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Metallaoxetanes as Intermediate in Oxygen-Transfer Reactions—Reality or Fiction?

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Contents

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1. Introduction

The transfer of oxygen atoms to and from transition-metal centers (reactions 1 and 2) is one of the fundamental processes in chemistry. These reactions take place under well-controlled laboratory conditions as well as in the complex reactions in the human being.

$$\mathrm{DO} \cdot \mathrm{M} \rightleftarrows \mathrm{MO} \cdot \mathrm{D} \quad (1)$$

$$\mathrm{MO} \cdot \mathrm{A} \rightleftarrows \mathrm{AO} \cdot \mathrm{M} \quad (2)$$

The oxygen-donor system (DO) donates an oxygen atom to the transition metal (M) leading to either an oxo-or a peroxotransition-metal complex (MO) which can transfer the oxygen atom further; either back to D (reaction 1) or to a new acceptor A (reaction 2).

The general type of reactions, as outlined in reactions 1 and 2, covers oxygen-transfer reactions from either an organic, an organotransition-metal, or an inorganic compound via various transition-metal systems to another organic, organotransition-metal, or inorganic species; areas which have been in very intensive development in the last few decades.[1-15] The oxygen-transfer reactions from MO (reactions 1 and 2) to organic systems have resulted in the development of selective oxidation reactions of a variety of compounds, e.g. alkanes can be oxidized to alcohols and carbonyls,[16-20] alcohols to carbonyls;[21-26] aldehydes to carboxylic acids;[27,28] alkenes to epoxides,[29] aldehydes,[30,31] diols,[32,33] carbonyls,[34-36] and carboxylic acids;[37,38] sulfides to sulfoxides and sulfones;[39,40] imines to nitrones;[41-43] and nitroso to nitro compounds.[44,45] Oxygen-transfer reactions from organic substrates to transition metals have also found useful applications, e.g. in the deoxygenation of epoxides to alkenes,[46] and in the formation of alkenes from a reaction between a compound with a carbonyl function and a carbene–titanium complex—"Tebbe-like" reactions.[47] The oxygen-transfer reactions to the metal center in an organotransition-metal compound or an inorganic species can lead to e.g. μ-oxo- or peroxotransition-metal complexes.

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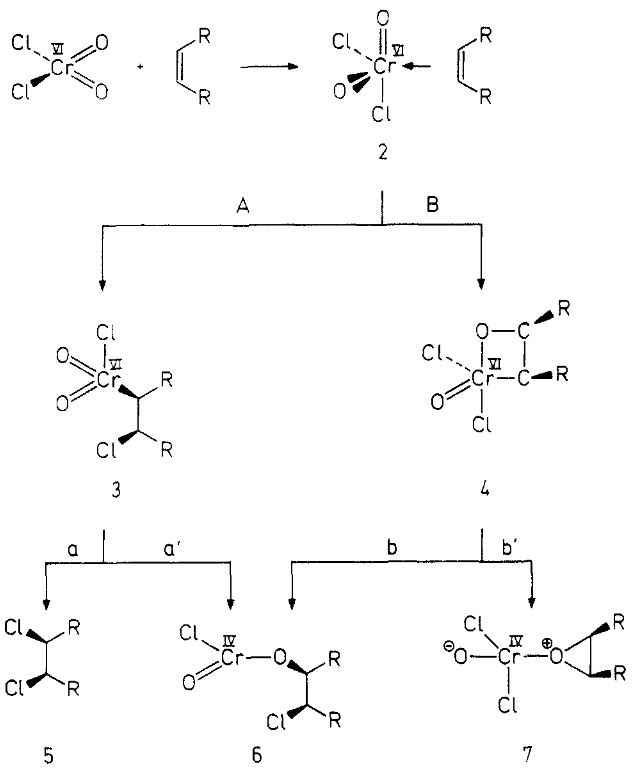
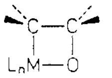
SCHEME 1



Much attention has been devoted to the mechanisms of the oxygen-transfer reactions. One of the most intriguing and often invoked intermediates is the four-membered metallaoxetane, 1. To quote one of the referees of this review: "Certainly there is no intermediate that has been so much invoked with so little evidence to support it—and I speak as an occasional culprit in this regard." The purpose of this account is to present and discuss the involvement of metallaoxetanes, 1, in oxygen-transfer reactions; we want to address to the chemistry, as well as, to a certain extent to discuss the frequent use of metallaoxetanes in oxygen-transfer reactions because, as we will see later, the metallaoxetane structure really has been invoked in many mechanistic discussions and often without any direct experimental evidence to support it.



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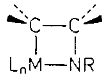
The involvement of metallaoxetanes, 1, in oxygen-transfer reactions was set forth by Sharpless et al.[48] It was found that the primary products in the oxidation of alkenes with chromyl chloride were epoxides, chlorohydrins, and dichlorides. To explain the formation of these products the mechanism in Scheme 1 was suggested.[48]

The first step in this mechanism is the formation of a chromyl chloride–alkene π-complex, 2, from which two possible reaction pathways were suggested (A and B in Scheme 1) both of which lead to chromium(VI) organometallic intermediates, 3 and 4, respectively. In reaction path A the alkene inserts into the chromium–chloride bond producing the alkylchromium intermediate 3. This intermediate can give the dichloride 5 (path a) by reductive elimination. By migration of the alkyl group from chromium to oxygen (path a′) intermediate 3 gives a chromium derivative of chlorohydrin, 6. The reaction path B in Scheme 1 produces by a (formally) [2 + 2] cycloaddition a four-membered intermediate 4, a chromaoxetane, which can yield either the chlorohydrin precursor 6 (path b) or the epoxide precursor 7 (path b′). The mechanism outlined in Scheme 1 is very much contrary to the previously suggested mechanism for this reaction, in which a direct interaction between the alkene and the oxo group of chromyl chloride is suggested.[49]

The mechanism for the oxygen transfer reaction, as depicted in Scheme 1, was extended to become more general:[48] the transfer of X from high-valent MX species (e.g. X =Cl, =O, =NR or =CR_2) to an alkene was suggested to involve a [2 + 2] cycloaddition, either as [$2\pi + 2\pi$] or [$2\pi + 2\sigma$], along the reaction path. The two metallacyclic intermediates containing the M–NR and M–CR_2 fragments are shown in 8 and 9, respectively.



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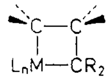

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The metallaoxetane reaction path was suggested by Sharpless et al. to compose *an alternative reaction path*[48] to the "classical/ordinary" mechanism[49] usually applied in oxygen-transfer reactions. Though, the metallaoxetane idea was within a few years very quickly adapted by many scientists in the discussion of reactions in which oxotransition-metal species were involved, as well as in other types of oxygen-transfer reactions. There might be several reasons why metallaoxetanes as intermediate have been so attractive: (i) they are able to account for observations which the "classical/ordinary" reaction mechanisms neglect and (ii) the sociological effect when some chemists proposed the metallaoxetane as an intermediate, which, together with the increased interest in oxygen-transfer reactions, made them "popular" thereby provoking even more chemists to use this intermediate in their papers.

Sharpless's introduction of the metallaoxetane as an intermediate in oxidation reactions was apparently not the first time this structure was presented; the reaction of epoxides and carbon dioxide catalyzed by a nickel(0) complex forming ethylene carbonate was suggested to involve either a nickelaoxetane or a η^2-CO_2–nickel complex.[50] But nobody took notice of this suggested metallaoxetane.

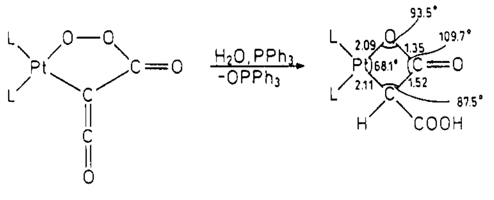
Reactions of alkenes with different substrates leading to four-membered rings containing an oxygen atom are well-known in other areas of organic chemistry. The reaction leading to 4 in Scheme 1 is essentially the reverse reaction of the alkene formation in the Wittig reaction where a trigonal-bipyrimidial oxophosphetane decomposes to the phosphine oxide and an alkene.[51] For this reaction the oxophosphetane intermediate has been characterized by X-ray diffraction measurements,[52] and this reaction mechanism is supported by theoretical calculations.[53]

2. Formation and Reactions of Known Metallaoxetanes

Four-membered cyclic compounds that contain a transition-metal atom, an oxygen atom and two carbon atoms, as in 1, were characterized by X-ray diffraction experiments before they were proposed as intermediates in oxygen-transfer reactions. Only few metallaoxetanes have been structurally characterized, and there is no trend in their formation concerning the transition metal. Metallaoxetanes with the metal atom from the early, the middle, and the late transition metals are all known.

Several metallaoxetanes with late transition metal have been prepared and characterized. The peroxopalladium(II) complex 10 reacts with ketene giving 11, which upon hydrolysis produces 12–the metallaoxetane.[54] In the presence of molecular oxygen 12 is able to oxidize triphenylphosphine to triphenylphosphine oxide and 13, which is transformed into the metallaoxetane 14 by treatment with triphenylphosphine or bases, such as pyridine, diethylamine, di-*n*-propylamine, or triphenylarsine.[54] Both 11 and 14 have been characterized by X-ray diffraction but only very few structural data were published.[54] The reaction sequence is depicted in Scheme 2.

A platinum analogue to 12 has been prepared by reaction of the dioxometallic adduct 15 with H_2O and PPh_3 (reaction 3); the structural data for the metallaoxetane are given in 16.[55] The platinaoxetane 16 undergoes a cleavage reactions in HCl, as depicted in reaction 4. Reactions 3 and 4 can both be considered as oxygen-transfer reactions.[55]



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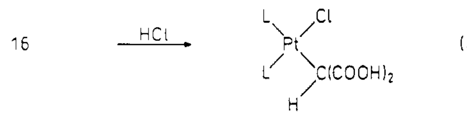
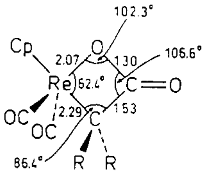


(4)

A metallacyclic complex similar to 14 and 16 with rhenium as the transition metal has also been prepared and characterized.[56] The complex is shown in 17 where the bond lengths and angles for the four-membered ring are given.[56] No reactions of 17 in relation to oxygen-transfer reactions was reported.



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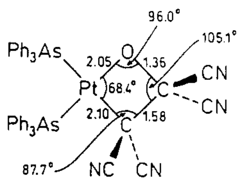
Stable metallaoxetanes containing late transition metals can also be prepared by reaction of tetra- and tricyano-substituted ethylene oxide with PtL_4 (L = PPh_3, $P(p\text{-}CH_3C_6H_4)_3$, $AsPh_3$).[57,58] Two characterized structures are shown in 18[57] and 19.[58]

The platinum atom and the four equatorial atoms (As, As, O, C) are essentially coplanar in 18. The dihedral angle between the planes C–Pt–O and As–Pt–As is 4.5°.[57] The distortion from planarity is due to a minimization of the nonbonding interaction between the cyano groups attached to the carbons in the metallaoxetane.[57] When comparing the structures of the metallaoxetanes, 16–19, it appears that the major difference is found in the metal–carbon bond length.



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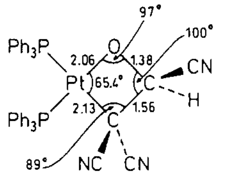

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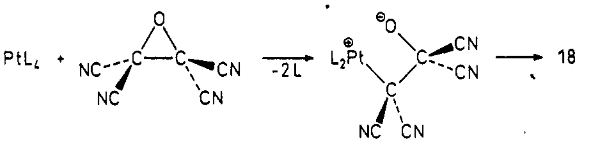
Different reaction mechanisms have been proposed for the formation of the metallaoxetanes 18 and 19.[57-59] The reaction leading to 18 and 19 can be described as an oxidative addition of tetra- or tricyano-substituted ethylene oxide to an intermediate PtL_2. It has been suggested that PtL_2 acts as a nucleophile, attacking the epoxide ring at the center of the lowest electron density—one of the two ring carbons.[57,58] This attack may lead to a cleavage of one C–O bond and the intermediate 20 may be formed (reaction 5). The 1,4-dipolar species 20 thus undergoes a cyclization reaction producing 18.[57,58]



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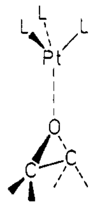
(5)

Another mechanistic suggestion, using theoretical calculations and the frontier orbital approach, has also been put forward to explain the formation of 18 and 19.[59] The reaction is suggested to take place via PtL_3 rather than PtL_2, as the former usually is known to be the reactive species in the oxidative additions of PtL_4.[60] It has been found that the most favorable reaction path is an end-on interaction by which the oxygen atom of the epoxide approaches the platinum atom in PtL_3. This leads to the cleavage of one of the C–O bonds in the epoxide which then adds oxidatively to the metal.[59] Two geometries from different parts of the reaction path are outlined in 21 and 22. The first part of this reaction (21) proceeds via an interaction between the highest occupied molecular orbital (HOMO) of the epoxide mainly located at the oxygen, and the lowest unoccupied molecular orbital (LUMO) of the PtL_3 located at the platinum atom.[59] When the reaction path changes from the end-on to the side-on coordination (21 to 22) the orbital interaction picture changes too, as the orbital interaction between the two systems at this part of the oxidative addition is dominated by the LUMO of ethylene oxide and the HOMO of PtL_3, as depicted in 23.[59] The side-on approach brings about a simulta-



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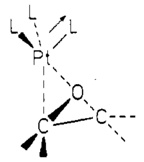

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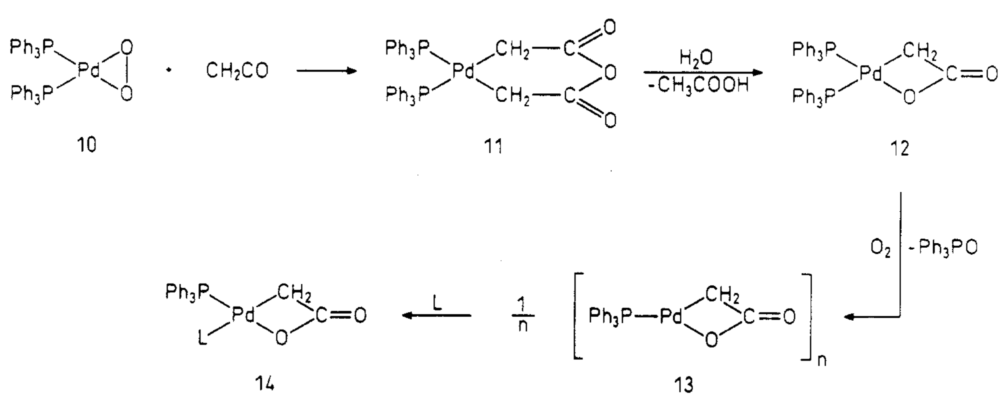
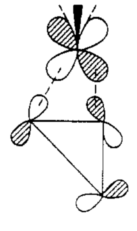
SCHEME 2



neous cleavage of one Pt–L bond, as indicated by the arrow in **22**.



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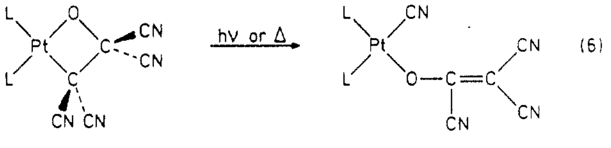
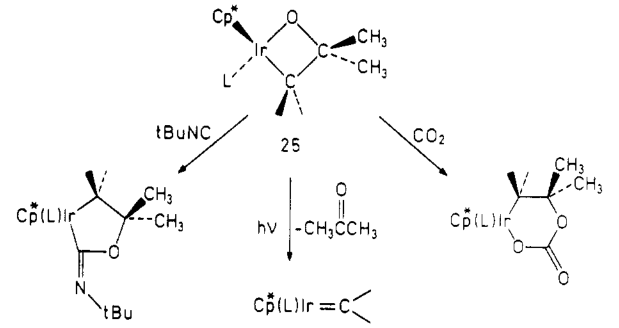
The metallaoxetane **18** undergoes both a thermal and a photochemical isomerization reaction to a (tricyanoethenolato)platinum complex, **24** (reaction 6).[61] The ring opening reaction (reaction 6) can also be initiated by addition of various phosphine ligands.[62] Reaction of a PdL_4 with tetracyanoethylene oxide affords the palladium analogues of **18** and **24**.[61] It has also been observed that a change of the ligands in PtL_4 to more basic ligands is conducive to the **18** to **24** transformation.[61] It should be noted that the platinaoxetane **18** shows no reactivity with carbon monooxide or carbon dioxide at room temperature (compare with the reaction of epoxides and carbon dioxide catalyzed by the Ni(0) complex[50]).[57]



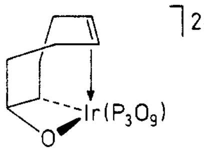
18 24

A few examples of metallaoxetanes with iridium as the transition metal are also known. An iridaoxetane has been prepared by irradiation of a mixture of Cp(L)IrH_2 and *t*-BuOH followed by treatment with chloroform and a sterically hindered base.[63] The iridaoxetane **25** has been partly spectroscopically characterized. Reaction with various substrates indicates that **25** is quite reactive toward electrophilic organic compounds, as shown in Scheme 3.[63] **25** undergoes also a photoextrusion reaction by which acetone is eliminated and an iridium methylene species is formed (Scheme 3).[64] This photochemical reaction can be considered as an oxygen transfer reaction via a metallaoxetane. Although insertion of organic molecules into the Ir–O bond of **25** appears quite readily, attempts to find conditions under which epoxides are formed have not so far succeeded.[63]

SCHEME 3



Reaction of the 1,5-cyclooctadiene complex $[(C_8H_{12})Ir(P_3O_9)](TBA)_2$ with molecular oxygen affords after a series of transformations the iridaoxetane shown in **26**.[65] The formation of the metallaoxetane **26** corresponds in principle to an insertion of an oxygen atom into the iridium–carbon bond in $[(C_8H_{12})Ir(P_3O_9)]$-$(TBA)_2$. The structure of **26** has been characterized by X-ray measurements.[65] Thermal activation of **26** leads to the formation of the η^3-allyl and alcohol iridium complex, **27**, reaction 7a, but no epoxide is formed (reaction 7b).[65]



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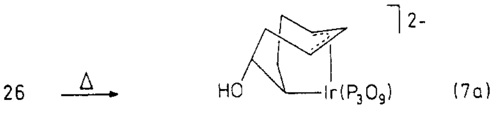

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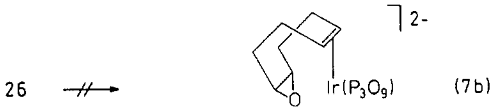
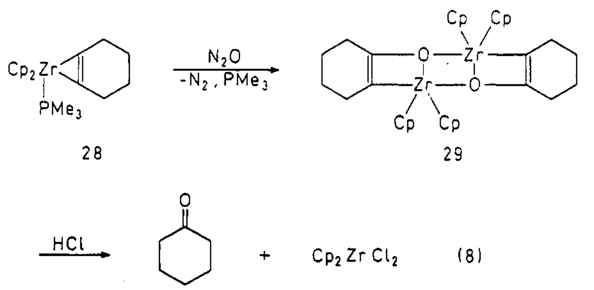
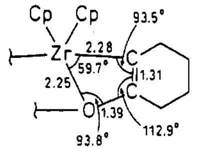


Some examples of oxygen-transfer reactions from metallaoxetene intermediates have been found.[66,67] Nitrous oxide reacts with $Cp_2Zr(C_6H_8)(PMe_3)$ (**28**) with elimination of molecular nitrogen under formation of **29**, a zirconaoxetene dimer.[66] Treatment of **29** with an excess of HCl results in the formation of cyclohexanone and Cp_2ZrCl_2 (reaction 8).[66] It should be pointed out that the oxidation of **28** to **29** is a facile reaction when



28 29 (8)

nitrous oxide is employed as the oxygen donor, it is not observed for other common oxidation reagents.[66] The structure of the zirconaoxetene part of **29** is shown in **30**.[66]



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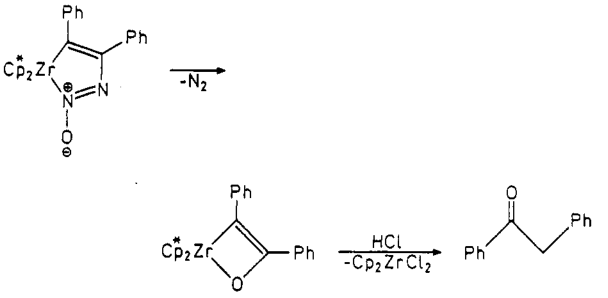
A nearly similar complex has been found in the reaction of $Cp_2^*Zr(C_2Ph_2)$ and N_2O giving a more reactive monomeric zirconiaoxetene (reaction 9) which was structurally determined by X-ray measurements.[67]



(9)

A reactive $Cp_2^*Zr{=}O$ intermediate formed by heating of $Cp_2^*ZrPh(OH)$ has also been trapped by e.g. alkynes, but no oxygen-transfer reactions were studied.[68]

3. Metallaoxetanes in Oxygen-Transfer Reactions from MO_x (x = 1–4) Species to Substrates

a. Transfer of One Oxygen

The metallaoxetane intermediate has been invoked in a variety of oxygen-transfer reactions from oxo-transition-metal and oxoorganotransition-metal species to organic substrates. We will here mainly consider oxygen-transfer reactions to alkenes leading to the transfer of one or two oxygen atoms.

As mentioned in the introduction the metallaoxetane was suggested as an alternative reaction path in the oxidation of alkenes by chromyl chloride (Scheme 1).[48] The proposal of the mechanism outlined in Scheme 1 was based on the observed products from the reaction. No direct (or indirect) evidence of a metallaoxetane intermediate was established.[48]

The metallaoxetane idea persuaded Rappê and Goddard to perform generalized valence bond plus configuration interaction calculations to obtain further insight into the reaction sequence that is depicted in Scheme 1.[69,70] The attention in their work was maintained on the energies of the intermediates in the oxidation of ethylene with chromyl chloride. The results are shown in Figure 1.[69b]

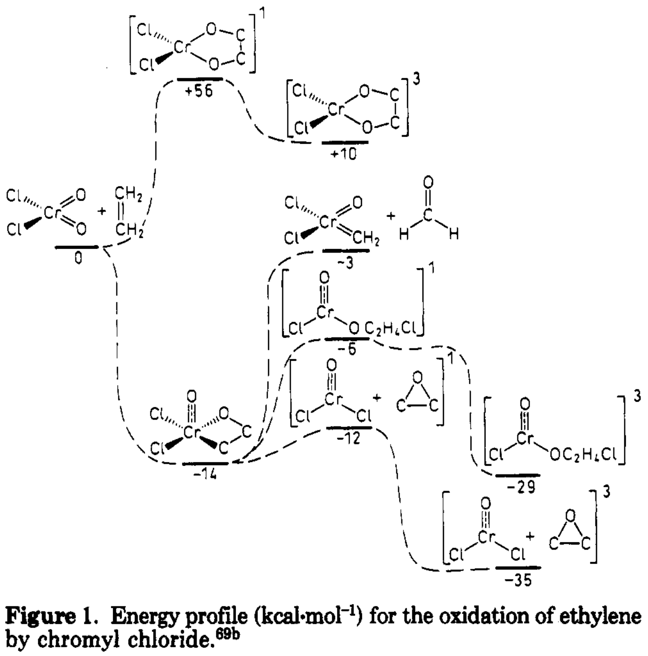


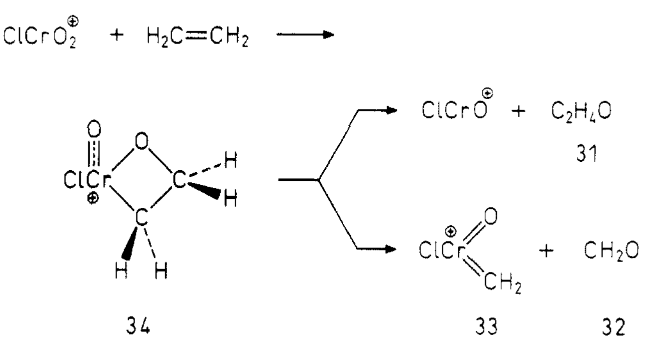
Figure 1. Energy profile (kcal·mol⁻¹) for the oxidation of ethylene by chromyl chloride.[69b]

The results show that the formation of the chromaoxetane is favored by 14 kcal·mol⁻¹ (the optimized structure of the chromaoxetane was not presented).[69,70] The oxygen transfer to ethylene under the formation to the ethylene oxide leads to further stabilization by 21 kcal·mol⁻¹ of the system.[69,70] The driving force in the reaction is the conversion of a spectator oxo double bond into an oxo triple bond.[69,70] The metallaoxetane approach was also extended to involve oxygen-transfer reactions to alkenes from the permanganate ion and osmium tetraoxide,[69] although no theoretical calculations were presented to support this.

Further theoretical support for a chromaoxetane has appeared from an ab initio study of the addition of ethylene to $Cr{=}O^{n+}$ (n = 1–3).[71] The heat of formation for chromaoxetane was calculated to 7.8 kcal·mol⁻¹ for the quartet and -70.7 kcal·mol⁻¹ for the triplet, respectively.[71] It was proposed that the concerted mechanism for the formation of the chromaoxetane as an intermediate in oxygen transfer reactions (epoxidation) was plausible unless steric repulsion prevents the concerted reaction.[71] The energies of formation for the manganaoxetanes were calculated to -20.7 kcal·mol⁻¹ and -83.1 kcal·mol⁻¹ for manganese in the triplet and doublet states, respectively.[71] Furthermore, it was indicated that a noncyclic manganese–alkoxy diradical intermediate could form along the reaction path; the formation of this intermediate was favored by 70 kcal·mol⁻¹ compared to the manganaoxetane.[71] In other words, the manganaoxetane is less stable than the manganese–alkoxy diradical.

Several gas-phase investigations support the chromaoxetane as an intermediate in the reaction of oxochromium species with alkenes.[72,73] $ClCrO_2^+$ reacts with ethylene to give two species that result from oxygen-transfer reactions, **31** and **32**, respectively, and one product containing both chromium and carbon, **33** (Scheme 4).[72] To account for **33** in which a chromium–carbon bond is formed, the chromaoxetane **34** was postulated as intermediate (Scheme 4).[72] The ethylene

SCHEME 4

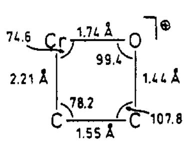


oxide **31** is formed by a reductive elimination, and **32** and **33** by a retro [2 + 2] cycloaddition.[72]

The gas-phase reactions of CrO^+ with different alkenes have also been studied.[73] Reaction of CrO^+ with ethylene gave Cr^+ and $CrCH_2^+$ as the ionic products and acetaldehyde and formaldehyde as the neutral products (compare Scheme 4).[73] For the reaction of CrO^+ with propene several neutral and ionic products were observed.[73] To account for some of the products two main reaction paths have been suggested; one reaction path (A) proposes an initial interaction between the oxygen in CrO^+ and the alkene part of propene, while the other path (B) involves an interaction between the chromium in CrO^+ and the alkene part of propene. To account for the products, the reaction path B has been postulated to proceed via the metallaoxetanes **35** and **36** which decompose as depicted in Scheme 5.[73]

The possible decomposition of **35** into the carbene–chromium, $CrCH_2^+$, and acetaldehyde is estimated to be endothermic by 28 kcal·mol^{-1} (not shown).[73] It has been suggested that the formation of the metal carbene product should become an energetically favorable process as the oxo–metal bond strength decreases relative to the carbene–metal bond.[73] This idea is supported by the formation of the manganese carbene, $MnCH_2^+$, as the major product in the reaction of MnO^+ (oxo–manganese bond strength is 57 ± 3 kcal·mol^{-1})[73] with ethylene,[74] when compared to the oxo–chromium bond energy of CrO^+ of 83.5 ± 1.3 kcal·mol^{-1}.[73]

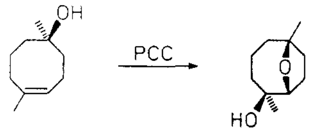
Ab initio calculations of the structure of the sextet state (the most stable state) of the chromaoxetane (which corresponds to the addition of ethylene to CrO^+) gives the structure as shown in **37**,[75] which is very similar to the X-ray structures determined for the other metallaoxetanes.[54-58]



37

Results that argue against the metallaoxetane mechanism, outlined in Scheme 1, have be presented by Barton et al.[76] Chromyl chloride and chromyl fluoride oxidation of steroid alkenes, as ergosteryl acetate, chlorosteryl acetate and 9,11-dehydrotigogenin acetate, gave products in which the absence of *cis*-halogenohydrins and the stereochemistry of the primary epoxidation was claimed to be inconsistent with the metallaoxetane intermediate.[76] The reaction of 9,11-dehydrotigogenin acetate gave e.g. the β-epoxide as the major product.[76] It was proposed that the reaction may involve more that one molecule of chromyl halide in the product-forming step.[76] However, no mechanistic details were presented to account for the observed products. The observation that no *cis*-halogenohydrins are formed in this reaction can possibly *not* be taken as evidence against the metallaoxetane mechanism, as stated by Barton et al.[76] The reaction path A in Scheme 1, which is responsible for the formation of *cis*-chlorohydrin, does not involve the chromaoxetane, but rather an intermediate where the alkene inserts into the chromium–chloride bond.[48]

The metallaoxetane has been invoked in different types of oxygen transfer reactions from other high-valent oxochromium compounds to alkenes although direct evidence for their presence in solution is still tentative.[77-79] An example of the chromaoxetane intermediate is given in Scheme 6 where it was suggested to account for the products in the substituent-directed oxidation of 1,5-dimethylcyclooct-4-en-1-ol (**38**) with PCC (reaction 10).[79]

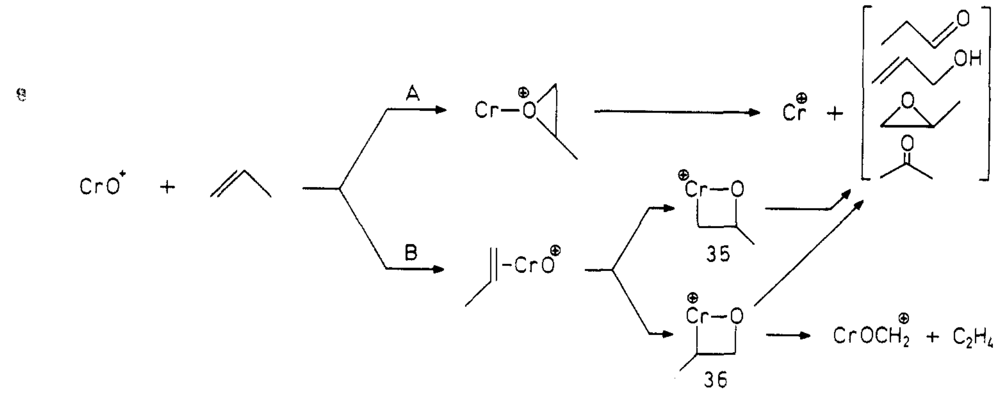


(10)

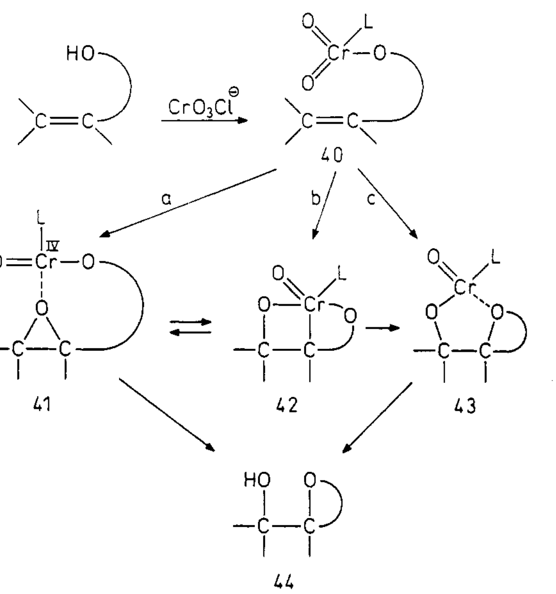
38 39

The oxidation proceeds as an overall syn addition. The first step has been suggested to be an addition of the chromium complex to the alcohol giving **40** which could give the product **44** either via reaction path a, b, or c, by which the intermediates **41**, **42**, or **43** are formed. However, **41** was excluded as an intermediate as it was not succeeded to convert the epoxide **45**, the

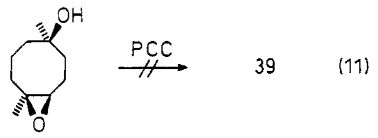
SCHEME 5



SCHEME 6



precursor to **41**, into **39** by treatment with PCC (reaction 11).[79] It was proposed that **42** provides a convenient mechanistic keystone since through ligand reorganization it could lead to either the epoxide complex, **41** or the hydroxy ether complex **43**.[79] Although, it was stated that no destinction between pathways b and c can be drawn.[79] It should be noted that the exclusion of **41** as an intermediate on the above basis is questionable due to the difference between the intermediate **41**, a Cr(IV) species, and the expected structure from reaction of **45** and PCC, namely a Cr(VI) fragment.

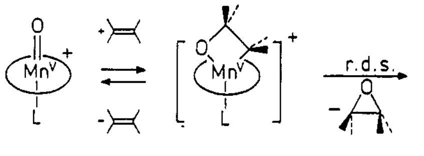


45

On the basis of the concept of least motion Kochi et al.[80] have argued for a direct interaction between the alkene and the oxygen in OCr(V)–salen complexes in the rds for the epoxidation of alkenes, rather than a chromaoxetane.

Metallaoxetanes have found their way into the current discussion of a mechanism for oxygen-transfer reactions from oxometallo porphyrins to predominantly alkenes.[12,81] The metallaoxetane was briefly introduced by Groves et al.[82] for the catalytic epoxidation of alkenes by Fe(TTP)Cl and iodosylbenzene as the oxygen source. It was argued that the metallaoxetane should be favored by oxidation of 1,1-disubstituted alkenes. However, a lower reactivity of methylenecyclohexane compared to cycloheptene was observed, thus arguing against the metallaoxetane reaction path.[82]

Several kinetic studies by Collman[83-86] and Meunier[84] lead to a more general introduction of the metallaoxetane intermediate in oxygen-transfer reactions from oxomanganese and oxoiron porphyrins. It was found that the reaction rate is independent of the concentration of alkenes, but that different alkenes are epoxidized at different rates.[83,84] Therefore, the alkene must be involved in the rds. Such an observation was proposed to be consistent with the Michaelis–Menten equation.[83,84] Here the alkene binds reversibly to the oxomanganese or oxoiron porphyrin complex followed by the rds that gives the epoxide and the manganese or iron porphyrin (reaction 12).[83,84]



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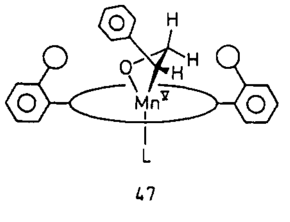
Kinetic studies with the hypochlorite system as the oxygen source showed that the oxygen-transfer process occurs in at least two steps. Binding energies for the formation of the intermediate and the rate constant for the decomposition of the intermediate have been obtained from a Lineweaver–Burk analyses.[84] The results reveal that the electron-rich alkenes bind somewhat more efficiently than the electron-poor alkenes.[84] It was suggested that since the decomposition of the intermediate to the manganese porphyrin and the epoxide is the rds of the catalytic cycle, the intermediate, **46**, must be reasonably stable. This rules out radicals and other reactive species.[84,85] The intermediate was proposed to be the metallaoxetane **46** formed by a formal concerted antarafacial [2 + 2] cycloaddition reaction. The loss of stereochemistry in the epoxidation of *cis*-alkenes was postulated not to be due to a decomposition of **46** via a transient radical species which would allow a rotation around the C–C bond, but rather represent the presence of a minor, parallel reaction path.[84] It should be mentioned that it has not been possible to characterize the metallaoxetane complex **46** spectroscopically, mainly due to its very poor EPR and NMR spectra.[86]

A detailed investigation of the oxygenation of styrene catalyzed by manganese and iron porphyrins showed phenylacetaldehyde as a product as well as the expected epoxide.[86] Isotopic labeling studies showed that one of the β-deuterium atoms of styrene migrate to the benzylic carbon in the course of the aldehyde formation. Furthermore it was shown that the oxygenation rates for styrene and styrene-d_8 were identical. However, when the same substrates were oxygenated in the same flask at equal initial concentrations, an inverse secondary isotope effect in the reversible formation of the oxometal–alkene complex was found.[86] Collman et al. argued that the production of phenylacetaldehyde form styrene was quite consistent with a metallaoxetane intermediate.[86] Two metallaoxetanes, **47** and **48**, were proposed and molecular modeling examinations indicated that the aromatic ring in **47** does not suffer from severe interaction with the tetrapyrrolic plane.[86] However, model studies indicated that introduction of an ortho methyl group would destabilize the manganaoxetane **47** resulting in drastic decrease in the amount of aldehyde product.[86] In **48** the metallaoxetane is not



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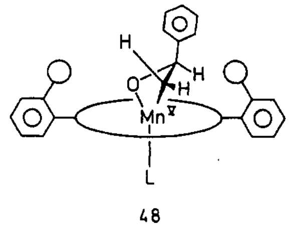


48

SCHEME 7

$$(F_{20}TPP)Fe^{III} + C_6F_5IO \rightleftarrows (F_{20}TPP)Fe^{III}{-}OIC_6F_5$$

$$(F_{20}TPP)Fe^{III}{-}OIC_6F_5 \rightleftarrows (^{+\cdot}F_{20}TTP)Fe^{IV}O + C_6F_5I$$

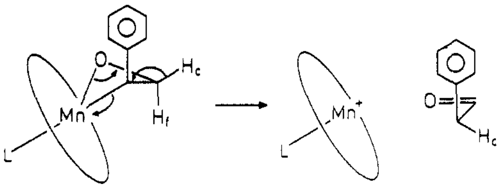
$$(^{+\cdot}F_{20}TTP)Fe^{IV}O + \text{alkene}_1 \rightarrow \text{metallaoxetane}_1$$

$$\text{metallaoxetane}_1 \rightleftarrows (F_{20}TPP)Fe^{III} + \text{epoxide}_1$$

$$(^{+\cdot}F_{20}TTP)Fe^{IV}O + \text{alkene}_2 \rightleftarrows \text{metallaoxetane}_2$$

$$\text{metallaoxetane}_2 \rightarrow (F_{20}TPP)Fe^{III} + \text{epoxide}_2$$

greatly affected, and the epoxide is still produced.[86] A possible mechanism for the decomposition of 47 to phenylacetaldehyde and Mn(TTP)Cl is depicted in reaction 13.[86] The epoxide/aldehyde ratio was proposed to reflect a competition between concerted (epoxide) and stepwise (aldehyde) breakdown of the metallaoxetane.[86]



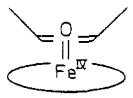
(13)

Collman et al. commented on the metallaoxetane intermediate in the conclusion of the paper:[86] "In the absence of spectroscopic information, of course, this remains a conjecture. But given that such an intermediate provides a simple rationalization for many metal-oxo-olefin reactions, both biological and biomimetic, we believe it should be given a careful consideration." It should also be noted that Groves et al. on basis of electron-donating para substituent effects have suggested that the production of phenylacetaldehyde takes place by a pinacol-like rearrangement of a cationic intermediate.[87]

Bruice et al.[88] have argued against the metallaoxetane as intermediate in oxygen-transfer reactions from oxomanganese and oxoiron porphyrins with the hypochlorite system as the oxygen donor. From computer simulations of the kinetic results obtained by Collman et al. for a competition epoxidation experiment of norbornene and cyclooctene, the reaction sequence shown in Scheme 7 can explain the following reported observations: (i) the reaction rate is independent of both the initial concentration of the alkene and the oxidant; (ii) the appearance of the epoxide is a zero-order process; (iii) one alkene inhibits the epoxidation of the other; and (iv) rates are different for different alkenes. Computer proanalysis of Scheme 7 established that a steady-state concentration of the metallaoxetane between 75 and 100% of the total concentration of the metalloporphyrin should be expected which consequently should lead to its detection.[88] Reinvestigation of the manganese and iron porphyrin catalyzed epoxidation concluded that the absorbance found at 424 and 523 nm could not be attributed to a metallaoxetane as this adsorbance is observed even in the absence of the alkene.[88] By lowering the concentration of the hypochlorite Bruice et al. found that the appearance of the epoxide for a given alkene became first order. Furthermore, it was found that norbornene oxide and *cis*-cyclooctene oxide were formed at the same rate, but that the yield of the former was twice the yield of the latter, i.e. norbornene was a better trap for the oxomanganese porphyrin species.[88] Rather than a metallaoxetane an alkene-derived carbocation radical intermediate was proposed.[89-91] On the basis of the epoxidation of alkenes catalyzed by a sterically hindered iron porphyrin it was argued that the formation of a metallaoxetane intermediate formed via a [2a + 2s] cycloaddition was disfavored because all alkenes, except terminal alkenes, were unable to approach the iron complex.[91] This argument was further supported by inspection of metallaoxetane structures constructed by X-ray-based computer graphics.[91,92]

On the basis of the rearrangement reactions found in the iron porphyrin catalyzed oxidation of *trans*-cyclooctene Traylor et al.[93] have argued against the metallaoxetane intermediate and proposed that the reaction takes place via a carbocation intermediate arising from an electron transfer followed by a cage collapse.[94] Further studies of iron porphyrin catalyzed oxidation of alkenes which are known to undergo rearrangement reactions through the intermediacy of an alkene cation radical supported the idea of an electron transfer from the alkene to the high-valent iron intermediate.[95] The epoxidation of adamantylideneadamantane catalyzed by chromium, manganese, and iron porphyrins has also been studied in the context to the metallaoxetane intermediate by Traylor et al.[96] The reason for choosing adamantylideneadamantane as the substrate was that the formation of the metallaoxetane is sterically impossible.[96] It was found that all three catalysts were capable of epoxidizing this alkene, and it was considered that the epoxidation of this alkene proceeds through the carbocation mechanism rather than the metallaoxetane pathway.[96]

Let us here mention a few other examples of postulated metallaoxetane intermediates in oxygen-transfer reactions from oxomanganese and oxoiron porphyrins to alkenes. To account for the loss of the deuterium label in the epoxidation of *trans*-1-deuteriopropylene and for the incorporation of deuterium in unlabeled propylene from D_2O by a reconstituted cytochrome P-450 system, a ferraoxetane porphyrin intermediate was invoked.[97] The epoxide could be formed directly by a reductive elimination from the ferraoxetane or this can lose a proton giving an iron carbene. This can either be protonated giving back the ferraoxetane porphyrin intermediate or form a metallaoxirane upon ring closure.[97] An intermediate of an alkene-oxoiron porphyrin has been observed by visible spectroscopy, and the reaction rate for the reaction of substituted styrenes correlates with the Hammett σ^+ ($\rho^+ = -1.9$).[98] Two possible structures for an intermediate were postulated, an alkene-π complex **49** and a ferraoxetane porphyrin **50**.[98]



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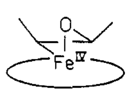
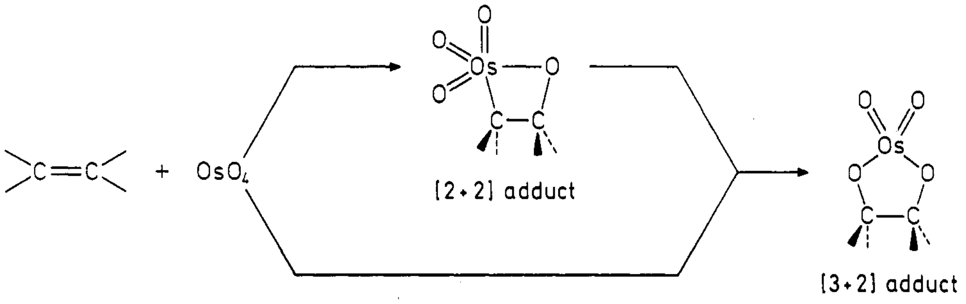


50

SCHEME 8

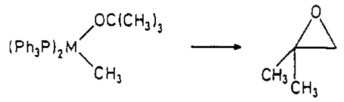


The metallaoxetane intermediate has also been proposed in other studies of oxygen-transfer reactions from oxomanganese and oxoiron porphyrins to alkenes,[99-101] but often without detailed mechanistic investigations.

Several theoretical investigations have also been put forward in an attempt to elucidate the possible involvement of metallaoxetanes in oxygen-transfer reactions from oxotransition-metal porphyrins and porphyrin-like systems.[102-104] By using extended Hückel calculations, with four hydrogens as a model for the porphyrin ring it was found that for the oxygen transfer from an oxoiron porphyrin to an alkene the ferraoxetane intermediate could be formed along the reaction course, but that the formation of the epoxide takes place via an open intermediate, rather than by a reductive elimination from the ferraoxetane.[102] Drago et al.[103,104] have analyzed the oxygen-transfer reaction to alkenes from an oxoruthenium(IV) glyoxaldiimine species using the INDO/1 method. Among the different approaches of ethylene to the oxo–ruthenium bond, two of which lead to the ruthenaoxetane namely a concerted and a nonconcerted [2 + 2] were considered. Optimization of the geometry from the concerted [2 + 2] cycloaddition resulted in a structure with almost no bonding between ethylene and the oxo–ruthenium fragment. A Ru–C bond length slightly longer (2.43 Å) than a typical Ru–C bond (2.12 Å) was calculated.[104] Neither the C–C nor the Ru–O bond lengths lengthened significantly.[104] The hydrogens atoms in the ethylene did not bend back toward tetrahedral angles by the approach to the oxo–ruthenium bond.[104] Optimization of a "forced" ruthenaoxetane, where the equatorial ligands (in this calculation a pentammine model was applied) were bent back and covalent Ru–C and C–O bond lengths were chosen as a starting point, resulted in the oxoruthenium complex and ethylene dissociating upon geometry optimization.[104] These results lead to the proposal that the formation of the metallaoxetane by a concerted [2 + 2] cycloaddition reaction was an unfavorable process.[104] The reason for the unfavorable pathway is traced to a two-orbital, four-electron repulsive interaction between the $\pi_{\mathrm{Ru-O}}$ and $\pi_{\mathrm{C-C}}$ orbitals.

The nonconcerted [2 + 2] cycloaddition pathway leading to the metallaoxetane by first a [1 + 2] pathway followed by a [2 + 2] reaction was also found unfavorable.[104] It this case a direct formation of the epoxide was found to be more favorable.[104] Optimization of a metallaoxetane with equivalent Ru–O and Ru–C, and C–C and C–O bond lengths leads to a five-membered Ru-O-C-C-N cyclic structure—the so-called suicide complex.[104,105] The oxygen-transfer reaction from the oxoruthenium complex was suggested to take place via an interaction of one of the carbons in the alkene with the oxygen first. This C–O bond is nearly entirely formed before the second C–O bond begins to form.[104]

The nickel and palladium complexes **51** decompose to afford 2-methylpropylene oxide (reaction 14).[106] Deuterium labeling of the methyl group bound to nickel showed that this group is not involved in the formation of the epoxide.[106] An intramolecular γ-hydrogen elimination from **51** (M = Ni) producing the metallaoxetane **52** and methane has been proposed to take place (reaction 15).[106]



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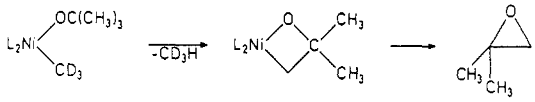
51



(15)

52

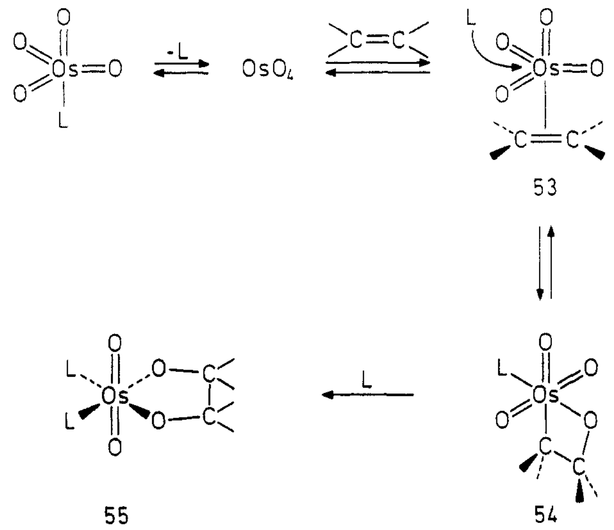
Changing the metal to titanium leads to a completely different reaction path as 2-methylpropene is formed as the major product with trace amount of the epoxide[106] (we will return to nearly similar reactions later—the "Tebbe-like" reactions). It appears thus that the titanium analogue to **51** yields the alkene by a retro [2 + 2] cycloaddition rather than taking the reductive elimination pathway. The proposed nickelaoxetane **52** is very similar to the palladium analogue **14** and the platinum analogues **16**, **18**, and **19** discussed in section 2, but their reactivities are different.

b. Transfer of Two Oxygens

A variety of oxometal complexes, such as osmium tetraoxide, ruthenium tetraoxide, and the permanganate ion, can provide an alkene with two oxygens. Osmium tetraoxide reacts with an alkene to give an osmium(VI) ester intermediate which can be hydrolyzed to give the corresponding *cis*-diol.[32] The osmaoxetane, which in principle is a [2 + 2] cycloaddition of the alkene to one of the oxo-osmium bonds in osmium tetraoxide, has become an often invoked intermediate in the discussion of a mechanism for the osmylation of alkenes. A [3 + 2] cycloaddition where the alkene adds directly to two oxo groups of osmium tetraoxide forming the osmium(VI) ester has also been proposed (Scheme 8).

Sharpless et al. have argued for the osmaoxetane as an intermediate in the dihydroxylation and oxoanimation reactions of alkenes by osmium tetraoxide.[48,107,108] The results obtained from the asymmetric dihydroxylation of alkenes with osmium tetraoxide in the

SCHEME 9

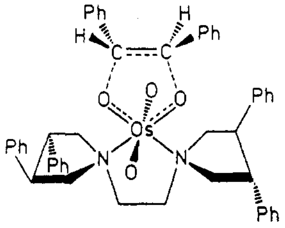


presence of dihydroquinine or dihydroquinidine acetate led to the formulation of the mechanism, as depicted in Scheme 9.[107]

The first step in this mechanism is the coordination of the alkene π-bond to the metal giving **53**, which in principle is the alkene analogue to the quinulicidine–osmium tetraoxide[109] and cinchona alkaloid–osmium tetraoxide[110] complexes. It should also be noted that there is spectroscopic evidence for the coordination of adamantylideneadamantane[111] and of aromatics[112] to osmium tetraoxide, which reminds a complex similar to **53**. The ligand L might also be present in the alkene addition step.[110] Reaction of **53** with the ligand provokes the insertion of the alkene giving the metallaoxetane **54**. Reaction of **54** with the second ligand produces the ligand–osmium(VI) ester **55**.[107] The coordination of the alkene to osmium in the first step can be thought of with two possible orientations of the prochiral alkene. He has suggested that the reaction with the chiral ligand proceeds with different rates resulting in the observed ee's for the reaction.[107,110] Sharpless has recently proposed a minor change to this outlined mechanism for the reaction between alkenes and osmium tetraoxide in the presence of labile ligands. It was suggested that the addition of the alkene to the oxo–osmium bond resulting in the osmaoxetane is the first step in the sequence followed by a coordination of the ligand to the metal introducing the asymmetry.[113] So far no direct evidence for an osmaoxetane in this class of reactions is available.

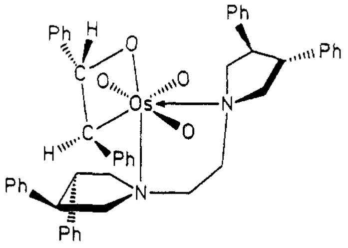
The discussion of the [2 + 2] pathway relative to the [3 + 2] cycloaddition pathway in the cis dihydroxylation of alkenes with osmium tetraoxide with and without the presence of tertiary amines as ligand(s) has formed the subject of other reports. The asymmetric induction obtained by using (−)-(*R*,*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine as chelating ligand was proposed to be introduced through a nucleophilic addition of the ligand to the alkene–osmium tetraoxide complex **53** (Scheme 9).[114] However, steric considerations between the axial type methyl group on the ligand and the substituents on the alkene part in a ligand–osmium(VI) ester complex obtained from a [3 + 2] cycloaddition can also account for the stereochemical outcome of the reaction.[114] It was thus concluded that neither of the proposed pathways could be ruled out by the results.[114]

Stereochemical considerations, using a chiral diamine with two *trans*-3,4-diphenylpyrrolidine units with C_2 symmetry at both ends of an ethylene chain, indicated a osmaoxetane as a possible intermediate for the dihydroxylation of alkenes with osmium tetraoxide.[115,116] The asymmetric oxidation was found to be kinetically controlled by the relative stabilities of the diastereomeric transition states and not to be a result of thermodynamic control determined by the resulting diamine–osmium(VI) ester complexes.[115,116] Reaction of the complex prepared from *trans*-stilbene–osmium tetraoxide in pyridine with the chiral diamine gave a nearly 1:1 mixture of the two diastereomeric complexes.[116] The [3 + 2] cycloaddition pathway leading to the sterically favored transition state **56** does not account for the observed stereochemical outcome. The intermediate **56** gives the wrong diastereomer compared to the structure of the osmium ester complex established from X-ray investigations.[116]



56

However, the [2 + 2] cycloaddition via the metallaoxetane intermediate **57** can explain the stereochemical outcome.[116] The metallaoxetane **57** places the phenyl rings of *trans*-stilbene in the space with least steric hindrance. This intermediate can rearrange to a diamine–osmium(VI) ester, similar to **56**, which produces the *cis*-diol in accordance with the observed stereochemistry. It should be noted that the rearrangement of **57** to a diamine–osmium(VI) ester gives the diastereomer which could not be formed by a direct [3 + 2] addition due to steric repulsion between the phenyl groups in the ligand and the phenyl groups attached to the alkene.



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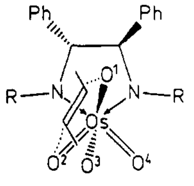
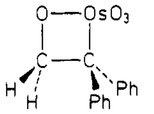
Corey et al.[117] have on the other hand argued against the [2 + 2] cycloaddition pathway in the osmium tetraoxide cis hydroxylation of alkenes when chiral 1,2-diphenyl-1,2-bis(mesitylamino)ethane is used as the ligand. The concerted [3 + 2] cycloaddition and the assumption that the oxygens in the ligand–osmium tetraoxide complex, which attacks the carbons in the alkene, are axial and equatorial, respectively, to the chelate ring **58** leads to a configuration of the product 1,2-diol which is in accordance with the experimental results.[117] The chelation of the diamine to osmium tetraoxide causes O(2) and O(4) to be electron rich due to electron donation from the nitrogens relative to the axial oxygens O(1) and O(3). The addition of the alkene to O(1) and O(2) is thus proposed as a concerted attack of the alkene by one relatively electrophilic and one relatively nucleophilic oxygen.[117] Calculation of the frontier orbitals of a ligand–osmium tetraoxide complex with C_2 symmetry supports Corey et al.'s hypothesis.[118] The metallaoxetane has been briefly introduced as an intermediate in the mechanism for the cis dihydroxylation of alkenes by osmium tetraoxide in several other cases.[119,120]



58

On the basis of ^1H NMR spectroscopic investigations of the reaction of 1,1′-diphenylethylene with osmium tetraoxide, two isomeric metallaoxetanes, **59** and **60**, were assigned on the basis of two sets of less intense coupled doublets (J 11 Hz each) at δ 5.83 and 5.355, and δ 5.72 and 5.35, respectively.[121]



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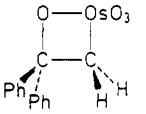


60

The assignment of the ^1H NMR results as **59** and **60** was later questioned.[122] An expected rapid pseudorotation of the OsO_3 group makes the protons of the hydrogens equivalent. Furthermore, it was stated that the chemical shift of the methylene group adjacent to the oxygen in **59** and adjacent to the osmium in **60** probably are not as identical as suggested.[122] Moreover, it would not be expected that **59** and **60** are formed at nearly equal amounts which is a consequence of the above interpretation.[122] Instead of assigning the ^1H NMR data to the metallaoxetanes, it was proposed that the data are more consistent with a mixture of dimeric osmium(VI) esters,[122] which are known to form in the reactions of alkenes with osmium tetraoxide.[123–127]

The reaction of alkenes with osmium tetraoxide has been investigated from a theoretical point of view in an attempt to obtain insight into the mechanism. By using extended Hückel calculations the interaction between an alkene and osmium tetraoxide has been studied.[128] Some of the frontier orbitals of osmium tetraoxide are shown to the left in Figure 2. It appears that these orbitals have symmetry to interact with the frontier orbitals of an alkene in a [3 + 2] cycloaddition reaction, as outlined in Figure 2.[128]

The LUMO π^* of the alkene is set up for the interaction with one of the HOMO's of osmium tetraoxide, and furthermore the π HOMO of the alkene can interact with both LUMO's of osmium tetraoxide. One of these interactions leads to the [3 + 2] cycloaddition product while the interaction with the LUMO with d_{z^2} symmetry might account for the coordination of an alkene to the osmium atom in osmium tetraoxide as observed by Nugent,[111] as well as proposed by others.[112] The interaction outlined in Figure 2 leads to a reduction of the osmium atom, Os(VIII), $d^0 \rightarrow$ Os(VI), d^2. The reaction of osmium tetraoxide depicted in Figure 2 as a [3 + 2] cycloaddition reaction takes place via an avoided crossing between the osmium d_{z^2} and the π-orbital of the alkene.[128] It has been found that the frontier orbitals of osmium tetraoxide are not directly set up for a [2 + 2] cycloaddition reaction with an alkene, but the [2 + 2] cycloaddition could not be excluded.[128] The observation that the proximity of chelating nitrogen bases increases the reactivity of osmium tetraoxide for alkene dihydroxylation was explained by the formation of a ligand–osmium tetraoxide complex with C_{2v} symmetry. The frontier orbitals of such a complex revealed an increase of the HOMO energy and a decrease in the LUMO energy of the osmium tetraoxide–ligand system when compared to osmium tetraoxide. This geometrical distortion makes the osmium complex a better donor and a better acceptor toward the LUMO and HOMO of an approaching alkene in the [3 + 2] cycloaddition manner.[128]

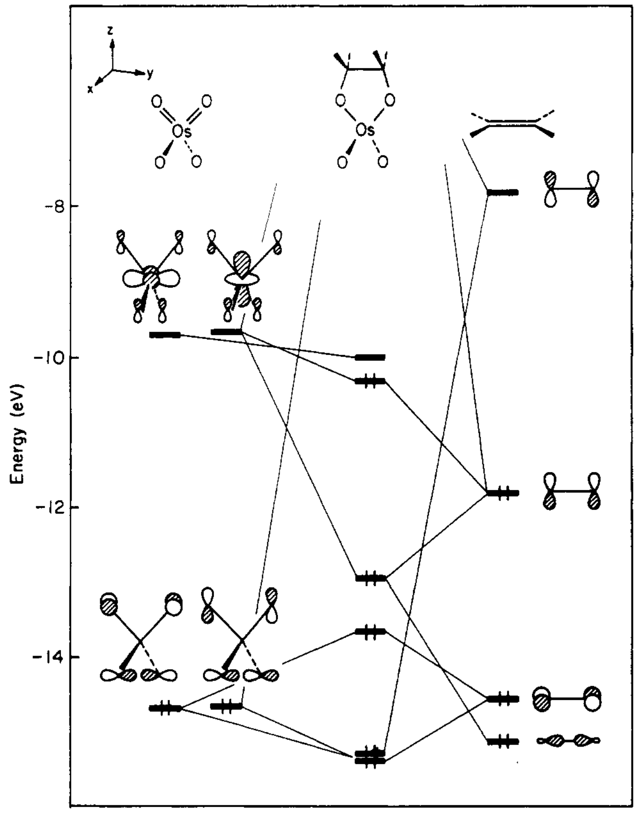
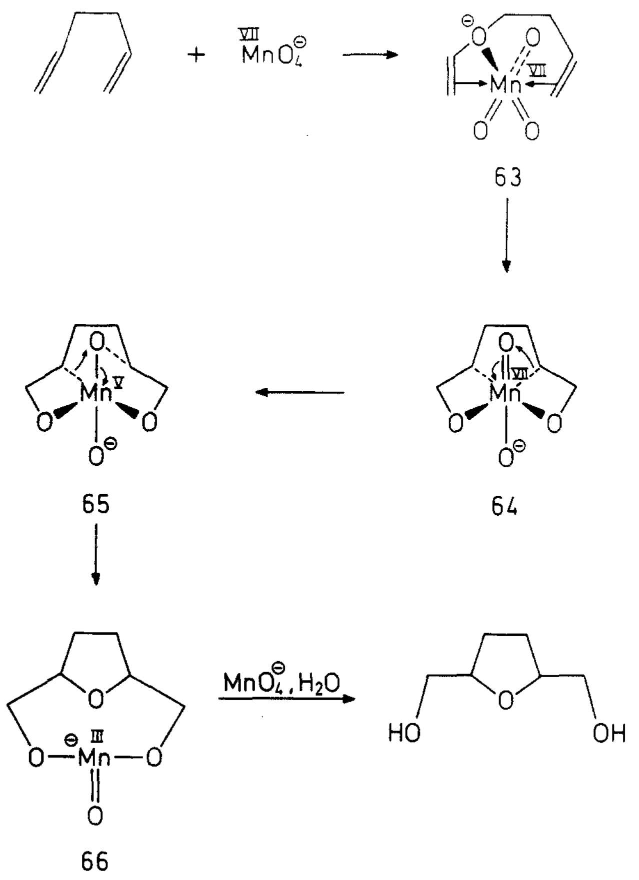


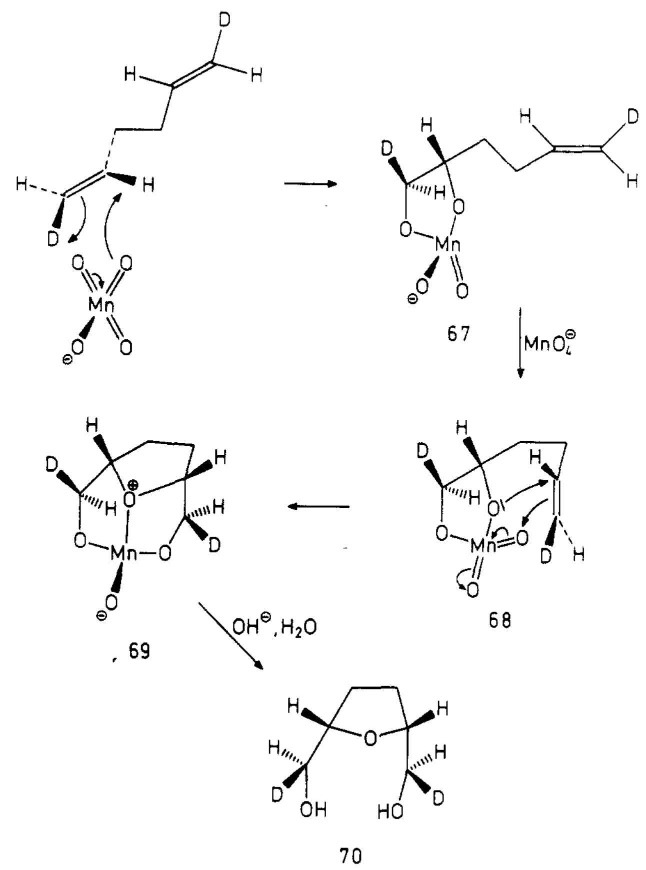
Figure 2. An interaction diagram for a [3 + 2] cycloaddition of ethylene to osmium tetraoxide.[128]

The [3 + 2] vs the [2 + 2] cycloaddition reaction has also been discussed in relation to the oxyamination of enopyranoside derivatives by N-tosylimidoosmium(VIII) trioxide.[129,130] On the basis of CNDO/2 and MNDO/3 calculations in relation to the observed regioselectivity, it was found that with the calculated π-electron densities of the model for *hex*-2-enopyranoside the [3 + 2] cycloaddition path was favored. With the assumption that steric hindrance plays a minor role during the reaction it has been found that the osmium–nitrogen bond needs to be polarized with osmium as the negative part and nitrogen the positive

SCHEME 10



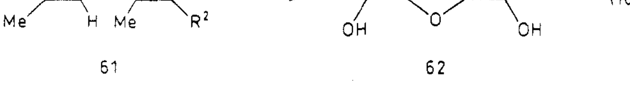
SCHEME 11



part, to account for the observed regioselectivity, if the reaction follows the [2 + 2] reaction path involving the metallaoxetane.[129,130]

To be able to say something significant about a [3 + 2] vs a [2 + 2] cycloaddition reaction mechanism in the reaction of osmium tetraoxide with alkenes either a characterization of the metallaoxetane to prove its existence or very detailed calculations of the activation energy for both the [3 + 2] and [2 + 2] and the possible reaction paths for the metallaoxetane intermediate are necessary.

The metallaoxetane intermediates have also become popular in the oxidation of alkenes and 1,5-dienes with the permanganate ion as the oxygen donor.[131] The metallaoxetane intermediate was probably first introduced in the permanganate oxidations of 1,5-dienes **61** to account for the stereochemistry of the formed 2,5-[1,1-bis(hydroxymethyl)ethyl]tetrahydrofurans (**62**) (reaction 16).[131]



61 62 (16)

It was pointed out that the classical ideas concerning the mechanism for the permanganate oxidations of alkenes did not help in the understanding of the reaction.[131] To account for the formation of **62** Walba et al. introduced the metallaoxetane intermediate as outlined in Scheme 10.[131]

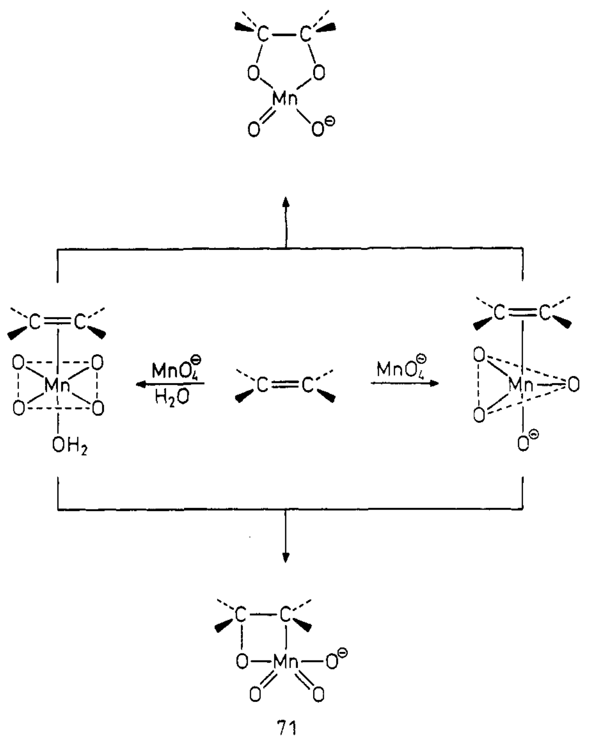
The first step in Scheme 10 is the formation of the bis-π-complex **63** between the diene and the permanganate ion followed by two [2 + 2] cycloadditions giving an octahedral Mn(VII) complex **64**, containing two metallaoxetanes. The reaction step, **64** → **65**, is an alkyl migration with retention of the configuration followed by a reductive elimination (also with retention), giving **66**, the Mn(III) diester.[131] Oxidation and hydrolysis of **66** affords the diol **62** with the correct stereochemistry.[131] It was later found that the same reaction also proceeds with Cr(VI) oxo species, and the [2 + 2] cycloaddition reaction path compared to the [3 + 2] cycloaddition path was discussed.[132]

The metallaoxetane mechanism for the permanganate oxidation of 1,5-dienes outlined in Scheme 10 was very much in contrast to the mechanism suggested at the same period of time by Baldwin et al.[133] They proposed the mechanism depicted in Scheme 11 for the oxidation of labeled hexa-1,5-dienes with the permanganate ion.[133]

The stereochemistry can be accounted for as follows:[133] the first step is a [3 + 2] cycloaddition of the alkene to the permanganate ion, giving **67**, which undergoes a rapid oxidation by another permanganate ion, producing **68** and manganate. An intramolecular cycloaddition of the Mn(VI) ester **68** produces **69**, as outlined in Scheme 11, followed by hydrolysis leading to the 2,5-bis(hydroxymethyl)tetrahydrofuran (**70**) with the correct stereochemistry.[133] It appears thus that the mechanism in Scheme 10 (the [2 + 2] cycloaddition), as well as the mechanism in Scheme 11 (the [3 + 2] cycloaddition), can account for the stereochemical outcome of the reaction.

^{18}O labeling experiments have indicated that a mechanism for the oxidation of 1,5-hexadienes in which all three oxygen atoms in the product are derived from a single molecule of the permanganate ion via a 1:1 diene–permanganate complex is incompatible with the

SCHEME 12



experimental results.[134] Though, no discussion of the [2 + 2] pathway relative to the [3 + 2] cycloaddition pathway was presented.

Freeman et al.[135-139] and Lee et al.[140-145] have frequently applied the metallaoxetane as an intermediate in reactions of alkenes with the permanganate ion as outlined in Scheme 12.

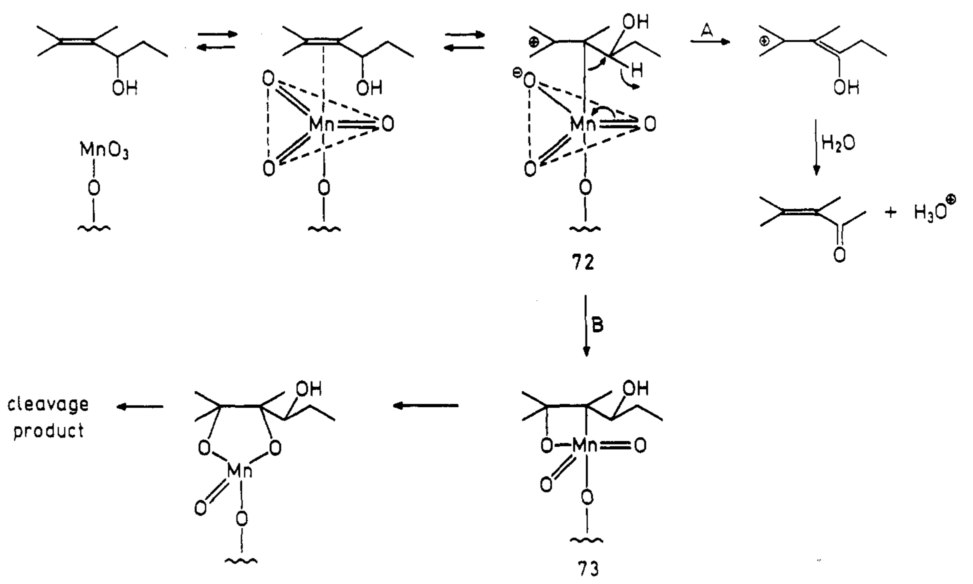
For the addition of the permanganate ion to the 5,6 double bond in the lactam form of substituted uracils, substituent effects, thermodynamic parameters, and salt effects were consistent with a concerted [3 + 2] cycloaddition.[135] But, the authors claimed that the experimental data did not exclude an initial fast transfer involving a charge-transfer complex and/or an organometallic intermediate having a Mn–C σ bond.[135] The kinetic data for the permanganate oxidation of substituted (*E*)-3-aryl-2-propenoates showed that both electron-donating and electron-withdrawing groups increased the rate of oxidation,[136] which could be indicative for a change in reaction mechanism. It was pointed out that charge-transfer complexes and/or the metallaoxetane 71 could be formed prior to the rds.[136] The five-membered cyclic manganese(V) ester was also found to be a plausible intermediate,[136] e.g. via **71**. Additional studies of the permanganate oxidation of different α,β-unsaturated carboxylic ion systems did not throw further light on the mechanism.[137-139]

The metallaoxetane has also been invoked as an intermediate in the oxidation of unsaturated alcohols by hydrated copper permanganate.[140] The first step was also here proposed to be a complex between the alkene and the metal as seen in Scheme 13. To account for some of the products observed the first step was suggested to be a slipping motion of the alkene toward one of the oxygens leading to a Mn–C bond and a positive charge at the other carbon in the double bond, **72**.[140,146] Reaction path A in Scheme 13 was proposed to have the largest activation energy due to the cleavage of a C–H bond in the rds.[140] The product from this reaction path, styryl ketone, is expected to be quite stable. The formation of the metallaoxetane **73** in path B in Scheme 13, was expected to proceed through a ts of lower energy, but giving rise to less stable cleavage products.[140]

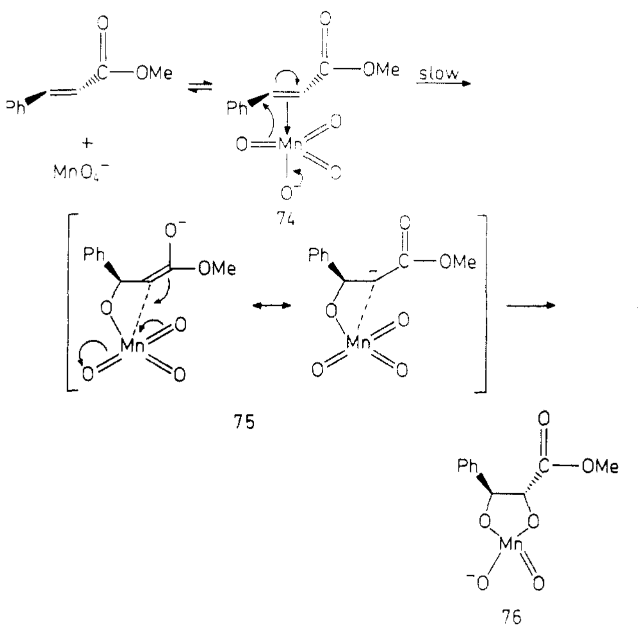
The Hammett plot for the permanganate ion oxidation of substituted methyl (*E*)-cinnamates gave ρ as 0.95.[141] These results indicate that the ts contains a greater concentration of negative charge near the aromatic ring than does the ground state.[141] It was proposed that the alkene–permanganate complex **74** was first formed, followed by a rate-determining nucleophilic attack by one of the oxygen atoms in the permanganate ion at the carbon atom nearest the aromatic ring initiated by a slipping motion of the alkene along the C=C bond, producing the metallaoxetane **75** (Scheme 14). The metallaoxetane then rearranges to the cyclic manganese(V) ester **76**.[141]

The idea with the slipping motion of the alkene toward one of the oxygens and subsequent formation of the metallaoxetane has been used by Lee et al. in several studies of the oxidation of different alkenes and alkynes by the permanganate ion,[142-145] but no direct

SCHEME 13

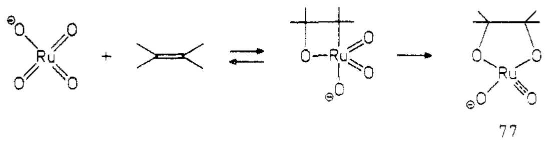


SCHEME 14



observation of the metallaoxetane has been reported in these reactions.

The spectator oxo bond introduced by Rappê and Goddard to be able to stabilize intermediates persuaded Lee et al.[147] to investigate the oxidation of *trans*-cinnamic acid by ruthenate (RuO_4^{2-}) and perruthenate (RuO_4^-). The purpose of using ruthenate and perruthenate was the following: it was assumed that the metallaoxetane intermediates were formed in rapid equilibrium reactions and that the perruthenate ion would react more rapidly with the carbon–carbon double bond to give the cyclic ruthenium(V) diester 77 (reaction 17) because 77 is stabilized by the spectator oxo group.[147] However, the similar reaction with ruthenate would not occur so readily (reaction 18), because of the formation of the cyclic ruthenium(IV) diester intermediate 78 could only be achieved by loss of the stability associated with the presence of the spectator oxo group in the metallaoxetane 79.[147]



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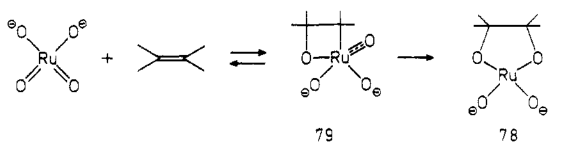
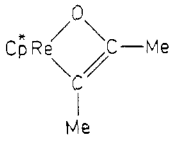


(18)

It was found that the reaction rate for the oxidation of cinnematic ion with perruthenate ion was 5×10^5 times faster than the corresponding ruthenate reaction.[147] The slow step in reaction 18 is the conversion of the metallaoxetane to the ruthenium(IV) diester as ruthenium changes from a d^2 to a d^4 state, compared to the previous steps which also are fast. The activation entropy for the ruthenate reaction is very similar to that for the oxidation of the cinnamate ion by permanganate, whereas the activation enthalpy is larger. The activation energy for the perruthenate oxidation is 7 kcal·mol^{-1} lower than for the ruthenate oxidation. It was concluded that the experimental observation was in agreement with the predictions made by Rappê and Goddard.[69]

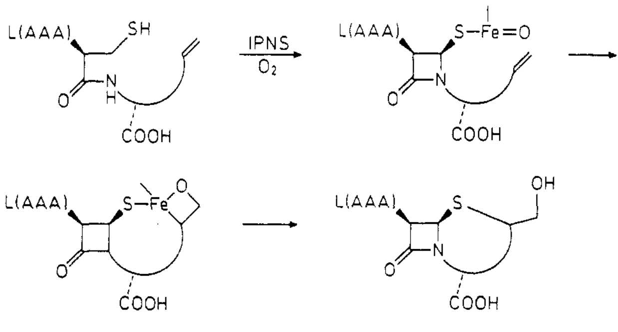
c. Other Reactions

The metallaoxetane intermediate has also been invoked in other types of oxygen-transfer reactions than discussed above. Cp^*ReO_3 reacts with PPh_3 in alkynes to produce compounds with the molecular formula $Cp^*ReO_2(R_1CCR_2)_2$.[148] $Cp^*ReO_2(CH_3CCCH_3)_2$ reacts with I_2 in benzene to give tetramethylfuran. A reaction mechanism with a rhenaoxetane intermediate (**80**) was proposed to account for the reaction.[148]



80

In a study of the mechanism of cyclization of tripeptides by the enzyme isopenicilin N synthase (IPNS) a ferraoxetane 81 formed by a [2π + 2π] cycloaddition of the oxo–iron species to the double bond has been postulated (reaction 19).[149]



(19)

Deuterium labeling studies have indicated that the last step in reaction 19 occurs by a syn [2π + 2π] cycloaddition followed by reductive elimination with retention.[149]

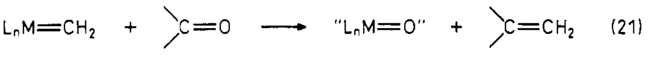
4. Metallaoxetanes in Oxygen-Transfer Reactions to Transition-Metal Complexes

Let us now discuss the possible formation of the metallaoxetane as an intermediate in reactions where an oxygen atom is transferred to the transition-metal complexes from various organic compounds.

We will start with the deoxygenation reaction of epoxides (reaction 20). As we have already seen, tetracyano- and tricyano-substituted ethylene oxide adds oxidatively to PtL_4, giving a platinaoxetane as the product.[56,57] Though, the metallaoxetane rearranges upon heating or irradiation to form 24, a platinum–alkoxy species.


(20)

A discussion of the proposed metallaoxetane intermediates in the reductive coupling of ketones and aldehydes to alkenes by various reagents, including Tebbe's reagent "CpTi=CH_2", (reaction 21) will also be presented here.

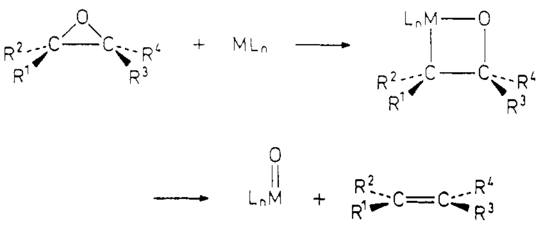


(21)

a. Oxidative Addition Reactions

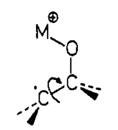
The metallaoxetane was proposed as an intermediate in oxidative addition reactions on the basis that deoxygenation of epoxides by transition-metal compounds formally is the reverse of the epoxidation of alkenes.[48] As we saw earlier the product distribution from an oxidation of alkenes by chromyl chloride lead to the "birth" of the metallaoxetane intermediate, and therefore also to the proposal of the metallaoxetane as an intermediate for the reduction of epoxides.[48]

Generally, the reduction of the epoxide goes with a high degree of retention of the stereochemistry. This was proposed to be consistent with the formulation of the mechanism as an insertion of the metal complex into one C–O bond in the epoxide, giving the metallaoxetane (reaction 22).[48]



(22)

Though, reduction of *cis*-stilbene oxide with WCl_6^{2-} gave only 8% retention of the configuration among the product stilbenes observed.[150] A zinc–copper couple gave 13% retention in the reduction of *cis*-stilbene oxide.[151] For this catalyst loss of the stereochemistry was found in the reaction of various *cis*- and *trans*-octenes.[151] To account for this observation a radical-like intermediate 82 was proposed,[151] in which the possibility of rotation around the C–C axis explains the observed limited stereoselectivity. The [Cr^{II}(en)] complex also shows nonstereoselective deoxygenation of epoxides.[46]

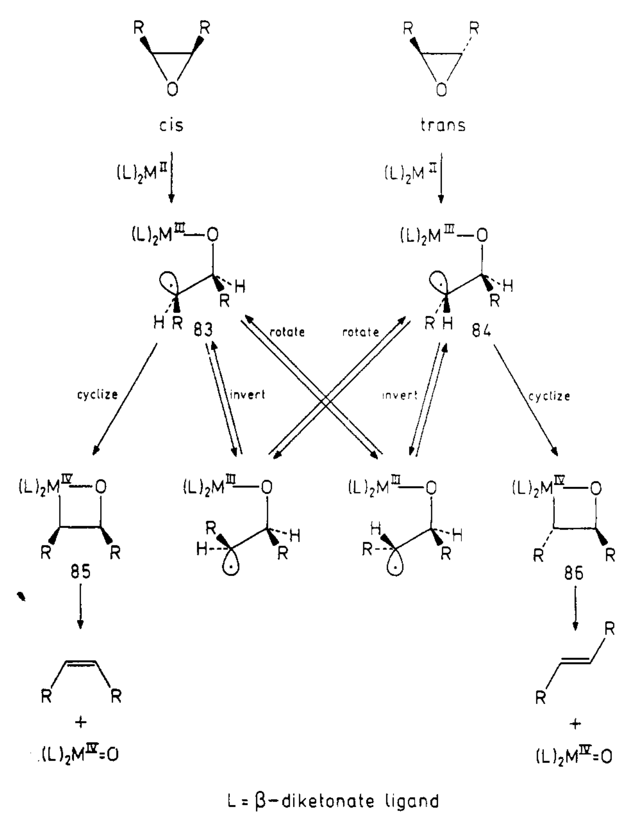


82

A system that catalytically deoxygenates epoxides was reported by Green et al.[152] When using sodium amalgam as reducing agent toward some metallocenes [$M(C_5H_5)_2X_2$] ($X_2 = Cl_2$; M = Mo, W, Ti, Zr; X_2 = O; M = Mo, W), these were able to reduce various epoxides.[152] The active-metal species was proposed to be the reduced low-valent reactive fragment "MCp_2".[152] This species was proposed to add oxidatively the epoxide to form the metallaoxetane. No experimental evidence for either the "MCp_2" or the metallaoxetane intermediate was reported.[152] Cis–trans isomerization is also observed for this system. *cis*-2-Pentene oxide gave *cis*:*trans*-2-pentene in ratios varying from approximately 1:1 (Ti, 80 °C) to 2:1 (W). Importantly, it was noted that the expected stereoselective product, *cis*-2-pentene, does not isomerize under the reaction conditions.[152]

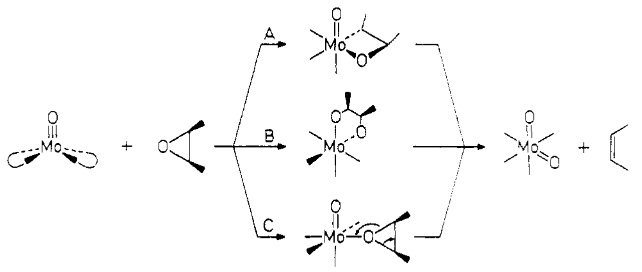
The loss of stereospecificity in relation to the metallaoxetane intermediate has been addressed in a contribution from Schwartz et al.[153] The active-metal species in the deoxygenation reaction is here several low-valent vanadium and molybdenum *β*-diketonate complexes. Schwartz et al. observed some trends in the evolution of the stereochemistry for the reaction. They noted that epoxides with large substituents on the three-membered ring lead to a larger degree of retention in the stereochemistry than those bearing small ones.[153] When the size of the ligands on the metal was increased a decrease in stereospecificity was observed.[153] The last thing they pointed out was that the reaction with molybdenum complexes proceeds with a larger degree of retention than observed for the vanadium systems.[153] From these established trends in the variation of the stereospecificity for the reaction they proposed a mechanism involving two intermediates as depicted in Scheme 15.[153] An initial radical intermediate, with the metal-oxidized one unit, was set forth. These radical species, 83 and 84, can either cyclize to the metallaoxetane intermediates, 85 and 86, or rotate around the C–C bond followed by an inversion at the radical center, as shown in Scheme 15. This latter reaction path accounts for the loss of stereospecificity for some of the reagents. Schwartz et al. explained the observed trends with varying ligand size, metal, and substituents accordingly to this proposed mechanism. Rotation around a C–C bond is speeded up by small substituents.[153,154] Providing more space around the metal center enhances the path with retention of the stereochemistry, because ring closure of the radical is facilitated.[153] In no case was complete retention observed with these metal complexes, nor was further evidence for the formation of a metallaoxetane given.[153]

SCHEME 15

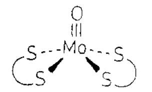


A stereoselective system for deoxygenation of epoxides has been reported by Moloy.[155] The active species is the d^2 $MoO(Et_2dtc)_2$ 87. When oxygen is removed from *cis*-2,3-epoxybutane, more than 98%

SCHEME 16



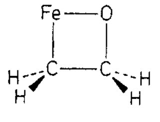
selectivity for the cis isomer, *cis*-2-butene, is observed.[155] A radical species, as **82**,—if formed—does for this system not rotate around the C–C bond. The author rationalized that the reaction must be concerted (Scheme 16, C) or proceed through a cyclic intermediate, as depicted in Scheme 16.[155]



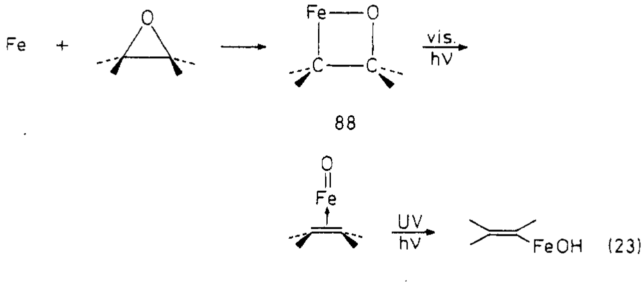
87

Two cyclic intermediates were proposed, namely the metallaoxetane (A) and a metallaglycol (B).[155] Moloy could not judge which of these three intermediates is the most likely; only say that if B is formed the back-reaction to **87** and the epoxide is slow due to no incorporation of ^{18}O into unreacted epoxide when $Mo^{18}O(Et_2dtc)_2$ is used as catalyst.[155]

A ferraoxetane, $FeOC_2H_4$ (**88**), was proposed on the basis of FTIR spectroscopy by Kafafi et al. as the product of an interaction of ethylene oxide and iron atoms in a solid argon matrix as 12.5–15 K.[156] The photochemistry of the ferraoxetane was followed; upon visible photolysis an oxo–iron π-complexed ethylene (**89**) species was formed (reaction 23).[156] An UV excitation of **89** resulted in a photorearrangement, inserting the oxometal function in a C–H bond of the π-complexed alkene, forming the vinyliron hydroxide **90**.[156] The assignment of the structures of the various intermediates was verified by an isotopical experiment with ethylene-d_4 oxide as starting material.[156] The symmetry (C_s or C_1) of **88** could not be determined on the basis of these spectroscopic measurements.[156]

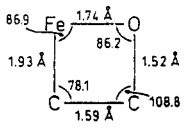


88



89 90

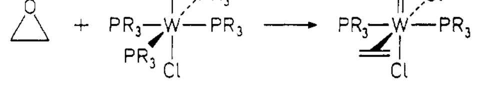
Ab initio calculations on **88**[157] revealed a planar ring with bond distances, as shown in **91**.



91

The theoretically obtained carbon–carbon distance is similar to the C–C bond distance in $Pt(As(Ph)_3)_2(C_2(CN)_4O)$ (1.58 Å) measured by X-ray crystallographic experiments.[57] The photochemical rearrangement reaction sequence in reaction 23 was confirmed by theoretical calculations, and the structures of **89** and **90** were optimized.[157]

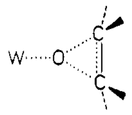
In a series of papers Mayer et al.[158–161] have demonstrated the oxidative addition reaction of various heterocumulenes, X=C=Y, and epoxides to a tungsten(II) complex, $WCl_2(PR_3)_4$ (R = C_6H_5, CH_3). Ethylene oxide gives upon reaction an oxotungsten(IV) complex, $W(O)Cl_2(PR_3)_2(CH_2{=}CH_2)$ (**92**), (reaction 24).[159]



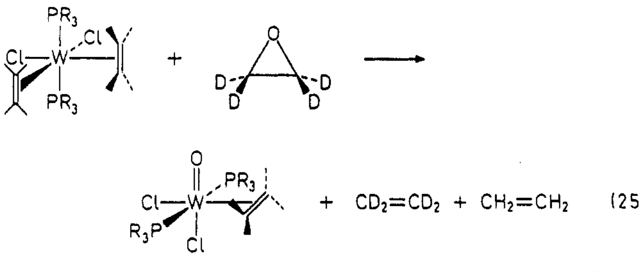
92

The product from this oxidative addition is unusual in the sense that a π-donor ligand (oxo) as well as a π-acceptor ligand (ethylene) are bound to the same metal center, the d^2 tungsten center. **92** is in principle the species suggested to be the first intermediate in the reactions of an alkene with an oxotransition-metal species.[48] More crowded terminal epoxides were found to yield mixtures of the alkene–oxo complex and a oxo–tris(phosphine) complex, $W(O)Cl_2(PR_3)_3$.[161] Epoxides of internal alkenes gave only the tris(phosphine) complex.[161,162] Both theoretical[163] and experimental[159] investigations showed that the formation of a tungstaoxetane from **92** was not feasible.

The oxygen transfer from the epoxide to the tungsten complex is suggested to proceed by a concerted mechanism involving a direct abstraction of the oxygen atom by the metal center **93**.[164] This mechanism is supported by following the reaction of ethylene-d_4 oxide with a similar W(II) complex, $WCl_2(CH_2{=}CH_2)_2(PMePh_2)_2$[165] (reaction 25).



93



The first step of this reaction is a loss of ethylene from $WCl_2(CH_2{=}CH_2)_2(PMePh_2)_2$, giving the 5-coordinated intermediate, $WCl_2(CH_2{=}CH_2)(PMePh_2)_2$, that is responsible for the reaction with ethylene-d_4 oxide.[164]

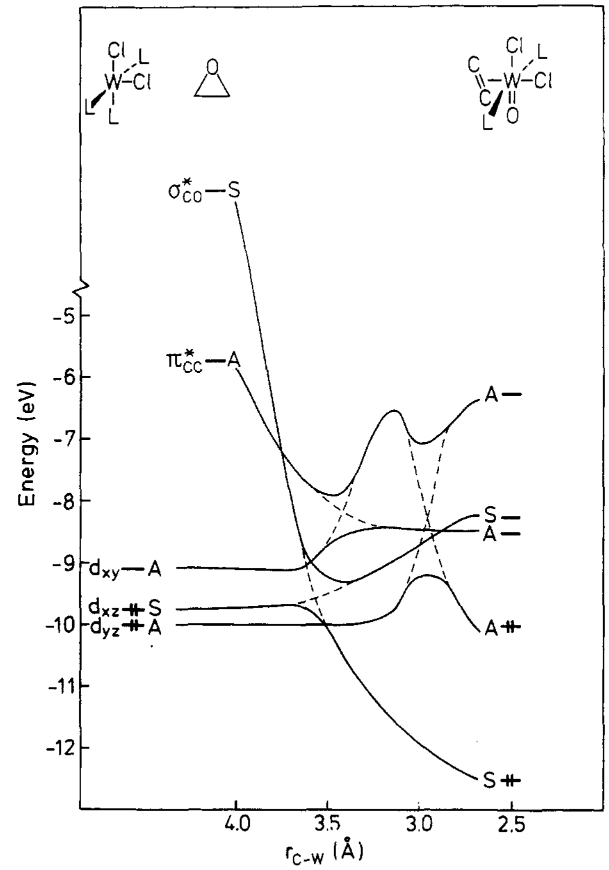
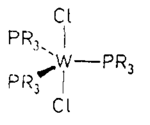


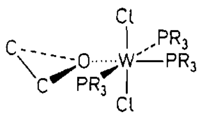
Figure 3. Energy correlation diagram for a concerted abstraction of oxygen from ethylene oxide by $WCl_2(PR_3)_3$.[59]

The alkene bound in the product is the one that was originally bound to the metal, no incorporation of $CD_2{=}CD_2$ is observed.[164]

A theoretical study based on the extended Hückel method is consistent with these two findings.[59] Because $WCl_2(PR_3)_4$ is coordinatively saturated the 14-electron complex $WCl_2(PR_3)_3$ (**94**) provides the most favorable opportunities for the oxidative addition to take place. From the calculations it was suggested that a concerted mechanism is responsible for the oxygen-atom transfer. The energetically most favored way to approach ethylene oxide to **94** was found to be "end-on", as shown in **95**. An energy correlation diagram for the concerted oxygen abstraction was presented and is shown in Figure 3.[59]



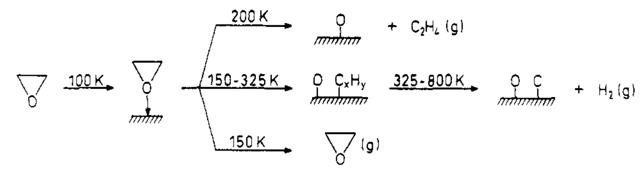
94



95

The most important thing to notice in this diagram is the avoided crossing of the d_{xz} (the HOMO) and an initially high-lying antibonding carbon–oxygen orbital, σ^*_{CO}, of ethylene oxide at $R_{C-W} \approx 3.5$ Å. This transfer of two electrons from tungsten to σ^*_{CO} leads simultaneously to the cleavage of the two carbon–oxygen bonds of ethylene oxide, to a strengthening of the carbon–carbon bond due to σ^*_{CO}'s C–C π-bonding character and to the formation of the tungsten–oxygen bond.[59] The deoxygenation of the epoxides by the tungsten(II) complex as outlined in Figure 3 is from an electronic point of view in principle the reverse process of the addition of an alkene to the oxo-ligands in osmium tetraoxide.[128] Tilting of ethylene oxide in an attempt to form a metallaoxetane causes an increase in energy and was found to be unfavorable compared with the approach shown in **95**.[59]

SCHEME 17



The (110) surface of Mo is also an active catalyst for deoxygenation of ethylene oxide.[166] Friend et al. exposed an Mo(110) surface with ethylene oxide at low temperature, heated the sample, and followed the evolution of desorbing species.[166] They could distinguish three different types of interactions between ethylene oxide and the surface depending on the temperature, as shown in Scheme 17.

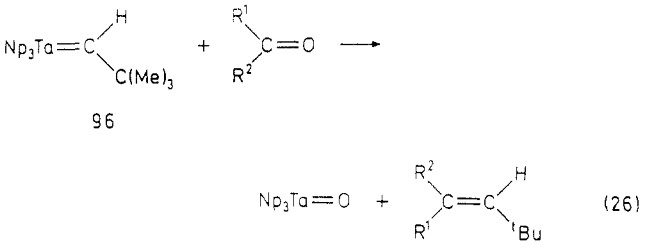
Below 150 K they observed only ethylene oxide. At 200 K a large peak in the mass spectrometer due to ethylene was seen.[167] Friend et al. concluded that ethylene was deliberated directly from adsorbed ethylene oxide into the gas phase. From a coadsorption experiment of ethylene oxide and ethylene-d_4 on the Mo(110) surface it was shown that the ethylene peak at 200 K originated from ethylene oxide, no deuterium containing products were detected. This excludes the possibility that ethylene oxide is cleaved at a lower temperature where the hereby formed ethylene sticks to the surface, before it is desorbs at 200 K.[166] For adsorption of ethylene sulfide on the Mo(110) surface Friend et al. have assigned the concerted mechanism as the most likely for the desulfurization reaction.[167]

Not all the ethylene oxide deliberates ethylene at 200 K; some decomposes nonselectively to surface-bound hydrocarbons at temperatures 150–325 K. At temperatures higher than 325 K molecular hydrogen is desorbed from these surface hydrocarbons, and surface carbides are left back.[166] The mechanism for this nonselective decomposition of ethylene oxide on Mo(110) is still unknown, it could proceed through a metallaoxetane. The third possibility connected to ethylene oxide decomposition reactions—the radical–alkoxide-like intermediate—was ruled out for ethylene production due to a missing incorporation of deuterium into ethylene in coadsorption experiments;[166] but again whether or not this species can lead to the nonselective decomposition products is unknown.

A theoretical analysis of the surface-catalyzed desulfurization of ethylene sulfide has appeared.[168] It was suggested that ethylene production follows a concerted mechanism which is very similar to the above outlined mechanism for the reaction of epoxides with $WCl_2(PR_3)_4$. The study indicates that this reaction might proceed easier on a surface than in model molecular compounds, due to the availability of more metal centers at the surface.[168]

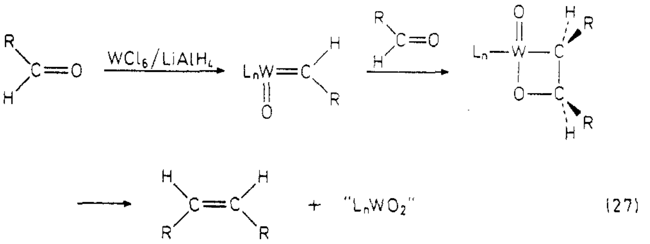
b. "Tebbe-like" Reactions

The reductive coupling of the carbonyl function of various organic substrates with a hydrocarbon ligand in high-oxidation-state early-transition-metal complexes has become a very syntheticly useful class of reactions.[47,169–171] Schrock showed that the transition metal ylide, $Ta(CH_2C(CH_3)_3)_3(CHC(CH_3)_3)$ (**96**), shows similar reactivity as phosphorus ylides—"Wittig-systems"—toward the carbonyl group of an organic compound[172] (reaction 26). This transition-metal compound was also able to attack esters and amides, a reaction that is normally unsuccessful with the phosphorus ylide systems, whereas **96** was reported to be unreactive toward ethylene oxide.[172] Schrock rationalized that the mechanism consists of at least two separate steps, one involving a coordination of the oxygen atom in the carbonyl fragment to Ta, followed by a metathesis reaction.[172]

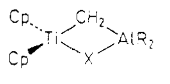

96

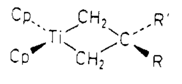
(26)

The mechanism for the Wittig reaction has been shown to involve a oxophosphetane intermediate.[52] An analogue intermediate was proposed by Fujiwara et al. for the reductive coupling of carbonyl-containing compounds to alkenes by a WCl_6–$LiAlH_4$ system.[173] This is the only system we are aware of that is active for the deoxygenation of epoxides as well as for the coupling of two carbonyl substrates to an alkene. A carbene–tungsten complex was set forth as active intermediate on basis of various model reactions that all revealed great similarities to typical carbene chemistry for this metal-catalyzed reaction.[173] The initially formed oxo-carbene–tungsten complex was suggested to add a second carbonyl group across the tungsten–carbon bond resulting in the formation of a tungstaoxetane. The reaction mechanism is outlined in reaction 27.[173] No evidence, spectroscopically or by reaction chemistry, was reported to support the formation of the metallaoxetane.[173]

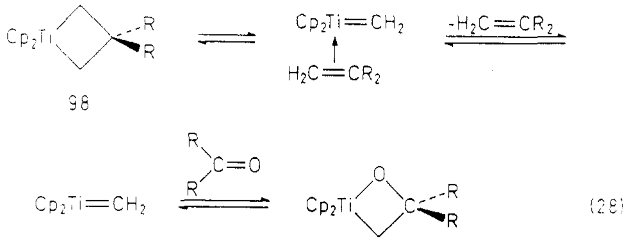

(27)

Tebbe's reagent, $Cp_2TiCH_2AlXR_2$ (**97**), is a versatile methylene transfer agent for the conversion of ketones to primary alkenes,[174] but no mechanistic features were published in the original paper by Tebbe et al.[174] The Tebbe reagent reacts with esters, giving vinyl ethers,[169] a species that Wittig-like reagent can not methylenate. A more stable aluminum-free source for "$Cp_2Ti{=}CH_2$" has been invoked,[175] namely the metallacycle **98** that has been characterized by Grubbs et al. by NMR spectroscopy[175] and by X-ray crystallographic[176] measurements. They found that this titanacyclobutane is planar and symmetrical. Puckering of the ring to relieve steric repulsion between the Cp rings and the substituents in the 2-position was shown to be unimportant,[175] whereas a rhomboid distortion is more likely on theoretical[177] as well as on experimental[176] grounds.


97

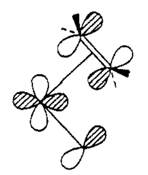

98

The reaction of the titanacyclobutane with carbonyls are shown in reaction 28.[47] The mechanism for the activation of "$Cp_2Ti{=}CH_2$" from **98** involves the metallacyclobutane to alkene–metal–alkylidene equilibrium and theoretical reports for this transformation have appeared.[177,178]


98

(28)

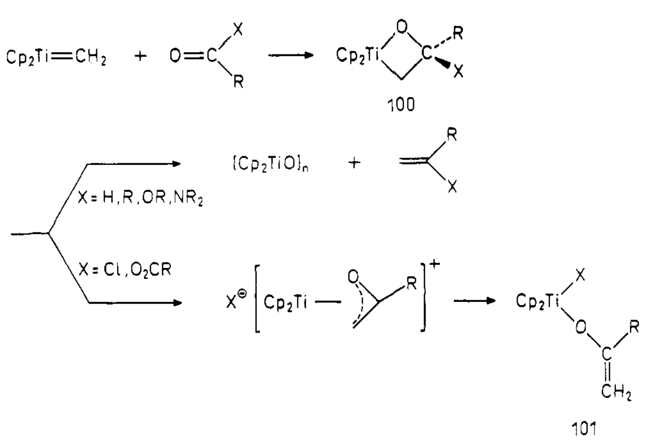
Hoffmann et al.[177] conclude that a specific alignment of the olefin and the carbene, as shown in **99**, is necessary for the coupling to proceed as to increase the interaction of the carbene p orbital with the LUMO of the olefin. This is not the conformation of the two coligands that results in the strongest π-bonds to these π-acceptors because of the competition of one of the d_π orbitals of Ti.[177] A minimum in total energy was found for an intermediate nonclassical structure.[177] A work by Upton and Rappé concludes that the formation of the titanacyclobutane is favorable by ~12 kcal·mol⁻¹.[178] Both reports agree on the point that the activation energy required for the metathesis to result is low from the metallacyclobutane.


99

The kinetics for the equilibrium has been studied by Grubbs and co-workers.[179,180] They concluded that the rds in the formation of the titanium–methylene intermediate is the reversible ring opening to a carbene–titanium–olefin complex (see reaction 28). This can reversibly exchange the olefin with another unsaturated organic substrate from the surroundings. This could be e.g. a substrate containing a carbonyl function that, upon ring closure, produces the titanaoxetane **100**. The mechanism for the reaction of "$Cp_2Ti{=}CH_2$" with carbonyls is shown in Scheme 18.[47]

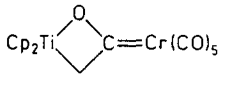
The final product for the reaction of "$Cp_2Ti{=}CH_2$" species with a carbonyl function is thus the olefin and an oxo–titanium species, $[Cp_2TiO]_n$, obtained after a metathetic ring opening.[47] Deviations from this general outlined reaction scheme is seen for substrates where the carbonyl function is substituted with very electron-withdrawing groups, such as chloride and anhydride.[171] The product for these species is an enolate–titanium complex, **101**. For these particular substrates the titanaoxetane **100** either does not form or it decomposes by another route than metathesis, by breaking only the Ti–C bond and transferring the X sub-

SCHEME 18

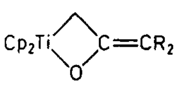


stituent to titanium.[171] The reaction for the decomposition of the titanaoxetane **100** is in principle the reverse reaction to the photoextrusion of acetone from **25** (Scheme 3).[64]

Spectroscopic evidence for the titanaoxetane has only recently been published by Grubbs et al.[181,182] Indications for two different titanaoxetanes were reported.[181,182] Both contain an sp^2-hybridized carbon bound to the oxygen, **102**[181] and **103**.[182]

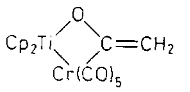


102



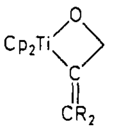
103

102 was formed by an insertion of a CO ligand of $Cr(CO)_6$ into "$CpTi{=}CH_2$".[181] Structure **102** was reported to be in equilibrium, through a zwitterionic intermediate, with **104**, a complex with a bridging μ^2-(η^2-ketene) ligand.[181]



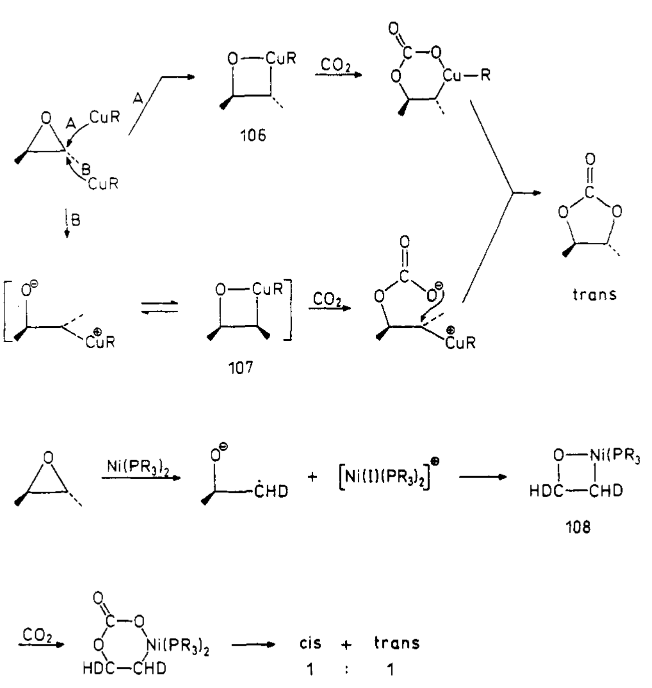
104

Two different routes giving **103** were reported by Grubbs et al.[182] Either coupling of a metal ketene with dimethylsulfoxonium methylide or reaction of a ketene with 3-*tert*-butyltitanacyclobutane gave the titanaoxetane **103** which was identified by dynamic ^{1}H NMR spectroscopy.[182] The ring is puckered with an inversion barrier of ~13–19 kcal·mol^{-1}.[182] It is suggested that the puckered structure is favored due to extra orbital interaction between an empty a_1 orbital of Ti and either the *exo*-methylene double bond or an oxygen lone pair.[182] The isomeric analogue to **103** with the sp^2-hybridized carbon in an α-position to titanium, **105**, is found to be unstable. It was impossible to obtain spectroscopic characteristics for this titanaoxetane.[170] The difference in stability is probably caused by the fact that **105** can not pucker and therefore is close to a planar geometry,[182] which has been shown to be the geometry required for cleaving of the corresponding metallacyclobutane.[180]

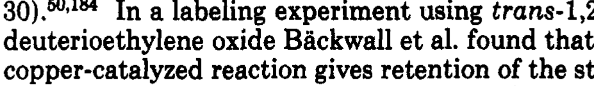


105

SCHEME 19



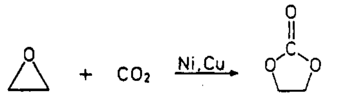
Schrock et al.[183] have reported that the high-valent tungsten–alkylidyne complexes $W(C_3Et_3)(DIPP)_3$ and $W(C\text{-}t\text{-}Bu)(DIPP)_3$ react with a variety of carbonylic species, forming the corresponding oxo–vinyl complexes $W(O)(vinyl)(DIPP)_3$. The reaction is proposed to involve a nucleophilic attack of the Lewis acidic alkylidyne carbon at the carbonyl function leading to a metallaoxetane-like intermediate, as outlined in reaction 29.[183]



(29)

c. Other Reactions

Late-transition-metal complexes of Cu(I) or Ni(0) catalyze the insertion of carbon dioxide into epoxides, giving the corresponding alkene carbonates (reaction 30).[50,184] In a labeling experiment using *trans*-1,2-dideuterioethylene oxide Bäckwall et al. found that the copper-catalyzed reaction gives retention of the stereochemistry, whereas a nickel catalyst yields nonstereospecific products; a 1:1 ratio of cis- and trans-dideuterated ethylene carbonate was observed.[184] Mechanisms for the transformations were proposed involving the metallaoxetane intermediates **106**–**108** as shown in Scheme 19.[184]

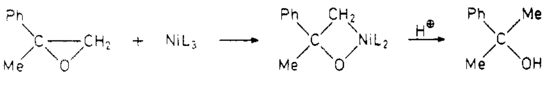


(30)

The observed retention for the copper-catalyzed reaction can be obtained by either double retention (path A) or double inversion (path B) of the two insertion steps involved in the reaction. The nickel-catalyzed reaction was suggested to proceed through an initial electron transfer from $Ni(PR_3)_2$ to the epoxide. The hereby formed anion radical can rotate around the C–C bond before collapsing to the nickelaoxetane intermediate.[184] For either catalyst CO_2 adds to the metallaoxetane through a coordination of the electrophilic carbon to the oxygen atom of the ring.

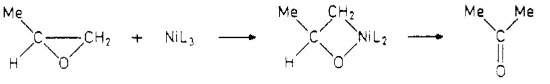
Reaction of $PtMe_2$(1,10-phenanthroline) with *trans*-2-deuteriostyrene oxide and CO_2 gave a metallacarbonate product which by NMR was shown to have a *cis*-2-D-1-Ph stereochemistry.[185] The reaction was suggested to take place by an S_N2 mechanism by which the metal attacks the less sterically hindered carbon atom leading to a open structure where rotation around the C–C bond and ring closure with retention of the configuration gives the metallaoxetane with the opposite stereochemistry as the substrate.[185] CO_2 then reacts with the metallaoxetane, and the metallacarbonate is formed.

The metallaoxetane intermediate has also been invoked in the nickel-catalyzed ring opening of epoxides.[186] $NiBr_2(PPh_3)_2$ was found to catalyze the ring isomerization of propene oxide to propionaldehyde, while $NiBr_2(PMe_2Ph)_2$ and $Ni(PPh_3)_3$ gave mixtures of acetone, propylene, and the aldehyde.[186] It was suggested that $NiBr_2(PPh_3)_2$ acts as a Lewis acid in an electrophilic attack at the epoxide oxygen followed by a C–O cleavage, whereas $Ni(PPh_3)_3$ was proposed to react with α-methyl styrene oxide and propene oxide as a nucleophile forming the metallaoxetanes **109** and **110** as depicted in reactions 31 and 32, respectively.[186]



109

(31)

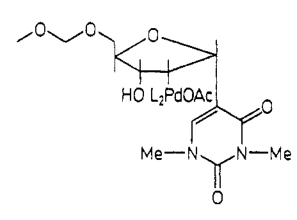


110

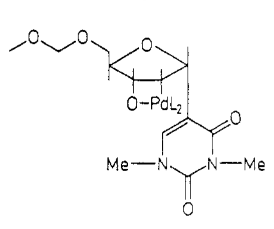
(32)

Related to reactions 31 and 32, it has been found that ML_4 (M = Ni, Pd, Pt) promotes the methylation of 2-methylpropene oxide with methyl iodide.[187] The first step was proposed to be the oxidative addition of methyl iodide, giving the divalent metal complex, $M(CH_3)IL_2$.[187] A metallaoxetane was set forth, as an intermediate, explaining the formation of the NMR-characterized product, a 2,2-dimethylpropoxy–platinum complex upon reaction with 2-methylpropene oxide.[187] The platinaoxetane structure was observed by NMR for the direct reaction of $Pt(PPh_3)_4$ with 2-methylpropene oxide in toluene-d_8.[187] Thus, it was pointed out that this structure might be a platinum–oxirane complex, although a large J_{Pt-H} (69 Hz) was observed.[187] A palladaoxetane has also been suggested as one of the possible intermediates in the palladium(0)-catalyzed reaction of α,β-epoxy ketones leading to β-diketones.[188]

Reaction of 1,4-anhydro-2-deoxy-5-*O*-(methoxymethyl)-D-*erythro*-pent-1-enitol with (1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)mercuric acetate in the presence of palladium(II) acetate afforded a product which possess adjacent hydroxyl and palladium substituents, **111**.[189] Decomposition of **111** to afford the C–C double bond in the furan ring was suggested to proceed via the palladaoxetane **112** from which an oxopalladium species was extruded.[189]

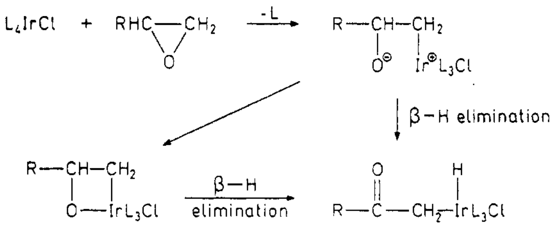


111



112

Reacting an epoxide with Ir(I)ClL$_4$ (L = PMe_3) leads to the formation of stable *cis*-hydridoacyl complexes, **113**, as depicted in reaction 33.[190] This reaction was proposed to be a nucleophilic attack of the Ir(I) complex at the epoxide on the least-substituted C–O bond. The hereby formed ionic intermediate can either β-hydrogen eliminate or close the ring to the iridaoxetane, which will β-eliminate the hydrogen to give the *cis*-hydridoacyl complex.[190]



(33)

113

5. Discussion

Certainly, the metallaoxetane structure does exist, but the evidence for its involvement in all the various types of oxygen-transfer reactions is still not convincing. The structures, **12**, **16**, **25**, and **26**, and the metallaoxetenes, **29** and the one shown in reaction 9, are all characterized and have been shown to be intermediates in different types of oxygen-transfer reactions. Other metallaoxetane structures, **17**–**19**, have been characterized by X-ray crystallography, whereas their ability to transfer oxygen atoms has either not been investigated or it was found that these complexes lead to rearrangement reactions. Recently, it has been found, by NMR spectroscopy, that a titanaoxetane probably is an intermediate in the "Tebbe-like" reactions.

The metallaoxetane has been proposed to be formed in reactions between alkenes and some oxometal complexes, and between organic substrates containing oxygen functions and various transition-metal complexes. The metallaoxetane structure has been invoked in the mechanisms of these reactions in an attempt to account for the different products observed: "The metallaoxetane, while not leading directly to the products observed, provides a convenient mechanistic keystone, since through ligand reorganization it leads to either the epoxide or ..."[79] In these reactions no conclusive evidence for the metallaoxetane has yet appeared, although it is still often used in mechanistic discussions of these oxygen transfer reactions.

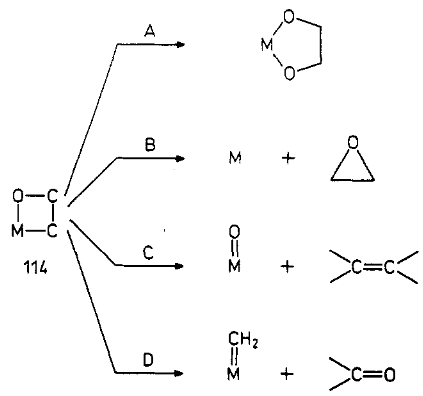
Let us here mention Sharpless et al.'s reservation when they first introduced the metallaoxetane: "We would be the first to admit that the arguments presented here in favor of carbon–metal bonded intermediates (the metallaoxetanes) in these olefin oxidations are inconclusive. In fact, as we tried to emphasize throughout, we have as yet no evidence which cannot also be rationalized by direct attack of the olefin on the ligands" ... "In spite of the inconclusive results at present, we have decided that our new hypothesis should be published since it offers an important alternative to those already in the literature."[48] Now more than a decade since Sharpless et al. proposed the involvement of the metallaoxetane in different oxygen-transfer reactions, the experimental evidence for its existence is still based mainly on the observed product distribution. Though, theoretical work by Rappé and Goddard has supported the mechanistic suggestions by Sharpless et al. Although, they only presented calculations for the chromyl chloride reactions the conclusions were extended to several other systems. Later it was theoretically shown by using ab initio calculations that oxochromium species with electron-withdrawing ligands favor the formation of a four-centered intermediate in the reaction with ethylene.[71] When moving from the oxochromium species to the oxomanganese and oxoiron porphyrin species it was found that these systems probably react with ethylene under formation of a diradical intermediate rather than a metallaoxetane.[71] Similar theoretical results were also obtained for various oxoruthenium systems.[103,104] Attempts to optimize ruthenaoxetane structure resulted in the formation of either ethylene and a oxoruthenium compound or a five-membered Ru–O–C–C–N cyclic structure, depending on the used ligands.[104]

Inspection of the different characterized metallaoxetanes reveals that no obvious trends in either the d electron occupation or in the oxidation state of the metal can be traced which will promote the formation of stable metallaoxetanes. The d occupation number for the characterized metallaoxetanes range from d^0 to d^8 (with all even numbers, except 2, found in between!). The oxidation state for the metal in the characterized metallaoxetanes varies from +2 to +5. It is thus not possible to predict whether a metallaoxetane is likely to form on basis of the d occupation number or the oxidation state of the metal in a hypothetical metallaoxetane.

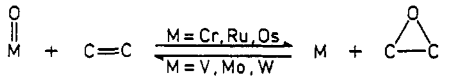
For the oxometalloporphyrin systems (manganese, iron, and ruthenium) recent experimental and theoretical results seems to favor a radical intermediate in the reactions with alkenes. However, for the "Tebbe-like" reactions it now seems reasonable to include titanaoxetanes (Ti(IV) and d^0) in the mechanistic considerations, although there is still no X-ray crystallographic evidence for the titanaoxetane. One has to be careful in predicting intermediates in this type of reactions: d^0 titanaoxetanes and zirconaoxetenes do form, whereas the evidence for e.g. d^0 osmaoxetanes is still inadequate.

If the metallaoxetane 114 is formed, there are at least four possible routes for its decomposition: (A) rearrangement to a metalladiester; (B) reductive elimination to the epoxide or its rearranged isomers; and two ways of ring opening, namely, (C) formation of an oxometal species and an alkene, or (D) formation of carbenemetal species and a carbonyl function, as depicted in Scheme 20.

SCHEME 20



The differentiation between route A and B in scheme 20 can be rationalized from the introduction of the spectator oxo bond.[69,70,147] The preference of either C or D can to some degree be traced to the bond energies of the resulting oxometal or carbenemetal species, respectively.[73,74] In the case of titanium route C will be favored, as the bond energy of Ti=O is larger than the $Ti{=}CH_2$ bond energy; this is probably the driving force in the "Tebbe-like" reactions. However, if a metallaoxetane is formed by reaction of ethylene and $Mn{=}O^+$, a carbenemanganese species and formaldehyde are formed, because of a stronger carbene-manganese bond in comparison with the oxomanganese bond.[74] A prediction based on the bond energies of the involved species weather reaction path C or D is preferred is probably very difficult due to a rather limited number of published oxometal and carbenemetal bond energies. Those known from gas-phase measurements indicate great similarities, except for the early transition metals.[73,74,191] A distinction between decomposition way B and C is most likely dependent on the metal. Those metals to the right of Cr, Ru, and Os (these included) tend to favor a reduced-metal complex and an epoxide (or its rearranged isomers), whereas the metals placed to the left of V, Mo, and W (included) give the oxometal species and the alkene, as outlined in reaction 34. It is interesting to notice that this separation of the metals is the same as the one found for the active-metal complexes in the epoxidation of alkenes.[29] There the metals to the left of the line form active epoxidation reagents as peroxo/peroxide–transition-metal complexes, whereas to the right of this line it is an oxotransition-metal species that promotes the epoxidation.[29]



(34)

When Sharpless et al. first introduced the metallaoxetane in connection with oxygen-transfer reactions, they suggested it as being involved in an alternative reaction path, although they could not exclude other reaction paths. However, later contributions to the metallaoxetane field have often neglected the possible existence of other reaction paths than the one involving the metallaoxetane. For example, in mechanistic proposals for the deoxygenation of epoxides, where often metallaoxetanes are invoked without taking the experimentally observed cis–trans isomerization into account. Also, in the reaction of high-valent oxometal species and alkenes the possibility of other reaction paths, as e.g. the [3 + 2] cycloaddition, are generally not offered as much attention, as the metallaoxetane path ([2 + 2] cycloaddition). As Sharpless et al. pointed out in their original paper introducing the metallaoxetane, "if formed, would constitute a new class of high-valent σ-bound organometallic species."[48] At that period of time, this was a new idea, that organometallic species could be involved in this type of organic oxidation reactions. The investigation of the chemistry of high-valent organometallic compounds was and still is in its early stages.[192] The proposal of an involvement of

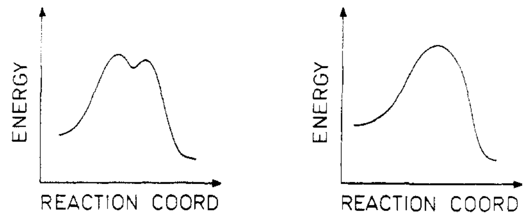


Figure 4. A reaction with an intermediate to the left and with a transition state to the right.

high-valent organometallic species in organic oxidation reactions resulted in a great number of contributions on various reactions, all confirming the possibility of metallaoxetanes. Never, though, has experimental observations been specific to rule out other reactions paths. Many authors did not really address the question of other reaction paths, rather they tried to explain all products as originating from the metallaoxetane. One can say that the metallaoxetane intermediate was adapted and accepted too quickly, hereby not stating that it is wrong, but only that more mechanistic investigations still are needed in order to trace possible intermediates. It should also be mentioned that other authors argued directly against the metallaoxetane intermediate.

An appropriate question to ask here is: Are metallaoxetanes intermediates formed during oxygen-transfer reactions? As it has been shown there is several examples of reactions involving characterized metallaoxetanes that can transfer an oxygen atom. But for the major number of reactions in which metallaoxetanes are suggested, the evidence for its existence is still incomplete. Before proceeding further into the question, which (probably) is very difficult to answer, let us first discuss what is understood by an intermediate. In Figure 4 two different reaction profiles are outlined.

In Figure 4a a reaction with an intermediate is shown, and in Figure 4b a reaction with a transition state is shown. In order to physically trace an intermediate, it has to exists enough time for detection to proceed. The practical limit is about 10^{-12} s. In the reactions where the metallaoxetane has yet not been characterized as an intermediate, the difficulties in its detection may be due to the fact that it is a very short-lived intermediate. Experimentally, it is not possible to distinguish a short-lived intermediate from a transition state (Figure 4b). So, maybe the metallaoxetane is a transition state in some reaction path rather than an intermediate?

6. Addendum

After submission of this review several papers dealing with metallaoxetanes have appeared. Bergmann et al. have prepared a metallaoxetane, $(Me_3P)_4Ru(\eta^2\text{-}CH_2C(Me)(Ph)O)$, which has been found to react with a variety of substrates.[193] In relation to oxygen-transfer reactions $(Me_3P)_4Ru(\eta^2\text{-}CH_2C(Me)(Ph)O)$ reacts with dihydrogen to give $(Me_3P)_4RuH_2$ and $HOC(Me)_2Ph$.[193] A rhodaoxetane, $(Me_3P)_3BrRh(\eta^2\text{-}CH_2C(Me)_2O)$, has also been prepared, but no oxygen-transfer reactions were studied.[194] The structure of the metallaoxetane part of $(Me_3P)_3BrRh(\eta^2\text{-}CH_2C(Me)_2O)$ is comparable with the other metallaoxetane structures. In the asymmetric epoxidation of alkenes catalyzed by a chiral Mn(salen) complex a direct interaction between the alkene and the oxygen in the oxomanganese complex have been suggested.[195] In contrast with hereto, the epoxidation of alkenes catalyzed by a ruthenium-substituted heteropolyanion, $SiRu(L)W_{11}O_{39}$, and the epoxidation of *cis*-1,2-dideuterio-1-octene catalyzed by *Pseudomonas oleovorans* mono oxygenase have both been suggested to proceed via a ruthenaoxetane[196] and a ferraoxetane,[197] respectively. The formation of allylic alcohols in the deoxygenation of 2,3-epoxy alcohols induced by $(Cp)_2TiCl$ has also been proposed to take place through a titanaoxetane.[198] In these papers where the metallaoxetane was invoked as the intermediate no other reaction paths were considered.

7. Abbreviations

acac	acetylacetone
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
dpm	dipivaloyl meronate
DIPP	2,6-diisopropylphenoxide
ee	enantiomeric excess
Et_2dtc	diethyl dithiocarbamate
Me	methyl
Np	neopentyl
PCC	pyridinium chlorochromate (py/CrO_3Cl^-)
Ph	phenyl
rds	rate-determining step
TBA	tetrabutyl ammonium
t-Bu	*tert*-butyl
tfa	(1,1,1-trifluoroacetyl)acetonato
TPP	*meso*-tetraphenylporphyrinato
ts	transition state

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