epoxides.^{259,260} The reaction yields can be improved by replacing the phenyl groups in the porphyrin moiety with perfluorinated phenyls.²⁶² The *cis*-alkenes are epoxidized much faster than the *trans* isomers, and it has been possible to selectively epoxidize the *cis* double bond of *trans,trans,cis*-cyclo-dodecatriene.²⁶⁰ This double bond is less well epoxidized by peracids than the *trans* double bonds.²⁶⁰ It has been found that besides epoxide formation, aldehydic products can be observed and that these do not

originate from a rearrangement of the epoxide, but from a hydrogen transfer during the primary reaction.²⁶²⁻²⁶⁴

Chiral "basket handle" iron porphyrins 82 with iodosylmesitylene as terminal oxidant achieve probably the highest asymmetric induction in isolated alkenes.^{262,265} Up to 51% ee in the epoxidation of *p*-chlorostyrene has been achieved when iron(III) [(binaphthylcarboxamido)phenyl]porphyrin chloride, 82, was used as chiral auxiliary.²⁶⁰ The steric environment



of the alkene has a pronounced effect on the asymmetric induction.²⁶⁰ Substitution of the double bond decreases the ee, and attempts to oxidize 1-methylcyclohexene with ee failed.²⁶⁰

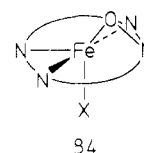
Iron(III) porphyrins have also been applied as catalysts with hypochlorite as oxygen source,^{219,266,267} but the catalytic activity is often lower than in the corresponding manganese systems. There are examples of successful epoxidations of alkenes by the iron(III) porphyrin-hypochlorite systems in the absence of an axial ligand, and it has been observed that the presence of 1-(triphenylmethyl)imidazole lowered the catalytic activity of some iron(III) porphyrins.²⁶⁷

The reactive oxoiron porphyrin intermediate 83, which probably achieves the epoxidation, can also be prepared with molecular oxygen, and it has been shown that acid anhydrides can help to break the oxygen-oxygen bond after the coordination of molecular oxygen to iron (Scheme 13).²⁶⁸ Complex 83 can also be prepared from $\text{Fe}(\text{Por})\text{Cl}/\text{O}_2/\text{H}_2\text{-Pt}$.²¹⁴

Alkyl and hydrogen peroxides have also been applied as terminal oxidants, but the catalytic activity of $\text{Fe}(\text{TPP})\text{Cl}$ is lower compared to that of $\text{Mn}(\text{TPP})\text{Cl}$.^{214,224} Also here the major problem is the homolytic fission of the peroxygen bond.

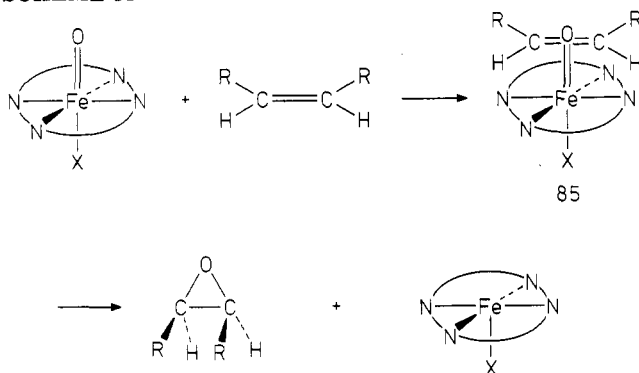
The mechanism for the transfer of oxygen from the oxoiron porphyrins to an alkene has received considerable attention, and many attempts from mainly experimental^{214,259,260,264,269-273} but also theoretical^{274,275} points of view have been performed to elucidate the mechanism.

Oxoiron porphyrins are very unstable and highly reactive species, and structural information is very restricted. Two structures have been suggested for the oxoiron porphyrin complex: one is the ferryl complex shown in 83²⁷⁶ and the other is one in which oxygen has been inserted into the iron-nitrogen bond, 84.^{212,275,277-280}



The ferryl complex 83 is similar to the oxochromium(V)-salen and -TTP complexes, which have been characterized by means of X-ray crystallography.¹²⁶⁻¹²⁸ The structure of 84 is related to the carbene

SCHEME 14



and nitrene analogue where it has been found that the carbene²⁷⁷ and nitrene²⁸¹ group can be inserted into the iron–nitrogen bond. A nickel analogue of 84 has also been characterized.²⁸² Several theoretical calculations indicate that 84 should be more stable than 83.^{275,278,280}

With a ferryl complex 82 as the reactive intermediate, several mechanisms, some of which are related to those for manganese porphyrins discussed previously, have been suggested. But to account for the stereoselective epoxidation of *cis*-alkenes catalyzed by iron porphyrins, as well as some other related complexes, the mechanism in Scheme 14 has been suggested.²⁶⁰

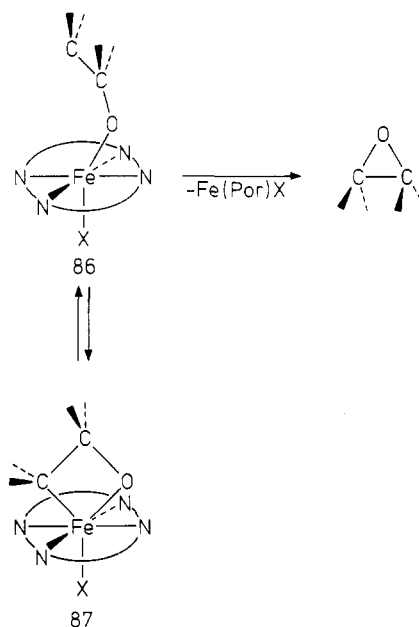
The alkene approaches the oxoiron bond from the side and parallel to the plane of the porphyrin ring, 85. The oxoiron porphyrin complex is characterized by having antibonding combinations of iron d_{π} and oxygen p_{π} orbitals, and the alkene interacts with one of these orbitals.²⁶⁰ The involvement of an acyclic metal–oxo carbocation has also been suggested.²⁷²

With 83 assumed to be the reactive intermediate for alkene epoxidation, attempts have been made to explain the oxygen-transfer process by means of extended-Hückel calculations.²⁷⁴ Four hydride ions were used as a model for the porphyrin ring.²⁷⁴ The preferred approach of ethene corresponds to only one carbon atom of the ethene interacting with oxygen, 86 (Scheme 15).²⁷⁴ The calculations indicate that the metallacycle 87 could be formed during the reaction course but that the formation of ethylene oxide takes place via the open intermediate rather than by reductive elimination from the metallacycle.²⁷⁴ The theoretical study also showed that along the various reaction paths one-electron-transfer mechanisms are likely to occur, and experimentally it has been observed that rearrangements of alkenes, known to proceed through the intermediacy of an alkene cation radical, accompany the Fe(TPP)Cl-catalyzed epoxidation of these alkenes.^{283–285} The approach of the alkene as outlined in 86 does not explain the stereoselectivity of the epoxidation.

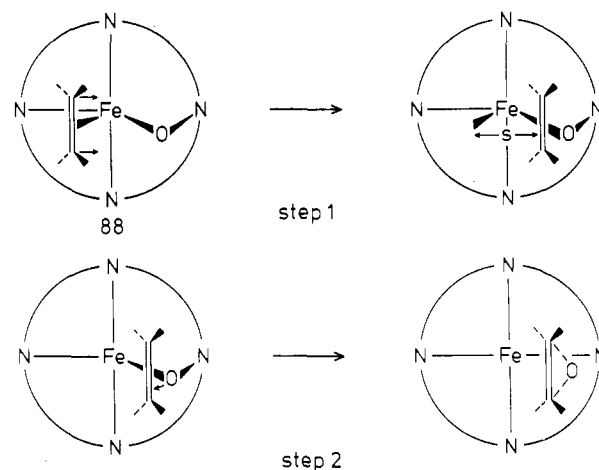
In an attempt to explain the stereoselective epoxidation of *cis*-alkenes by oxoiron porphyrins, extended-Hückel and INDO calculations have been performed.²⁷⁵ This investigation takes its starting point in 84 as the reactive intermediate. The approach of an alkene to 84 is shown in 88 in Scheme 16.²⁷⁵ The most favorable orientation of the alkene is perpendicular relative to the iron–oxygen bond.²⁶⁸

The next step in this reaction mechanism is then a slipping motion of the alkene toward oxygen (step 1, Scheme 16). This motion is controlled by favorable interaction between the π^* orbital of the alkene and the

SCHEME 15



SCHEME 16



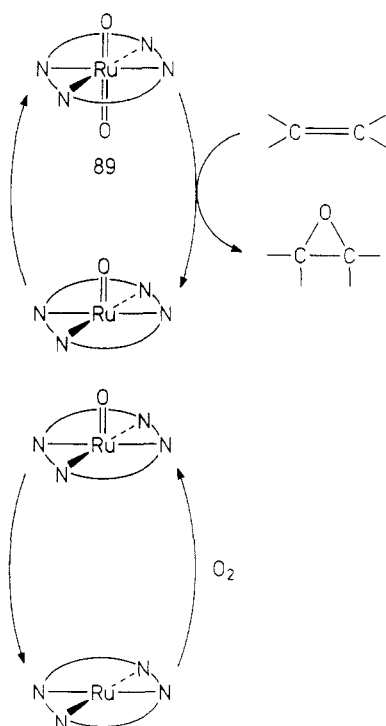
electrons at oxygen, which is antisymmetric with respect to the iron–oxygen–nitrogen plane. Interaction between the π orbital of the alkene and an acceptor orbital at oxygen is also observed, making the attack of the alkene a nucleophilic character. With this reaction mechanism *cis*-alkenes will thus have a preference for interaction with the oxygen since substituents in the *trans*-alkenes will interact repulsively with the porphyrin ring or substituents in the 5 α , 10 α , 15 α , and 20 α positions of the porphyrin ring.²⁷⁵

The mechanism suggested for the stereoselective epoxidation of *cis*-alkenes outlined in Scheme 16 is to a certain extent similar to the one shown in Scheme 14, the main difference being that the oxygen in the oxoiron porphyrin in 88 in Scheme 14 is tilted toward one of the nitrogens.

2. Ru and Os

Ruthenium(II) complexes such as RuCl₂(PPh₃)₃ in combination with molecular oxygen or TBHP epoxidize alkenes in low yields.^{147,286,287} With a ruthenium(III) bipyridyl complex as catalyst and sodium periodate as oxidant, it has been found, with the exception of substrates with terminal double bonds, that alkenes can be

SCHEME 17



oxidized to epoxides in a stereospecific way, rather than to ketones or carboxylic acid.²⁸⁸ With bipyridyl as ligand, ruthenium(II) can also be applied as catalyst.²⁸⁹

Dioxo(tetramesitylporphyrinato)ruthenium(VI) (89) is able to catalyze the epoxidation of alkenes with molecular oxygen²⁹⁰ or iodosylbenzene²⁹¹ as oxidant. The epoxidation is nearly stereospecific; cf. the corresponding iron and chromium systems.²⁹⁰ It has also been observed that the *cis*-alkene is much more reactive than the *trans*-alkene. The mechanism in Scheme 17 has been suggested.

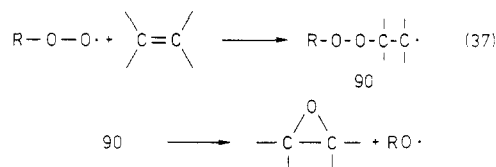
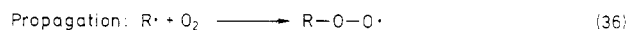
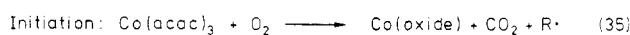
A dioxo(phenanthroline)ruthenium(VI) complex has also been applied as catalyst for alkene epoxidation with molecular oxygen as oxidant.²⁹² The oxo(phenanthroline)ruthenium(IV) complex also shows catalytic activity.²⁹² A ruthenium(III)-phenanthroline complex is also an epoxidation catalyst, but with iodosylbenzene as terminal oxidant.²⁹³ Coordination of a tetraanionic chelating agent (1,2-bis(3,5-dichloro-2-hydroxybenz-amido)ethane) to ruthenium(IV) affords a complex that shows catalytic properties with iodosylbenzene as oxidant.²⁹⁴ Photochemical epoxidation by *trans*-dioxo complexes of ruthenium(VI) and osmium(VI) has also been reported.²⁹⁵

A few osmium(III) porphyrins have also been prepared and found to possess catalytic activity, but compared to the iron porphyrins the reaction time is longer and the yield of epoxides lower.²⁹⁶ Replacement of iodosylbenzene by TBHP gave cyclohexenol as the major product in the catalyzed oxidation of cyclohexene, indicating a radical reaction path.²⁹⁶ An osmium(III) complex containing 1,2-bis(2-pyridinecarboxamido)benzene as ligand can also catalyze the epoxidation of cyclohexene in the presence of iodosylbenzene.²⁹⁷

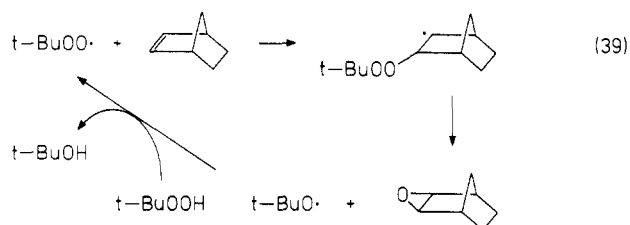
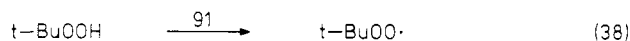
VII. Co, Rh, and Ir

The use of cobalt, rhodium, and iridium complexes as catalysts for alkene epoxidation is rather limited. However, cobalt complexes are very effective catalysts

SCHEME 18



SCHEME 19



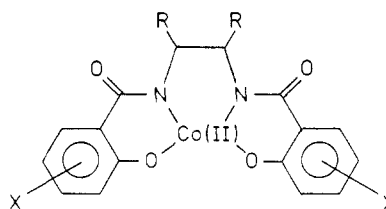
for autoxidations, and some of the work done with alkene epoxidations is related to the autoxidation of molecular oxygen.⁸

1. Co

Co(acac)_2 and Co(acac)_3 catalyze the epoxidation of alkenes with TBHP as oxygen donor, but yields are low and long reaction times are required.²⁹⁸ Co(acac)_3 and molecular oxygen epoxidize alkenes in which abstraction of an allylic hydrogen is disfavored compared to addition to the $\text{C}=\text{C}$ double bond.²⁹⁹ Azobis(isobutyronitrile) increases the yields of epoxides without significantly changing the distribution of the products whereas radical inhibitors retard the formation of epoxides.²⁹⁹ The cobalt complex serves as an initiator by the generation of radicals (Scheme 18, (35)).²⁹⁹ The next step is formation of a peroxy radical by reaction with molecular oxygen (reaction 36), followed by addition of the peroxy radical to the alkene, leading to **90** (Scheme 18, (37)). The epoxide is formed by fragmentation of **90**.

The cobalt system is also able to form an oxo-cobalt complex which can achieve epoxidation of alkenes. The use of cobalt(II) triflate or nitrate as catalysts and iodosylbenzene as terminal oxidant allows epoxidation of a variety of alkenes.²¹⁶ The yields of epoxides are <77% and the reaction is nonstereoselective.²¹⁶ In the epoxidation of *cis*-stilbene, *trans*-stilbene was found as the major product.²¹⁶

Cobalt(II) bis(salicylamide) (91) and related complexes are able to catalyze the epoxidation of alkenes by two different pathways.³⁰⁰ With TBHP as terminal



91

oxidant, a radical chain mechanism is operative by which the *tert*-butylhydroperoxy radical adds homolytically to the C=C double bonds of systems in which the allylic hydrogen is less reactive than the C=C double bond (reaction 39).³⁰⁰ This reaction is effectively inhibited by ionol.³⁰⁰ The mechanism in Scheme 19 has been proposed.³⁰⁰

The reaction outlined in Scheme 19 is associated with the Co(II)/Co(III) interconversion in the one-electron redox process by which the *tert*-butylperoxy radical is formed (reaction 38).

Complex **91** can also undergo a two-electron oxidation by iodosylbenzene, forming an oxocobalt(IV) species that can epoxidize a variety of alkenes.³⁰⁰ The oxygen atom transfer to the alkene proceeds with very high, but not exclusive, stereospecificity.³⁰⁰ The cobalt catalysis of epoxidation by **91** has been compared with the catalytic properties of chromium(III)-salen and manganese(III)-salen complexes, and **91** seems to be slightly more active than the two other complexes.³⁰⁰ The mechanism for the oxygen transfer from the oxocobalt complex to the alkene is probably very similar to that of the oxygen transfer from the oxochromium and oxomanganese complexes to an alkene.

Cobalt porphyrins have also been used as catalysts of alkene epoxidation: propylene has been epoxidized with perbenzoic acid generated in situ in the presence of Co^{II}(*p*-CH₃-TTP) as catalyst and oxygen as terminal oxidant.³⁰¹ Styrene has been converted to styrene oxide with sodium hypochlorite catalyzed by Co^{III}(TPPP)Br, but the catalytic activity of the cobalt complex is lower than that of the corresponding manganese complex.²¹⁹ Molecular oxygen in the presence of cobalt porphyrins can also epoxidize styrene.³⁰²

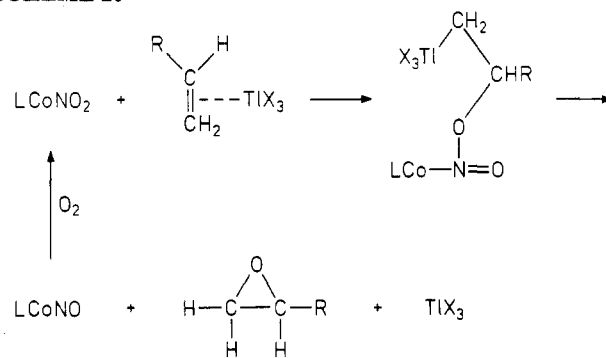
Alkene epoxidation in the presence of cobalt(II) as well as some other transition-metal complexes by peroxyacids has been found to proceed via two distinct processes, one initiated by the peroxyacid and cobalt(II) and the other by the peroxyacid alone.³⁰³ The reaction is nonstereospecific and the first step in the cobalt(II)-initiated reaction proceeds via a one-electron reductive cleavage of the peroxyacid by cobalt(II).³⁰³ The oxy radical reacts with the alkene to give a β -hydroxyalkyl radical that cyclizes to the epoxide.³⁰³ The radical-initiated reaction is observed to proceed faster than the peroxyacid epoxidation, but the latter gives the highest yields of epoxides.³⁰³

The one- and two-electron pathways involving cobalt complexes for alkene epoxidation are not the only way cobalt complexes can mediate alkene epoxidation. Cobalt-nitro complexes can transfer an oxygen atom to alkenes activated by thallium(III) (Scheme 20).³⁰⁴ The cobalt-nitrosyl complex can be reoxidized to the nitro complex by molecular oxygen.³⁰⁴ The first step in the reaction depicted in Scheme 20 is probably a nucleophilic attack of one of the oxygens in the nitro group on the activated alkene in a similar way to the nucleophilic attack on metal-activated alkenes.³⁰⁵

2. Rh and Ir

Rhodium(I) complexes can activate molecular oxygen and oxidize cyclohexenes to a variety of products, the epoxide being one of them.^{147,306-308} A series of rhodium(II) carboxylate-*d*⁰ transition metal complexes can also act as catalysts for alkene epoxidation with mo-

SCHEME 20



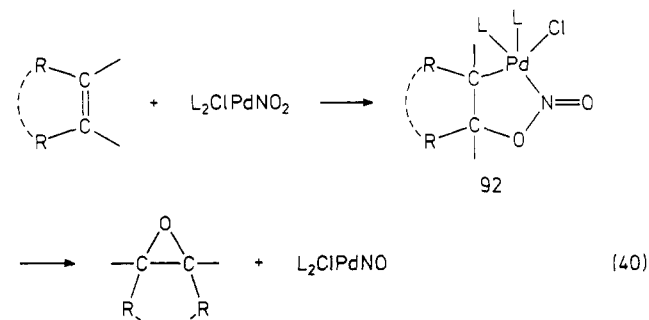
lecular oxygen as oxidant.³⁰⁹ It has been suggested that the two complexes act separately in a stepwise mechanism of the oxidation. Each step corresponds to a particular catalyst:³⁰⁹ the rhodium complex promotes in the case of cyclohexene the formation of cyclohexenyl hydroperoxide (autoxidation), which then is used by the *d*⁰ transition metals in their reaction with the alkene.

Iridium complexes can also utilize molecular oxygen as oxidant, and epoxidation of cyclic alkenes and of styrene has been observed together with the formation of other oxidation products.^{310,311}

VII. Ni, Pd, and Pt

Only a few investigations have focused on nickel catalysis of alkene epoxidation. Soluble nickel(II) salts are, unlike their iron(II), manganese(II), cobalt(II), and copper(II) counterparts, completely ineffective in the catalytic epoxidation of alkenes with iodosylbenzene as terminal oxidant.²¹⁶ However, the complexation of nickel(II) to tetraaza macrocycles as well as to other ligands affords systems that can act as catalysts for alkene epoxidation.^{147,312} The nickel(II) system was found to be a better catalyst than the nickel(III) system.³¹² The nickel(II) ligand complexes can achieve catalytic epoxidation of a variety of alkenes with iodosylbenzene as terminal oxidant,³¹² but the reaction is nonstereospecific as epoxidation of *cis*- β -methylstyrene afforded a ~2:1 mixture of the *cis*- and *trans*-epoxides.³¹² Iodosylbenzene and the nickel(II) complex probably form an oxonickel(IV) intermediate that transfers oxygen to the alkene in a similar way as the other oxotransition-metal complex systems.

Palladium(II)-nitro complexes are able to epoxidize cyclic alkenes, but low yields of the epoxides are obtained (reaction 40).³¹³⁻³¹⁵ The epoxide is probably



formed by fragmentation of a palladacycle intermediate, **92**, formed by the addition of the alkene to one of the oxygens in the nitro group and to palladium.³¹³⁻³¹⁵ The palladium-nitrosyl complex can be reoxidized to the

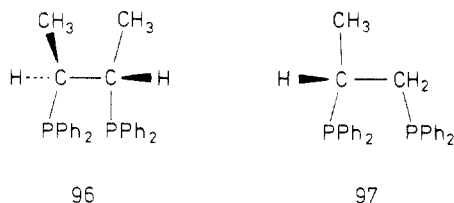
nitro complex by molecular oxygen. Molecular oxygen can also be utilized as oxidant in another way:³¹⁶ reaction of azibenzil with molecular oxygen in the presence of palladium(II) acetate gives an intermediate that can transfer an oxygen atom to alkenes.³¹⁶ The reaction is nonstereospecific and byproducts are often observed.³¹⁶ Other palladium(II) compounds are also effective catalysts for this reaction.³¹⁶ Copper(II) and nickel(II) complexes need longer times and higher temperatures to accomplish the reaction, and yields are lower than with palladium.³¹⁶

α -(Silyloxy)alkyl peroxobenzoates **93** can act as terminal oxidants in the presence of palladium(II) catalysts to give epoxides.³¹⁷ The epoxidation is nonstereospecific, and a stepwise mechanism with an intermediate that can rotate has been suggested.³¹⁷ Based on ¹⁸O-labeling studies and the structures of rearranged products, the mechanism in Scheme 21 has been outlined. It is assumed that it is an oxopalladium(IV) complex, **94**, that acts as the oxygen-transfer reagent,³¹⁷ but a palladium(II)-peroxobenzoate species similar to that observed for platinum(II)-dioxygen complexes might also be involved.³¹⁸

Platinum(II)-dioxygen complexes do not react with alkenes, but in the presence of stoichiometric amounts of benzoyl chloride a smooth reaction takes place, probably via a benzylperoxy-platinum(II) intermediate.^{318,319}

Diluted hydrogen peroxide and hydroxy-platinum(II) complexes are effective systems for the selective epoxidation of terminal alkenes,^{320,321} whereas attempts to epoxidize cyclohexene and *cis*-2-hexene failed.³²⁰ The hydroxy-platinum(II) complex is in equilibrium with the platinum cation and the hydroxide anion, which abstracts a proton from hydrogen peroxide. The alkene coordinates to the platinum cation, and the hydrogen peroxide anion performs a nucleophilic attack on the coordinated alkene, which leads to **95**.^{305,321} The suggested mechanism for the formation of the epoxides is shown in Scheme 22.³²¹

Introducing chiral phosphines, e.g., (-)-2(*S*),3(*S*)-bis(diphenylphosphino)butane (**96**) or (+)-2(*R*)-bis(diphenylphosphino)propane (**97**) in the hydroxy-platinum(II) complex leads to catalysts that are capable of asymmetric epoxidation of simple alkenes.³²² The

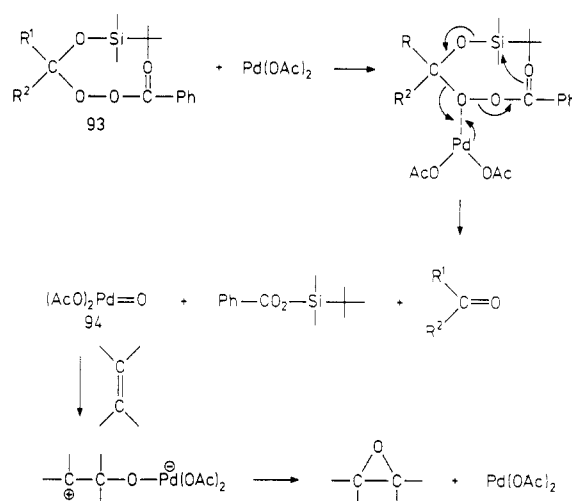


highest asymmetric induction was obtained with **96** as chiral ligand in the epoxidation of propene, where 41% ee of the *S* enantiomer was obtained.³²² Under similar conditions the complex with **97** as chiral ligand afforded 35% ee, but of the *R* enantiomer.³²² The *S* enantiomer is always preferentially produced with **96** as chiral ligand, while the *R* enantiomer is preferred with **97** as chiral ligand at platinum.³²²

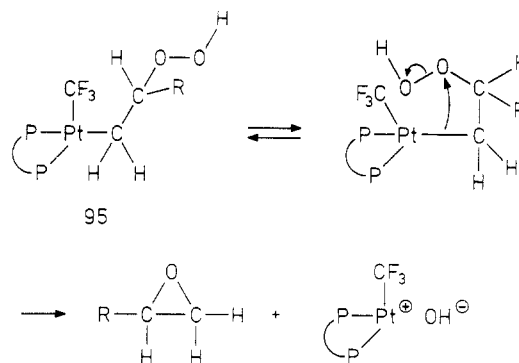
IX. Cu, Au, and Ag

Copper and gold complexes have not been intensively studied as epoxidation catalysts, whereas silver, in

SCHEME 21



SCHEME 22



different forms of single crystals and surfaces, has been very intensively studied. The selective epoxidation of ethylene to ethylene oxide is an important process from both a fundamental and practical point of view, and silver catalysts are used in industry for this reaction.

1. Cu and Au

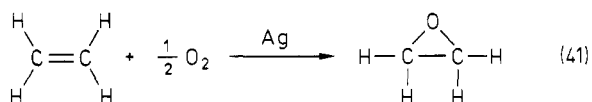
Copper(II) nitrate and triflate can catalyze the epoxidation of alkenes with iodosylbenzene as terminal oxidant.^{216,323} The reaction is nonstereospecific; the only oxidized product obtained from *cis*-stilbene was *trans*-stilbene oxide together with *trans*-stilbene.^{216,323} Several mono- and binuclear copper complexes have also been tested for catalytic activity, and the binuclear complexes were found to be more active than the mononuclear complexes.³²⁴ A reaction utilizing $\text{Cu}(\text{OCO}-\text{CF}_3)_2$ instead of $\text{Pd}(\text{OAc})_2$ (Scheme 21) as catalyst with α -(silyloxy)alkyl peroxobenzoates as terminal oxidant for alkene epoxidation has also been described.³²⁵

Low yields of epoxides can also be obtained when β -hydroxyalkyl radicals are oxidized by copper(II)³²⁶ or in a mixed palladium(II)-copper(II) system.³²⁷

Gold complexes such as $\text{Au}(\text{PPh}_3)_3\text{Cl}$, a d^{10} complex, can achieve epoxidation of cyclohexene in low yield with molecular oxygen as oxidant.³⁰⁶ The gold complex $\text{Au}(\text{PPh}_3)_3\text{Cl}$ was found to be slightly more active as catalyst than the isoelectronic platinum complex $\text{Pt}(\text{PPh}_3)_3$, but the activity of the d^{10} complexes is generally lower than that of the d^8 complexes.³⁰⁶

2. Ag

Silver is a uniquely effective catalyst for heterogeneous epoxidation with molecular oxygen as oxidant, but the reaction is mainly restricted to the selective oxidation of ethylene to ethylene oxide (reaction 41).³²⁸⁻³³⁰ The epoxidation of alkenes other than



ethylene results in low epoxide yields, and little use of silver catalysts has been made for other alkenes. But it should be noted that styrene with no β -hydrogen is reported to give good yields of styrene oxide.³³¹ The selectivity of the reaction (number of moles of ethylene oxide produced divided by the total number of moles of ethylene consumed) has been found to be about 45% on a clean silver catalyst.³³² However, in the presence of moderators such as chlorine, alkali metals, or alkaline earth metals the selectivity increases to 87%.^{328-330,332-334} The remaining ethylene undergoes combustion to carbon dioxide and water.³²⁸⁻³³⁰

The epoxidation of ethylene catalyzed by a silver surface with molecular oxygen as oxidant is not stereoselective. Epoxidation of *cis*-1,2-dideuterioethylene leads to a substantial amount of the *trans*-epoxide, and the corresponding *trans*-alkene produces some *cis*-epoxide.³³⁵⁻³³⁷ In one study about 70% retention³³⁵ of the original conformation was found in the product epoxide, whereas others have observed that the epoxide products are nearly equilibrated.^{336,337}

Two fundamental questions remain unanswered for silver-catalyzed epoxidation of ethylene: (a) what is the identity of the surface oxygen species responsible for the epoxidation and (b) how does the oxygen-transfer process take place?

Most data obtained when silver is exposed to oxygen are consistent with the occurrence of more than one adsorption process. Three types of oxygen have been observed, molecular, atomic, and subsurface oxygen; the adsorption processes have also been described as an "almost nonactivated" dissociative adsorption and a nondissociative adsorption.^{328,338,339} The chemisorbed molecular oxygen on silver has been known for some time and characterized by a variety of techniques.^{326,328} The adsorbed molecular oxygen has been described as "superoxide-like" (O_2^-),^{328-330,338,340,341} and the ESR signal of oxygen adsorbed on silver shows g values typical of the suboxide radical;³⁴² however, a "peroxide-like" species (O_2^{2-}) has also been suggested.^{328,343-346} Adsorbed atomic oxygen on silver has also been characterized by a variety of techniques.³³⁰

Both mechanisms involving atomic^{330,347} and molecular oxygen³²⁹ for the epoxidation of ethylene have been suggested.

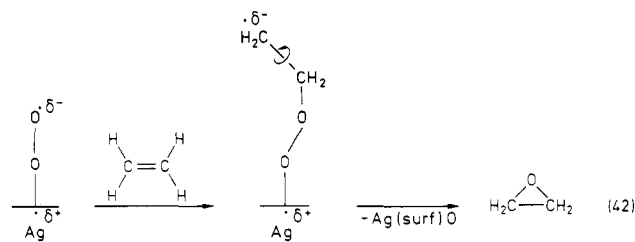
The evidence for molecular oxygen as the active species for epoxidation is rather indirect with respect to reaction selectivity or promoter effects, but more direct evidence for this mechanism has been obtained by several studies: e.g., nitrogen oxide as an oxygen atom donor afforded only the combustion reaction.^{348,349} Increasing the nitrogen oxide pressure favors the formation of molecular oxygen and the epoxidation is then the primary reaction.^{348,349} The principal argument against the molecular oxygen mechanism has been the

low coverages of suboxide species detected on silver surfaces.^{350,351}

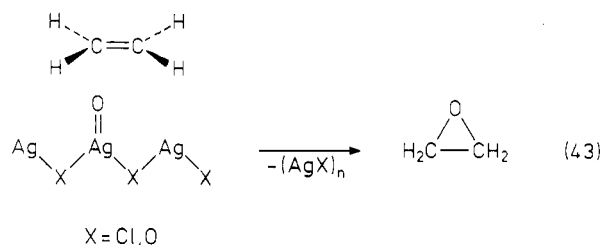
Considerable attention has been devoted to the effect of moderator species upon the catalyst activity and selectivity for ethylene epoxidation. It has been shown that elements that are more electronegative than silver tend to increase the selectivity of the reaction while those that are electropositive relative to silver have the opposite effect.^{328-330,352} However, the use of alkali promoters has also been shown to increase the selectivity, but not necessarily the activity, of the catalyst.³⁵³ The catalyst activity and selectivity may be well correlated with the surface work function, with electronegative moderators increasing the work function,³⁵⁴ which is consistent with a model in which ethylene is epoxidized by a molecular oxygen species.³²⁸ The effect of alkali moderators, e.g., cesium, is to block acidic sites on the surface, thereby inhibiting isomerization of ethylene oxide to acetaldehyde and further oxidation.^{353,355}

Ag(110) and Ag(111) surfaces are found to be better catalysts than those that have been reported for high-surface-area catalysts, the former being the most active.^{328-330,356,357} However, by using a single-crystal Ag(111) surface it has been demonstrated that stable molecular oxygen plays no direct role in the epoxidation reaction, but that it is chemisorbed atomic oxygen that is the surface species that selectively oxidizes ethylene to ethylene oxide.³⁴⁷

A mechanism involving addition of molecular and atomic oxygen adsorbed on a silver surface to ethylene has been suggested. IR investigations reveal a surface peroxy species: $\text{H}_2\text{C}-\text{CH}_2-\text{O}-\text{O}-\text{Ag}(\text{surface})$, which on heating gives a spectrum identical with that obtained when ethylene oxide was absorbed on a reduced silver surface.^{358,359} These results together with the stereochemistry of the reaction, could indicate the following path:



The mechanism involving atomic oxygen is outlined in (43).³²⁹



With oxygen coordinated to the silver surface as peroxygen, a mechanism involving a peroxometallacycle like the one suggested for epoxidation by molybdenum-peroxo complexes, has been invoked.³⁶⁰

The mechanistic details of the silver-catalyzed epoxidations are far from understood. The mechanism depicted in (42) might have some similarities to the epoxidation of alkenes by peroxy radicals formed by

electron transfer from the transition metal to TBHP. The other mechanism, (43), is similar to the transfer of an oxygen atom from the oxomanganese complexes to alkenes, which also is known to take place in a nonstereospecific way.

Epoxidation of ethylene and propylene can also be achieved electrochemically on polycrystalline silver.^{361,362}

Halogen in combination with Ag₂O has been found to epoxidize steroidal alkenes.³⁶³

X. Epilog

At this point several questions arise: e.g., how many different types of mechanisms are operating in the transition-metal-catalyzed epoxidations? In this epilog the attention will mainly be devoted to this question. Three main types of complexes are involved in the transfer of an oxygen atom from the reactive intermediate to an alkene: (i) transition-metal-peroxide/peroxo complexes, (ii) oxotransition-metal complexes,³⁶⁴ and in some cases (iii) peroxo radical.

The transition-metal-peroxide (peroxo) complexes are operating in the beginning of the transition-metal series, where the transition metal is in its highest oxidation state, d⁰, making a coordination of the peroxide/peroxo possible. The oxotransition-metal complexes act as catalysts from the middle toward the end of the transition-metal series and in some cases side by side with the peroxo radicals. The transfer of the oxygen atom from type (i) complexes to an alkene is described as an interaction of the alkene either with one of the electrophilic peroxygens or via a peroxometallacycle; the former type of mechanism is related to epoxidation of alkenes by peracids. Many arguments seem to favor a mechanism by which the alkene interacts with the electrophilic peroxygen, but a peroxometallacycle as intermediate cannot be excluded. Two types of intermediates have also been proposed for the transfer of the oxygen atom from type (ii) complexes to an alkene. One of the mechanisms is an interaction of the oxygen in the oxotransition-metal complex with the alkene and the other is interaction of the alkene with both the oxygen and the metal forming a metallacycle. The transition metal in these complexes has a partly filled d-electron block that can be perturbed by structural and electronic changes at the metal center, making several electronic states of the oxotransition-metal complex possible. These changes in electronic structure might have some influence on the transfer of the oxygen atom, and some data seem to indicate a transfer process in which the oxygen interacts with either one or both carbons in the alkene, whereas other data support the metallacycle as intermediate. The peroxo radicals (iii) are mainly operating where the systems can undergo electron-transfer processes and the epoxidation takes place for alkenes in which abstraction of an allylic hydrogen is disfavored compared to addition to the C=C double bond. Besides these three main types of complexes involved in epoxidation reactions, some complexes in which the oxygen attacking the alkene seems to be of nucleophilic character have also recently appeared in the literature.

XI. Abbreviations

| | |
|------|-----------------|
| Ac | acetyl |
| acac | acetylacetonate |

| | |
|---------|--|
| Bu | butyl |
| Cp | cyclopentadienyl |
| dipic | 2,6-pyridinedicarboxylate |
| DMF | <i>N,N</i> -dimethylformamide |
| ee | enantiomeric excess |
| ESR | electron spin resonance |
| HMPA | hexamethylphosphoric acid triamide |
| HOMO | highest occupied molecular orbital |
| IR | infrared |
| L | ligand (generalized) |
| LUMO | lowest unoccupied molecular orbital |
| M | metal |
| MCPBA | <i>m</i> -chloroperbenzoic acid |
| Me | methyl |
| oxinate | 8-hydroxyquinoline |
| Ph | phenyl |
| PhIO | iodosylbenzene |
| pic | pyridine-2-carboxylate |
| Por | porphyrin |
| Py | pyridine |
| R | alkyl |
| salen | <i>N,N</i> -bis(salicylidene)ethylenediamino |
| TBHP | <i>tert</i> -butyl hydroperoxide |
| TPP | <i>meso</i> -tetraphenylporphyrinato |
| tritox | tri- <i>tert</i> -butylmethoxide |
| X | anionic ligand |

XII. Acknowledgments

A part of this work was done during stays at Cornell University, Ithaca, NY. I want to thank Professor Roald Hoffmann for the support during these stays—"thanks Roald!". Thanks are also expressed to Professor Kurt Torssell for fruitful discussions. The Danish Natural Science Research Council and Thanks to Scandinavia, Inc. (especially Mr. Richard Netter), are acknowledged for financial support. I also want to thank Hanne Kirkegaard for the word processing and Arne Lindahl and Leif Mortensen for the drawings.

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