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## Reactivity by Design—Metallaoxetanes as Centerpieces in Reaction Development

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### 1. INTRODUCTION

The development of new catalytic reactions that perform chemical transformations with high selectivity and efficiency is a key goal in chemical research. Many new reactions are discovered serendipitously, but increasing mechanistic knowledge permits the rational design of new reactions of key intermediates. We feel that 2-metallaoxetanes can serve as key intermediates in the design of new reactions. We present herein

a review of the synthesis, structure, and reactivity of 2-metallaoxetanes.

2-Metallaoxetanes have been postulated as intermediates in numerous reactions and have been the subject of many experimental and computational studies. In several cases, the intermediacy of 2-metallaoxetanes has not been supported by subsequent mechanistic investigations.<sup>1,2</sup> Nevertheless, there are many reactions where 2-metallaoxetanes have been established as intermediates in the lowest energy pathway. As a result, the reactivity of 2-metallaoxetanes has received increased attention in recent years and these complexes have enormous potential for development of novel catalytic reactions. The goal of this review is to provide a resource for those wishing to design new reactions based on 2-metallaoxetanes as reagents, intermediates, or transition states in catalytic reactions. This review will begin with a description of catalytic and stoichiometric reactions in which 2-metallaoxetanes have been identified as likely intermediates. In the course of this discussion, the properties of 2-metallaoxetanes will be described, as well as general methods for their preparation. Metallaoxetane reactivity will then be described, which will hopefully provide the foundation for future discoveries.

Schiøtt and Jørgensen reviewed the early developments in the field of metallaoxetane chemistry 20 years ago.<sup>1</sup> In the work at hand we want to build on their seminal review and describe the developments in the field since 1990. Although our focus will lie on the more recent progress, we will at times still point to the early stages when the context demands it. We excluded non-transition metallaoxetanes,<sup>3</sup> nonanionic metallaoxetanes,<sup>4</sup> and 3-metallaoxetanes<sup>5</sup> from the discussion but included well-defined 2-metallaoxetanes, 2-metallaoxetenes, and 2-metallalactones.<sup>6</sup> See Figure 1 for an illustration of the scope of the review.

The first time the structural motif of a 2-metallaoxetane (metallaoxetane from here) was reported in a publication was as early as 1900.<sup>7</sup> When Biilmann investigated the oxymercuration of olefins, he found that  $\alpha$ - $\beta$  unsaturated carboxylic acids such as cinnamic acid (**1**) converted into a compound that he described as an inner salt of a 3-phenyl-3-hydroxy-2-mercuripropanoic acid (**2**; Scheme 1).

Treatment with aqueous sodium hydroxide led to cleavage of the Hg—O bond and yielded the ring-opened product **3**. This structure was brought up again in related reports by Biilmann<sup>8</sup> as well as Schrauth et al.<sup>9</sup> and later by Park and Wright.<sup>10</sup>

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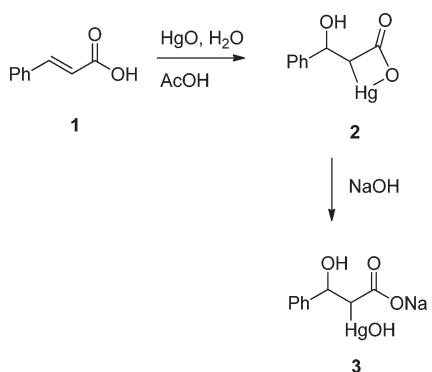
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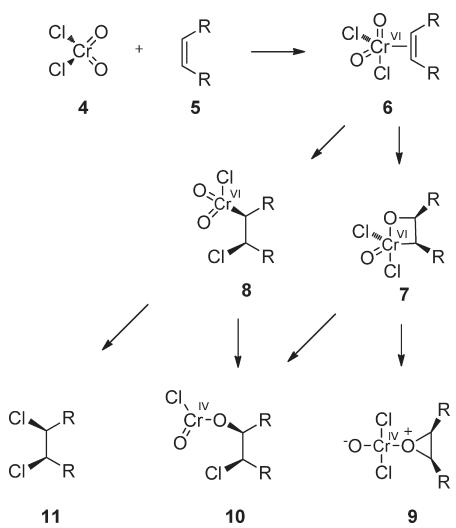
Included		Excluded	
$[M] \square O$	2-metallaacetane	$[M] \square O$	$[M] =$ no transition metal
$[M] \square O$	2-metallaacetene	$[M] \square OR$	non anionic metallaacetane
$[M] \square O$	2-metallalactone	$[M] \square O$	3-metallaacetane

Figure 1. Scope of the review.

## Scheme 1. First Reported Metallaacetanes



## Scheme 2. Chromyl Chloride Catalyzed Epoxidation of Olefins



Over 70 years after these initial reports, De Pasquale invoked the intermediacy of a nickelaoxetane in the Ni catalyzed formation of cyclic carbonates from epoxides and  $CO_2$ .<sup>11</sup> Shortly after that, Sharpless proposed a metallaacetane intermediate in the chromyl chloride catalyzed epoxidation of alkenes.<sup>12</sup> This report can possibly be regarded as the hour of birth for many

mechanistic speculations about an involvement of metallaoxetanes in transition metal catalyzed reactions.

## 2. METALLAOXETANES AS TRANSIENT INTERMEDIATES

## 2.1. Olefin Oxidation Reactions

**2.1.1. Epoxidation.** The intermediacy of metallaoxetanes in the epoxidation of olefins has been proposed in multiple cases.<sup>1,13</sup> In fact, the postulate of such an intermediate in the chromyl chloride catalyzed epoxidation of alkenes reported by Sharpless et al. in 1977 had significant impact.<sup>12</sup> As mentioned earlier, it marked the onset of many mechanistic speculations regarding the potential intermediacy of metallaoxetanes in transition metal catalyzed or mediated oxygen-transfer reactions. But the mechanism of this classic reaction is still under debate/investigation.

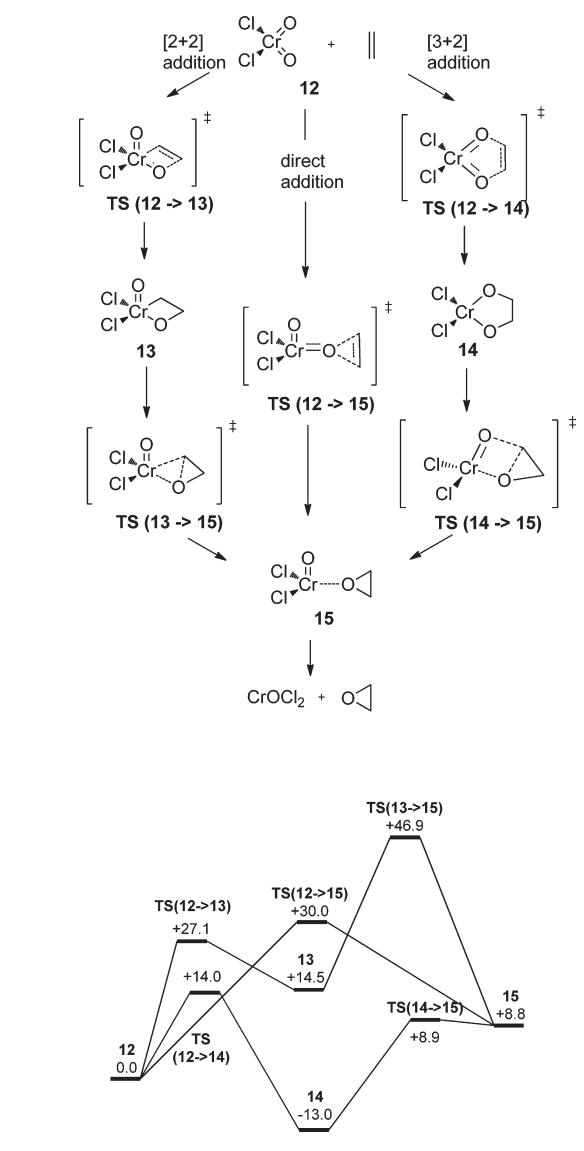
In their initial report, Sharpless and co-workers stated a chromaoxetane intermediate 7 formed after olefin-metal pre-coordination (6), and subsequent [2 + 2] addition with an oxo ligand would best explain the product distribution in the reaction of chromyl chloride 4 with olefins.<sup>12</sup> The main products observed were the epoxide 9, a chlorohydrin 10, and a vicinal dichloride 11 (Scheme 2). Several theoretical studies have been conducted to further elucidate this reaction mechanism.

The first theoretical studies of this reaction mechanism were ab initio calculations performed by Goddard and Rappé<sup>14</sup> which supported the formation of a chromaoxetane intermediate. Further calculations by Yamaguchi<sup>15</sup> and gas-phase studies by Bierbaum<sup>16</sup> and Beauchamp<sup>17</sup> corroborated this reaction pathway. The same intermediate was proposed in olefin oxidations performed with other oxochromium compounds, albeit without direct experimental evidence.<sup>18,19</sup> Arguments against an oxametallacyclic intermediate in this reaction were voiced by Barrett based on product distribution analysis but without further spectroscopic or theoretical support.<sup>20</sup> (All of the above are mentioned in detail in Jørgensen's reviews.<sup>1,13</sup>)

Further scepticism arose with the onset of the animated discussion about the reaction mechanism of transition metal catalyzed olefin dihydroxylation (section 2.1.2). Detailed DFT calculations by Ziegler et al. contradicted the original hypothesis of Sharpless. After optimization of the substrate and product geometries, the authors were unable to detect a minimum for a precoordination of the ethylene fragment to the chromium complex. In contrast to Goddard's earlier work,<sup>14</sup> Ziegler reported that a [3 + 2] addition of ethylene to chromyl chloride was kinetically and thermodynamically favored over the [2 + 2] addition (Scheme 3).<sup>21</sup>

The transition states for the [3 + 2] and [2 + 2] additions lie at 14.0 and 27.1 kcal/mol relative to the substrates and the energies of the metalladioxolane, 14, and the metallaacetane, 13, -13.0 and 14.5 kcal/mol, respectively. On the [3 + 2] pathway the system crosses from the singlet to the triplet state, which was rationalized by possible spin-orbit coupling.<sup>22</sup> The second step consists of rearrangement of the oxametallacycles to the epoxide precursor complex, 15, in which the fully formed epoxide is coordinated to the metal center. This complex had already been postulated by Sharpless<sup>12</sup> as a direct precursor to the final products and had been widely agreed on in other studies earlier.<sup>14</sup> Limberg and co-workers finally reported IR spectroscopic proof for the existence of 15 in low temperature photolytic matrix experiments.<sup>23</sup> For this second step the [3 + 2] pathway had an

**Scheme 3.** Ziegler's DFT Calculations on the Chromyl Chloride Epoxidation



activation barrier of 21.9 kcal/mol and the product **15** was 21.8 kcal/mol energetically higher than dioxolane (**14**) while the activation barrier for the [2 + 2] pathway was calculated to be 34.4 kcal/mol and exothermic by −5.9 kcal/mol. As the product complex **15** in these calculations was assumed to be in the triplet state, spin crossover had to occur in the second step for the [2 + 2] pathway. A direct addition pathway without intermediates was considered also but showed the highest of all initial activation barriers to be 30.0 kcal/mol; consequently, this pathway was regarded as highly unlikely (among the following steps, the barrier from **13** to **TS(13 → 15)** is energetically even more demanding).

In a short review of the chromyl oxide catalyzed oxidation of organic compounds, Limberg pointed out that the failure to detect the [3 + 2] adduct **14** during their low temperature photolytic matrix experiments meant that it cannot represent an essential intermediate—at least under these conditions, as **14** is more stable than the product complex **15** and should thus be readily detected.<sup>23c</sup>

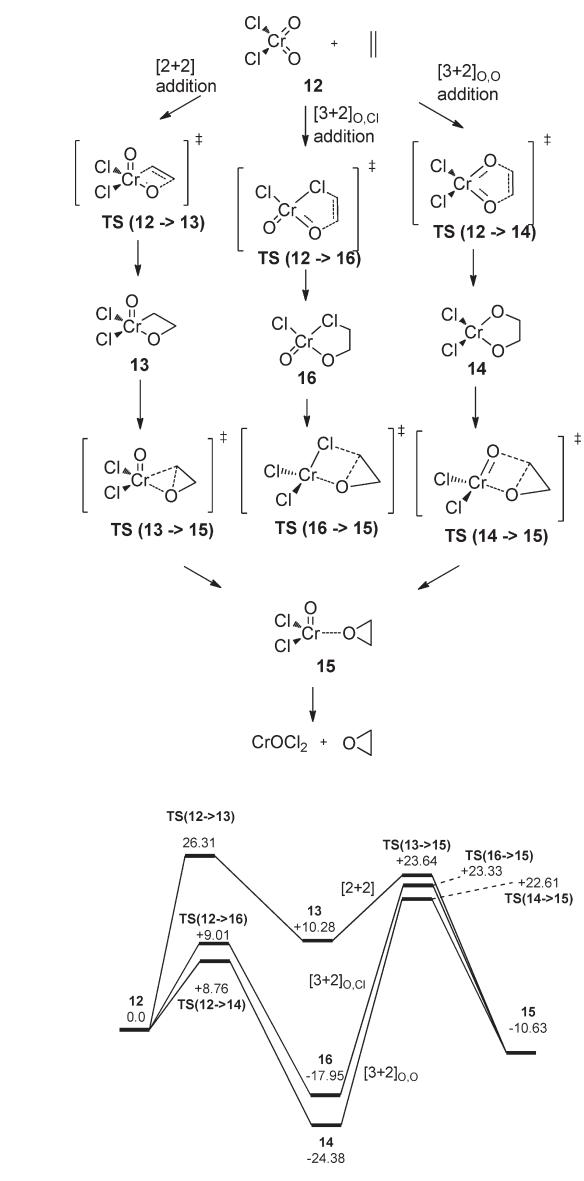
Recent gas phase studies of the interaction between alkenes and high valent chromium-oxo species also invoked chromaoxetanes as possible reaction intermediates.<sup>24</sup> In a theoretical study (UB3LYP/6-311++G level) of C=C double bond activation by CrO<sub>2</sub><sup>+</sup>, Wang and co-workers found that the activation of the double bond only involved one metal-oxo ligand in an initial [2 + 2] addition, with formation of a chromaoxetane. No evidence was found for a competing [3 + 2] addition involving both oxo ligands to form the dioxolane.

More recently, Tia et al. used hybrid DFT at the B3LYP/LACVP\* level to carry out a theoretical study of this reaction.<sup>25</sup> Similar to Ziegler's findings, no transition state could be detected for precoordination of the olefin to the metal. For the direct addition pathway, an almost thermoneutral triplet intermediate (+0.12 kcal/mol) was found, but no valid transition state either on the singlet or the triplet surface could be located. Thus, a direct addition pathway was also ruled out. For the stepwise mechanisms, the [2 + 2] and [3 + 2]<sub>O,O</sub> dioxo pathways, already investigated by Ziegler, were considered, in addition to a separate [3 + 2]<sub>O,Cl</sub> oxochloro addition in which one chloride and one oxo ligand attacked the olefin (Scheme 4).

The activation barrier (26.31 kcal/mol) and endothermicity (10.28 kcal/mol) calculated for the [2 + 2] pathway were similar to those reported by Ziegler (27.1 and +14.5 kcal/mol, respectively) and both the [3 + 2]<sub>O,O</sub> (TS = 8.76 kcal/mol, intermediate **14** = −24.38 kcal/mol) and [3 + 2]<sub>O,Cl</sub> pathways (TS = 9.01 kcal/mol, intermediate **16** = −17.95 kcal/mol) were found to be kinetically and thermodynamically favored regarding the formation of the oxametallacyclic intermediates. No spin crossover was reported for these transitions. The second step—the rearrangement to the epoxide precursor complex **16**—was decisively different from the work of Ziegler (Figure 2). Ziegler reported a very high energy barrier from the metallaoxetane **13** to the products, potentially due to the necessary spin crossover (34.4 kcal/mol barrier, TS = 46.9 kcal/mol above reactants). Tia's calculations still showed that the [2 + 2] pathway had the highest transition state energy for the three pathways (23.64 kcal/mol above reactants compared to 22.61 kcal/mol for [3 + 2] dioxo and 23.33 kcal/mol for [3 + 2] oxochloro), but the relative activation barrier was lower due to the energetically higher lying intermediate. The activation energies for the three pathways compared were [2 + 2] = 13.36 kcal/mol, [3 + 2]<sub>O,O</sub> = 46.99 kcal/mol, and [3 + 2]<sub>O,Cl</sub> = 41.28 kcal/mol. Moreover, the transition from the intermediates to the product was only exothermic in the [2 + 2] case (**13** → **15** = −20.91 kcal/mol) but endothermic for the [3 + 2] pathways (**14** → **15**, [3 + 2]<sub>O,O</sub> = 13.75 kcal/mol, **16** → **15**, [3 + 2]<sub>O,Cl</sub> = 7.32 kcal/mol). All the reported structures and transition states lay on a singlet state surface, and no spin crossover was reported. Although the product was calculated to be 19.54 kcal/mol more stable in its triplet state, no triplet transition states from either the metallaoxetane or the five-membered oxametallacycles could be found. As a consequence, Tia et al. concluded that the [2 + 2] pathway is the most favored overall reaction path in spite of its high first activation barrier.

The lower stability of the formed intermediate **13** allowed the reaction to proceed to completion faster over a smaller second activation barrier, which was significantly higher for the more stable [3 + 2] adduct intermediates, **14**. This was also in accordance with the failure to observe another intermediate in low temperature photolytic matrix experiments, as the metallaoxetane was energetically higher than the detected epoxide precursor complex.<sup>23c</sup>

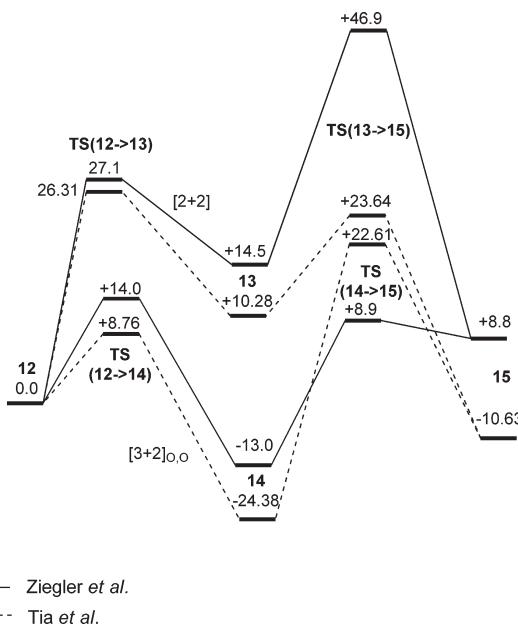
**Scheme 4.** Tia's DFT Calculations on the Chromyl Chloride Epoxidation



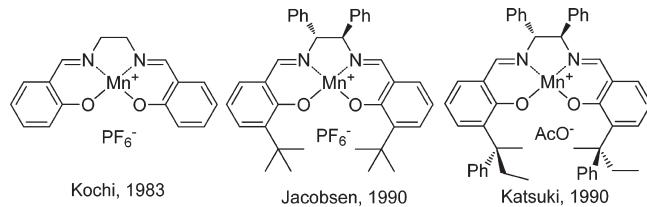
However, the overall energy needed to proceed along the  $[2 + 2]$  pathway is higher and only if the excess energy dissipates at the stage of the intermediate can the lower second barrier affect the course of the reaction. In addition, DFT is known to have some severe deficiencies in calculating relative energies of different spin surfaces and crossover between these is often undetectable with traditional methods and algorithms.<sup>26</sup>

Another important class of olefin epoxidation where metallaoxetanes have been invoked along the reaction coordinate include metalloporphyrin systems. These are of special interest due to their similarity to oxidizing enzymes such as cytochrome P450.<sup>27</sup>

Groves et al. introduced the idea of a metallaoxetane intermediate for the iron-porphyrin catalyzed asymmetric epoxidation of olefins, but in the same report they dismissed it. They had predicted a preference for 1,1-disubstituted alkenes, but this was not consistent with experimental results.<sup>28,29</sup> Schiøtt and Jørgensen



**Figure 2.** Comparison between the  $[2 + 2]$  and  $[3 + 2]_{O,O}$  pathways as calculated by Ziegler and Tia.

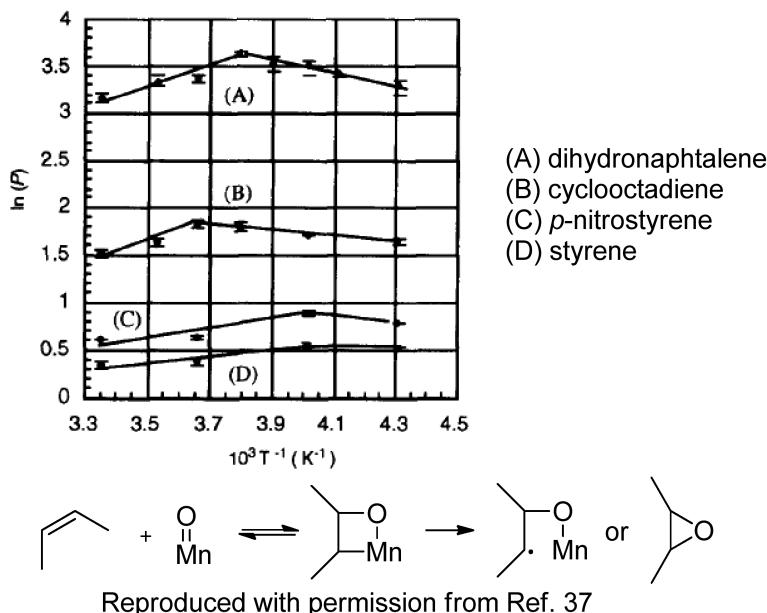


**Figure 3.** Pioneering Mn-salen catalyst systems used in olefin epoxidation.

give a good overview of the early mechanistic considerations regarding metallaoxetanes in their review.<sup>1</sup> The quintessential message from these investigations is that no convincing spectroscopic or theoretical evidence for a metallaoxetane intermediate in metalloporphyrin-promoted epoxidations has been found. In later accounts the role of a metallaoxetane as an intermediate was further dismissed, although a transition state metallaoxetane was still considered possible.<sup>28b,30</sup>

More recently, Broadbelt and Snurr have reported on quantum chemical studies of stable intermediates for the alkene epoxidation employing Mn-porphyrin catalysts.<sup>31</sup> A metallaoxetane intermediate would be very high in energy compared to other possible intermediates, such as a radical species. Consequently, these authors concluded that a metallaoxetane is unlikely to be involved in the reaction mechanism.<sup>31</sup>

Related to the transition metal porphyrin systems mentioned above are transition metal salen complexes. The asymmetric catalytic manganese-salen/derivative based epoxidation of alkenes first reported by the groups of Jacobsen<sup>32</sup> and Katsuki<sup>33</sup> is perhaps the most prominent olefin oxidation employing these complexes. Even earlier, Kochi et al. had reported nonstereoselective catalytic epoxidation of unactivated alkenes employing a chromium-salen system with iodosobenzene as stoichiometric oxidant (Figure 3).<sup>34</sup> A subsequent report described a manganese-salen system that displayed increased reaction rates and a broader substrate scope.<sup>35</sup> These and related Mn and Cr-salen



**Figure 4.** Nonlinear Eyring-plots in the Mn-salen catalyzed epoxidation of olefins indicate two distinct operational mechanisms.

systems gained considerable interest with respect to their utility as well as for purposes of elucidating the active mechanism.<sup>13,36</sup>

Kochi proposed a radical intermediate for the Mn-salen system<sup>35</sup> but was reluctant to stipulate a particular intermediate for the Cr case. Instead, he tentatively offered two possible intermediates, one of which was a chromaoxetane, with the other being a complex where the fully formed epoxide was coordinated to chromium. In either case, the  $C_{\alpha}$ —O bond would need to be sufficiently polarized to account for the buildup of positive charge on the alkene.<sup>34b</sup>

After the discovery of the asymmetric versions of this reaction by Jacobsen and Katsuki, more and more mechanistic studies were performed and the discussion about the involved pathways intensified. The main question was whether the reaction proceeded via a concerted or stepwise mechanism; if the latter, the question of which intermediates were involved would arise. Without going into the details of all proposed pathways,<sup>36b</sup> we will highlight those which invoke metallaoxetanes. It must be clarified, though, that no definitive answer to the mechanistic question has been found to date. Indeed, most probably several mechanisms are operational and competing with each other in the individual cases.<sup>36b</sup> Jacobsen suggested in his original report the direct transfer of the oxo ligand to the alkene, similar to the mechanism reported for related iron-porphyrin systems,<sup>28</sup> but left open whether it was a concerted or stepwise one-electron transfer mechanism.<sup>32</sup> Katsuki and co-workers initially rationalized the stereochemical results with a radical intermediate but later reviewed their mechanistic proposal to invoke a metallaoxetane intermediate.<sup>37</sup> This rationale was based on the observation of a nonlinear relationship between reaction temperature and enantioselectivity, as well as on the effect of substituents on the modified salen ligand on the enantioselectivity (Figure 4). Such nonlinearity in the Eyring plot of a reaction indicates two different operational mechanisms,<sup>38</sup> as had been predicted by Norrby et al. for this reaction.<sup>39</sup> In this proposal, the reversible formation of a manganoxetane was followed by irreversible formation of a radical intermediate. Brun and co-workers also speculated about the existence of a metallaoxetane in their  $H_2O_2$

promoted epoxidation of alkenes. The observation of an aldehyde and a tertiary alcohol as a side product of the reaction could best be explained if the reaction path went through such an intermediate.<sup>40</sup>

The most noteworthy opposition against metallaoxetane intermediates in these reactions came from the Jacobsen group.<sup>41</sup> This lab reported linear Eyring correlations with mCPBA as oxidant. Moreover, the main argument presented was that in the case of a metallaoxetane intermediate **18** the Mn center in this species would have to be heptacoordinate Mn, which is unusual.<sup>41b</sup> This is the case when pyridine N-oxide additives are present in the reaction mixture, taking up the sixth coordination site on **17** (Scheme 5). These additives led to increased yield and stereoselectivity of the reaction, which implies that they are in some interaction with the metal.<sup>42</sup> Even in the case of a ligand with a tethered pyridine N-oxide derivative that presumably cannot decoordinate, the reaction rate was not affected and the Mn center would have to accommodate seven bonds in the case of metallaoxetane formation. Heptacoordinate Mn complexes have been reported, but only for Mn(II) complexes.<sup>43</sup>

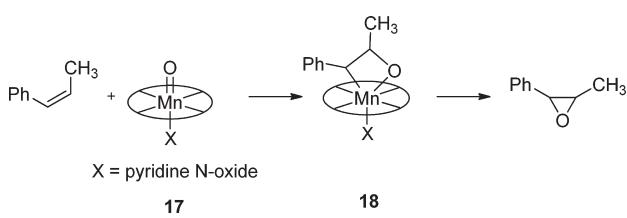
Linde et al. performed Hammett studies which provided experimental evidence for separate pathways for cis- and trans-epoxide formation from substituted cis-stilbenes. In this report they favor competing concerted and radical pathways over a manganoxetane involvement.<sup>44</sup>

Katsuki also proposed a metallaoxetane intermediate for the Cr-salen systems although the same considerations as with the Mn catalyst arose regarding the necessity of a heptacoordinate chromium species to accommodate the metallaoxetane.<sup>45</sup>

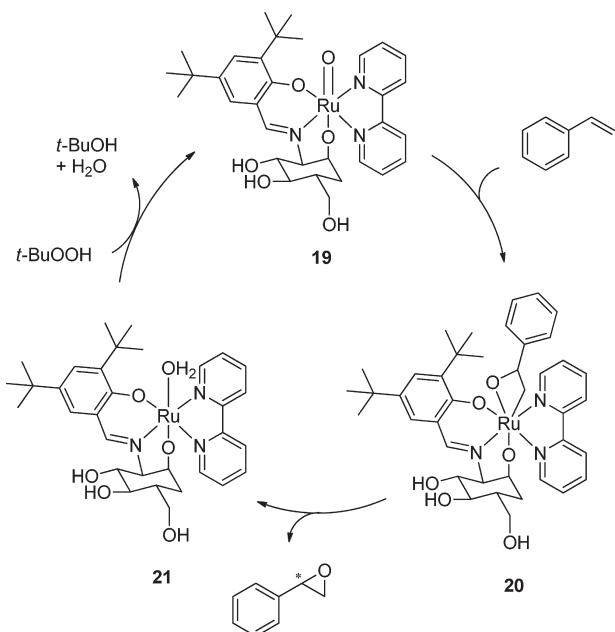
The same lab further developed catalytically active Ru,<sup>46</sup> Ti,<sup>47</sup> and Nb systems<sup>48</sup> based on their salen-derived ligands. Thus far, no mechanistic proposals have been given for any of these systems as to whether a metallaoxetane intermediate might be formed in the transformation.

Asymmetric olefin epoxidation with a Ru complex containing a sugar based ligand was reported by Chatterjee et al. in 2005.<sup>49</sup> The reported enantioselectivities are modest, and no detailed mechanistic study regarding possible intermediates was carried

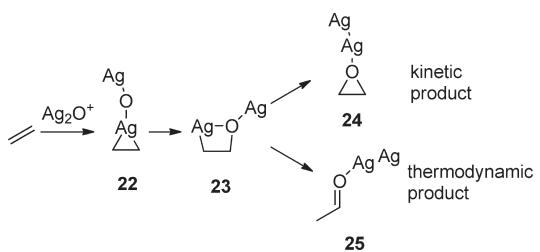
**Scheme 5. Heptacoordinate Mn-Species as Metallaoxetane Intermediates**



**Scheme 6. Styrene Epoxidation with a Chiral Ru Catalyst**



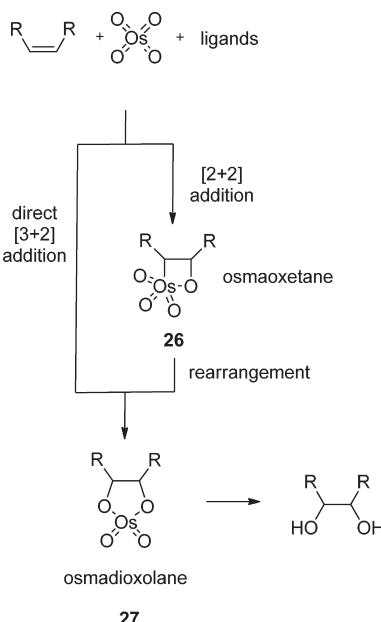
**Scheme 7. Gas-Phase Epoxidation of Ethylene with  $\text{AgO}^+$**



out. Based on the retention of stereochemistry and precedence in its postulation, a metalla-oxetane intermediate **20** was proposed (Scheme 6).<sup>49b</sup> In a later report, this intermediate was still mentioned,<sup>50</sup> whereas a radical intermediate was suggested for their related Mn based system.<sup>51</sup>

Heterogeneous epoxidation of simple olefins is an industrially relevant process. In an effort to understand the mechanism behind this and related transformations, various systematic theoretical and experimental studies on heterogeneous systems have been performed. Madix proposed the intermediacy of a

**Scheme 8. [2 + 2] and [3 + 2] Addition Pathways in Olefin Dihydroxylation**



surface metallacycle for the oxidation of *tert*-butanol to isobutylene oxide on  $\text{Ag}(110)$ .<sup>52</sup>

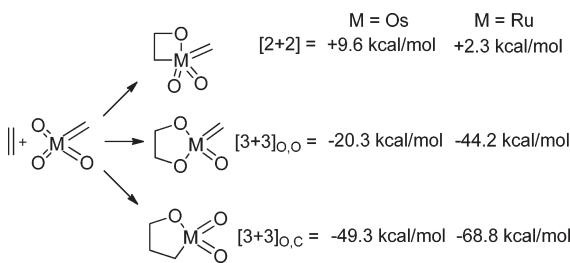
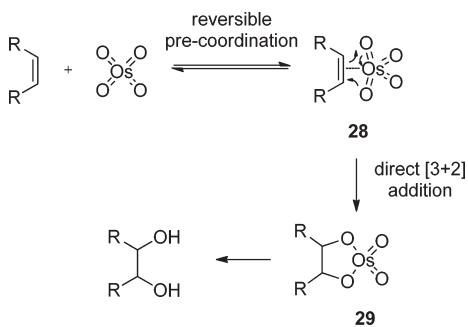
Schröder and Roithová used gaseous  $\text{Ag}_2\text{O}^+$  as a model to study the epoxidation of ethylene by heterogeneous silver catalysts.<sup>53</sup> A combination of ESI tandem mass spectrometry and DFT calculations was used to investigate the active species in this transformation; an argentaoxetane was found to be a reasonable intermediate (Scheme 7). Initial coordination of ethylene to one silver atom (**22**) is followed by attack of the bridging oxygen on a carbon, leading to the metallaoxetane **23**. The decomposition of the metallacycle can lead either to the desired epoxide **24** via direct oxygen atom transfer or to the byproduct acetaldehyde (**25**) if a hydrogen migration occurs. Even though acetaldehyde is the thermodynamic product, the latter transition state is calculated to have a higher energy, which is in good agreement with the observed reaction outcome.<sup>53b</sup>

Reductive elimination of an epoxide from an isolated auraoxetane<sup>54</sup> as well as platinaoxetanes<sup>55,56</sup> was later verified experimentally (sections 3.6 and 3.7).

**2.1.2. Dihydroxylation.** When Sharpless proposed a metallaoxetane intermediate in his report on the chromyl-chloride epoxidation of alkenes,<sup>12</sup> the involvement of this structure in other metal mediated oxidation reactions of olefins, such as the dihydroxylation of alkenes by osmium tetroxide, was also considered. [2 + 2] Addition of an  $\text{Os}=\text{O}$  and  $\text{C}=\text{C}$  double bond would form osma-oxetane **26**, which then could rearrange to the 2,5-osmadioxolane **27**. Up to that point, a direct [3 + 2] addition mechanism was generally considered for this transformation (Scheme 8).<sup>57</sup>

The challenge to this mechanistic proposal<sup>12,58</sup> triggered extensive experimental and theoretical studies along with controversial reports thereof over the following two decades.<sup>2,59</sup> Initial support for a stepwise mechanism including formation of an osma-oxetane came from the observed nonlinearity of Eyring plots of temperature vs stereoselectivity, which indicated a change in mechanisms throughout the reaction<sup>58c</sup> (also observed

**Scheme 9.** [3 + 2] Addition after Reversible Olefin Precoordination



**Figure 5.** Calculated energy levels for the different products of [2 + 2] and [3 + 2] additions of olefins and metal-oxide species.

for related epoxidation reactions, section 2.1.1) and kinetic considerations.<sup>58e,60</sup> A direct [3 + 2] mechanism was considered unlikely based on the observed electronic effects of bases and substrates employed in the reaction.<sup>58f,i,61</sup> Similar proposals were made by Tomioka<sup>62</sup> and others.<sup>63–65</sup> Early theoretical studies<sup>58g,66</sup> supported the possibility of initial formation of the oxetane and subsequent rearrangement to the dioxolane, but transition state energies were not calculated.

Corey et al. rejected a stepwise [2 + 2] mechanism, arguing instead for a direct [3 + 2] addition.<sup>67</sup> The observed Michaelis–Menten kinetics were attributed to a fast, reversible coordination of the olefin to the metal center, as in structure 28, which then underwent direct [3 + 2] addition to yield the metalladioxolane 29 (Scheme 9).<sup>67k</sup> The nonlinearity in Eyring plots reported earlier by Göbel et al. was thus ascribed to this pre-equilibrium.<sup>58c</sup>

Theoretical orbital symmetry studies by Jørgensen and Hoffman<sup>68</sup> were likewise in support of a [3 + 2] addition. In 1996 and 1997 three groups independently reported DFT studies comparing the [2 + 2] and [3 + 2] pathways.<sup>69–71</sup> These calculations unequivocally disfavored the [2 + 2] mechanism involving the metallaoxetane formation, based on prohibitively high activation barriers for oxetane formation as well as rearrangement to the dioxolane. In the same time period, the Corey and Sharpless groups published results on kinetic isotope effect measurements which revealed a highly symmetric transition state.<sup>67l,72</sup> These theoretical and experimental findings, along with some later reports on OsO<sub>4</sub><sup>73–76</sup> and similar systems,<sup>59,77</sup> established that the osmium tetroxide mediated olefin dihydroxylation and its asymmetric analogue<sup>58b</sup> do not proceed through an osmaoxetane intermediate.

Another longstanding dihydroxylation protocol employs permanganate salts. Similar to the case of OsO<sub>4</sub>, the mechanism was

considered to follow a direct [3 + 2] addition pathway<sup>57a</sup> even though some reports at least did not rule out the possibility of a manganaoxetane intermediate.<sup>78–80</sup> The concerted mechanism was corroborated by several theoretical and experimental studies,<sup>81–85</sup> and the metallaoxetane intermediate was dismissed in light of the collected data.

Closely related to the osmium and manganese systems are ruthenium tetraoxide and analogues as dihydroxylation reagents. But again, a mechanism involving a ruthenaoxetane was not found favorable, particularly due to the calculated high activation barriers of the necessary [2 + 2] additions of the metal oxide and the double bond.<sup>66a,86–88</sup>

The situation was similar when oxo groups on the metal were substituted by methyldiene ligands. The [3 + 2]<sub>O,O</sub> mechanism was energetically favored over a [2 + 2] addition, although in this case, interestingly, a [3 + 2]<sub>O,C</sub> addition involving one methyldiene ligand and one oxo ligand was calculated to be the lowest overall energy reaction pathway (Figure 5).<sup>89</sup>

Various rhenium oxides have also been shown to dihydroxylate olefins.<sup>90,91</sup> For the didehydroxylation of diols, the intermediacy of a rhenaoxetane has been proposed by Gable and co-workers. Rhenadioxolane 28 decomposed to rhenium oxide 30 and olefins, which was suggested to occur through a retro [2 + 2] addition of an intermediate rhenaoxetane 29 (Scheme 10). It was postulated that dihydroxylation as the microscopic reverse of the studied reaction could follow through the same pathway in the opposite direction.

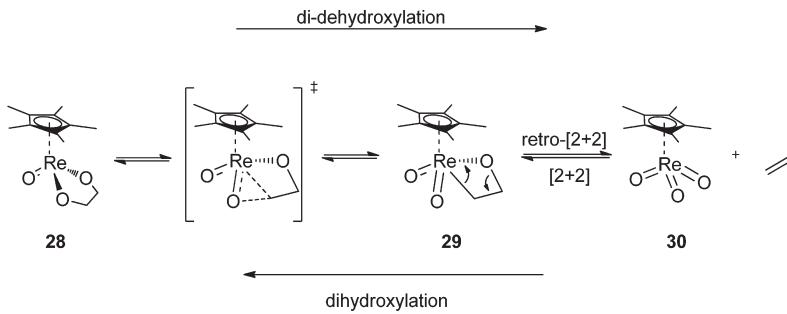
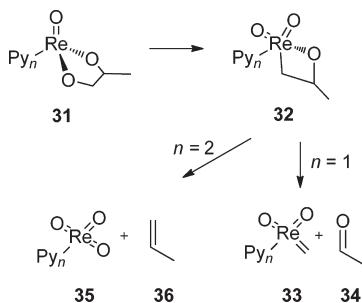
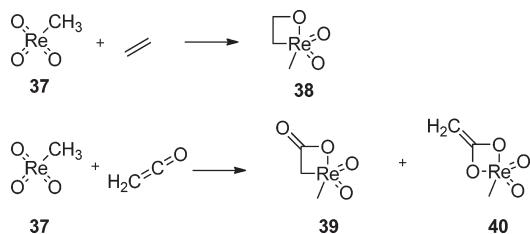
Experimental support was given by kinetic investigations<sup>92</sup> and frontier orbital calculations.<sup>93</sup> In mass spectrometric studies, Chen and co-workers observed the dissociation of rhenium dioxolanes 31 to rhenium carbene complexes 33 and carbonyl compounds 34 or rhenium oxide 35 and olefins 36 depending on the number of bound pyridine ancillary ligands. Their experimental results indicated two different retro [2 + 2] addition pathways from an intermediate rhenaoxetane 32 (Scheme 11).<sup>94</sup> These findings were in agreement with computational studies of the same authors and corroborated the involvement of the rhenaoxetane 32 in this reaction path.<sup>94c,95</sup>

Computational work by the groups of Rappé and Frenking compared several LReO<sub>3</sub> species in their reactivity toward ethylene<sup>96,97</sup> and ketene.<sup>98</sup> It was found that the transition states as well as the reaction energies were lower for a [2 + 2] addition pathway only in the case of L = Me (methylrhenium trioxide, MTO (37)) for the reaction with ethylene and for all studied rhenium oxides in the reaction with ketene to give rhenaoxetanes 38 and 39. In the latter case, a [2 + 2] addition with the ketene carbonyl was also calculated to be favorable (40) (Scheme 12).

Several other group 6,<sup>99,100</sup> 7,<sup>82</sup> and 9<sup>101</sup> transition metal oxides have been studied with computational methods regarding their reaction with alkenes by Frenking and others. In all cases, the formation of metallaoxetanes is energetically significantly more demanding than competing formations of metallacyclobutanes or five-membered oxametallacycles.

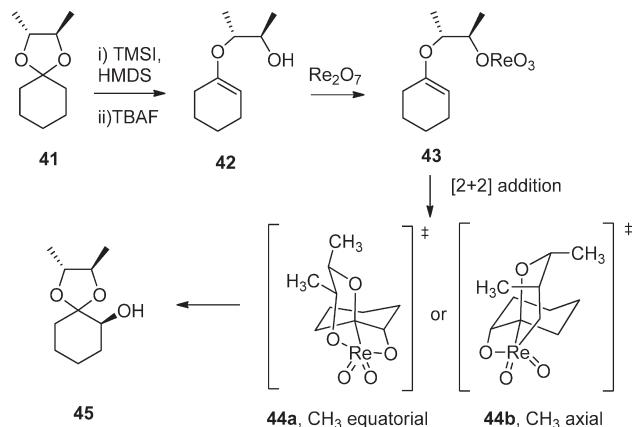
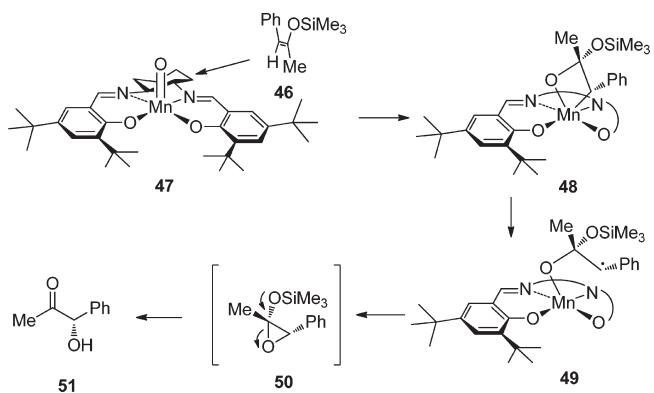
In general, [2 + 2] addition of olefins and mid- to late transition metal–oxo bonds are energetically disfavored by most modern theoretical methods.<sup>2</sup> Among the few exceptions are ketenes and selected rhenium oxide systems.

**2.1.3.  $\alpha$ -Hydroxylation.** In the Re<sub>2</sub>O<sub>7</sub> mediated oxidation of homochiral ketals (e.g., 41) to  $\alpha$ -hydroxylated products (45), Kennedy and co-workers proposed a rhenaoxetane as the intermediate (Scheme 13).<sup>102</sup> After opening of the ketals to their enol ethers, 42, and precoordination of the metal center to the free

**Scheme 10.** Dihydroxylation and Didehydroxylation with Rhenium Oxides**Scheme 11.** Decomposition of a Rhenadioxolane via a Rhenaoxetane**Scheme 12.** Formation of Rhenaoxetanes from MTO

hydroxyl group of the diol, 43, a [2 + 2] addition of the double bond with a Re=O bond was postulated. The good to excellent diastereoselectivities of this transformation were attributed to a tricyclic transition state 44 in which the methyl groups of the protecting diol are preferably oriented in an equatorial fashion (44a). No further spectroscopic evidence was provided for the intermediacy of the rhenaoxetane. This mechanistic proposal would have to be re-examined in light of later computational work related to [2 + 2] additions of Re=O with olefins which only seems to be viable in select cases (section 2.1.2).

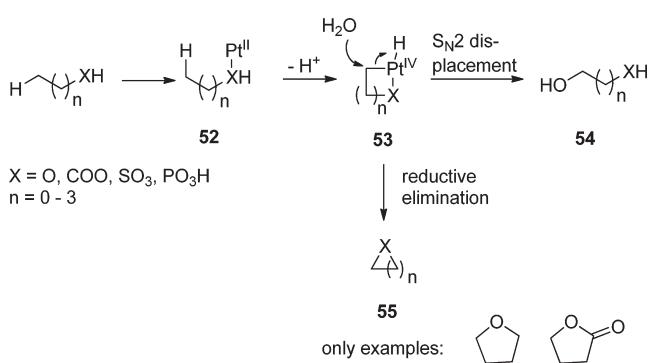
A few years later, Fell and co-workers reported the catalytic enantioselective  $\alpha$ -hydroxylation of silyl enol ethers (i.e., 46) and ketene acetals with (salen)manganese(III) complexes (47).<sup>103</sup> Based on product distribution in relation to the substrates, they proposed a skewed side-on approach of the enol ether to the metal center followed by a concerted [2 + 2] addition to the Mn=O bond. This leads to the formation of manganaoxetane 48, analogous to the reports of Norrby and Åkermark<sup>39,104</sup> and

**Scheme 13.** Re Mediated  $\alpha$ -Hydroxylation of Ketals**Scheme 14.** Mn-salen Catalyzed  $\alpha$ -Hydroxylation

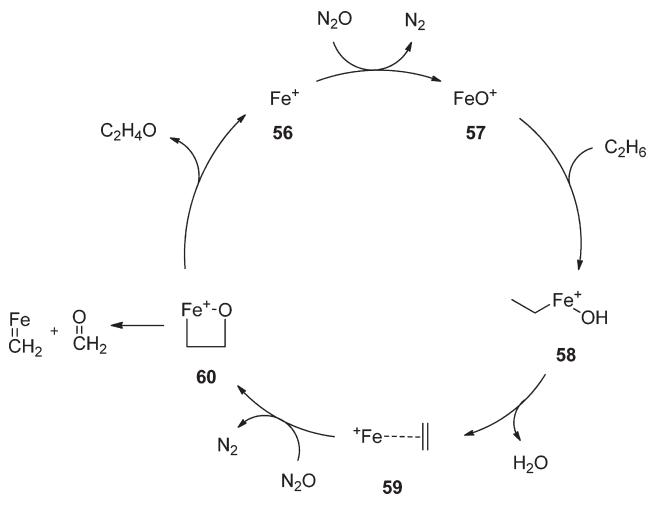
Katsuki<sup>37</sup> regarding olefin epoxidation by Mn(salen) complexes. The further reaction steps were proposed to occur via radical intermediate 49, which collapses to epoxide 50. The epoxide in turn opens to form the  $\alpha$ -hydroxylated product 51 (Scheme 14).

A second mechanism that was investigated leads stepwise through radical intermediates.<sup>41b,105</sup> However, it was found not to account adequately for the observed increased enantioselectivity of olefins with remote bulky silyl substituents. No further stoichiometric studies have been carried out, although these could serve to intercept or spectroscopically detect the intermediate.

**Scheme 15. Oxaplatinacycle Intermediates in Alkane Oxidation**



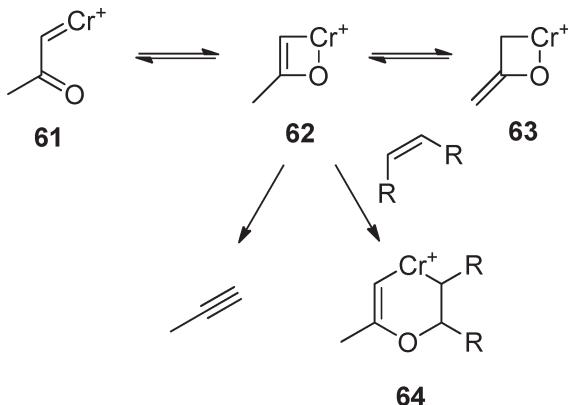
**Scheme 16. Gas Phase Oxidation of Ethene with  $\text{Fe}^+$**



**2.1.4. Oxidation of Alkanes.** A platinaoxetane was proposed as the reaction intermediate in the Pt(II) mediated oxidation of C—H bonds in substrates that have coordinating functional groups such as alcohols or carboxylic, sulfonic, or phosphonic acids.<sup>106</sup> The authors proposed that C—H oxidative addition would occur after initial coordination of the Pt center to the hydroxy or carboxy group (52), resulting in the formation of an oxametallacycle (53). Hydrolysis then would liberate the oxidized product 54 (Scheme 15). Support for this mechanism comes from the observation of byproduct 55. Formation of five-membered cyclic ethers and lactones can be attributed to C—O reductive elimination from a six-membered oxametallacycle. However, an epoxide arising from such a reductive elimination pathway through a hypothetical platinaoxetane was not observed.

Gas phase oxidation of ethane by  $\text{N}_2\text{O}$  is occurring in the presence of  $\text{Fe}^+$  (56), as reported by Schwarz and co-workers in Fourier transform ion cyclotron resonance studies (FT-ICR).<sup>107</sup> After the formation of  $\text{FeO}^+$  (57) by reaction with  $\text{N}_2\text{O}$ , the metal oxide inserts into a C—H bond of ethene and the resulting complex 58 eliminates water to give 59, a  $\pi$ -bound ethene fragment on  $\text{Fe}^+$ .  $\text{N}_2\text{O}$  oxidation gives rise to ferraoxetane 60, which then eliminates the oxidation product and  $\text{Fe}^+$  (Scheme 16). The formation of the metallaotetane was

**Scheme 17. Chromaoxetene/Chromaoxetane Isomerism**



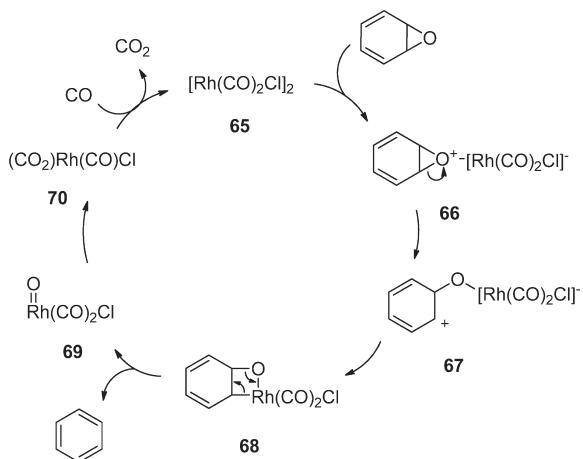
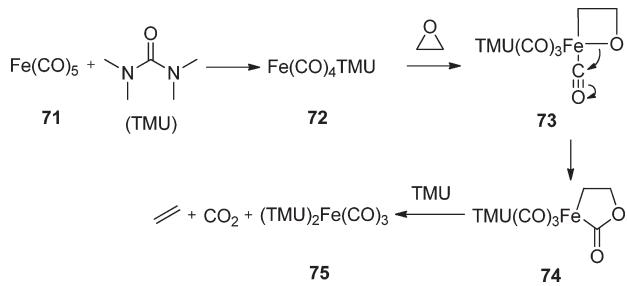
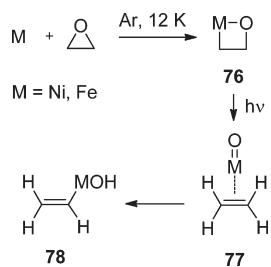
supported by the observation of  $\text{Fe}^+=\text{CH}_2$  and  $\text{CH}_2\text{O}$ , which are the products of a [2 + 2] cycloreversion of the oxetane. Later work in the same lab on the oxidation of norbornane with  $\text{FeO}^+$  in the gas phase led to the proposal of a similar ferraoxetane based on collision induced dissociation experiments in an FT-ICR mass spectrometer.<sup>108</sup> Again, the observation of the iron carbene  $\text{Fe}^+=\text{CH}_2$  and an aldehyde as [2 + 2] ring-opening products corroborated the presence of such a ferraoxetane.

**2.1.5. Other Reactions.** Schwarz et al. also reported on the potential involvement of a chromacyclobutene in the reaction of gaseous  $\text{CrC}_3\text{H}_4\text{O}^+$  with alkenes.<sup>109</sup> The reaction was followed by Fourier transform ion cyclotron resonance mass spectrometry. The chromium complex was assumed to have a carbene structure with a  $\beta$ -carbonyl group (61). This compound could undergo electrocyclic closure to metallaotetane 62, which could isomerize and be in equilibrium with the corresponding chromaoxetane 63, bearing an exocyclic double bond. The chromacyclobutene can eliminate propyne through  $\beta$ -H elimination or undergo alkene insertion into the Cr—O bond to form 64 (Scheme 17).

## 2.2. Other Oxygen-Transfer Reactions

**2.2.1. Deoxygenation of Epoxides.** The deoxygenation of epoxides with transition metal complexes is formally the reverse reaction of olefin epoxidation with transition metal oxo complexes. Thus, it is of little surprise that metallaotetane intermediates have been postulated for this transformation as well. In the same year as Sharpless' proposal of metallaotetane intermediates, Ashworth and Berchtold described the deoxygenation of arene-oxides to aromatic products under Rh(I) catalysis.<sup>110</sup> They postulated the formation of rhodaoxetane intermediate 68 after precoordination of the epoxide oxygen (66) and stepwise insertion of the metal into the C—O bond (67). A retro [2 + 2] ring-opening would yield the arene and Rh(III)-oxo species 69, which is regenerated to the active catalyst through migratory insertion to CO (70) and subsequent loss of  $\text{CO}_2$  (Scheme 18).<sup>110</sup>

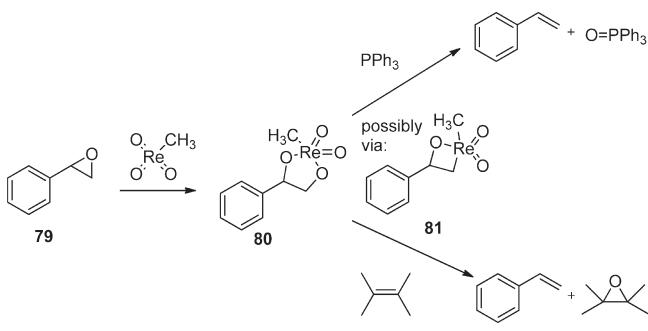
In the same year, Alper suggested a ferraoxetane as a possible intermediate in the deoxygenation of epoxides with a stoichiometric amount of iron pentacarbonyl (71). After oxidative addition to the C—O bond, the metallaotetane 73 could rearrange to the five-membered metallactone 74, from which  $\text{CO}_2$  and ethylene could be eliminated (Scheme 19).<sup>111</sup> Unfortunately, however, these reports did not receive their due attention.

**Scheme 18. Rh Catalyzed Deoxygenation of Arene Oxides****Scheme 19. Deoxygenation of Epoxides with  $\text{Fe}(\text{CO})_5$** **Scheme 20. Low Temperature Deoxygenation of Ethylene Oxide**

Other early deoxygenation protocols that discussed metallaoxetane intermediates<sup>112–117</sup> are presented in the Jørgensen review.<sup>1</sup>

Similar to their matrix isolation experiments with an iron/ethylene oxide system,<sup>1,116</sup> Margrave and co-workers observed the insertion of Ni into a C–O bond of ethylene oxide in a solid argon matrix via FTIR spectroscopy.<sup>119</sup> The resulting nickelaoxetane 76 underwent metathesis to an ethylene Ni oxide complex  $\text{NiO}(\text{C}_2\text{H}_4)$  77 upon irradiation. The Ni could then insert into one of the ethylene C–H bonds and rearranged to vinylnickel hydroxide 78 with UV photolysis (Scheme 20).<sup>119</sup>

Bäckvall and Blomberg performed quantum chemical calculations on the deoxygenation of ethylene oxide with a number of transition metals (Cr, Mo, Fe, Co, Ni, Cu, Ag) involving a

**Scheme 21. Oxygen Transfer from Epoxides to  $\text{PPh}_3$  or Alkenes**

metallaoxetane intermediate.<sup>120</sup> For all metals except silver, the metallaoxetane was more stable than metal + epoxide. When comparing the energy of metal + epoxide to metal oxide + ethene, again the former is less stable for all metals apart from silver and copper. Although transition states were not considered in their calculations, the authors concluded that the involvement of a metallaoxetane in these deoxygenation reactions is a valid assumption.

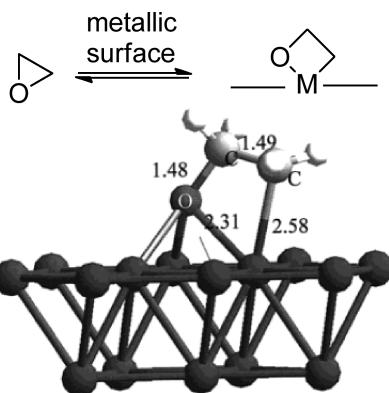
Rhenium oxides such as methyltrioxorhenium (MTO),  $\text{CH}_3\text{ReO}_3$ , besides their employment in olefin epoxidation<sup>96,121,122</sup> and dihydroxylation,<sup>96,122–124</sup> could also be used for epoxide deoxygenation.<sup>93,125–127</sup> Espenson and co-workers described the transfer of an oxygen atom from epoxides to triphenylphosphine<sup>125a</sup> as well as from styrene oxide (79) to 2,3-dimethyl-2-butene under MTO catalysis.<sup>125b</sup> They found that rhenadioxolane 80 was formed in this process and hypothesized that the decomposition of this structure could lead via rhenaoxetane 81 before the alkene is expelled (Scheme 21).<sup>125b</sup> Alkene extrusion from rhenadioxolanes has been studied by Gable and co-workers<sup>92d,93</sup> as well as Chen and co-workers,<sup>94,95</sup> and the intermediacy of metallaoxetanes has been corroborated through these experimental and computational investigations (section 2.1.2).

In a later report, Gable described catalytic deoxygenation of epoxides with  $\text{Tp}'\text{ReO}_3$ . In this case, a rheniumdioxolane was not proposed as intermediate; instead, oxidative addition to form a rhenaoxetane directly and subsequent [2 + 2] cycloreversion were put forward as a possible pathway.<sup>126a</sup>

Recently, MTO catalyzed deoxygenation of epoxides and diols with  $\text{H}_2$  as reductant was reported by Ziegler et al.<sup>127</sup> Based on the analogy of previously reported reactions by Espenson<sup>125b</sup> and Gable<sup>92d,93</sup> and the selectivity for *cis*-cyclic diols, a mechanism involving a rhenaoxetane was proposed.

## 2.2. Heterogeneous Interactions of Simple Epoxides.

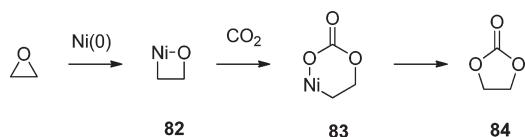
Friend and co-workers suggested formation of a surface metallacycle from the olefin and adsorbed atomic oxygen as intermediate in their study of the oxidation of propylene to acetone on a  $\text{Rh}(111)$  surface. Extended Hückel calculations gave support for this proposal.<sup>128</sup> Barteau and co-workers successfully adsorbed 1-epoxy-3-butene to a  $\text{Ag}(110)$  surface. Temperature programmed desorption (TPD), surface spectroscopical methods (HREELS), and DFT calculations were in agreement with the formation of a surface metallacycle that contains only one metal atom—the surface analogue of a metallaoxetane.<sup>129</sup> This structure released the epoxide again upon further heating. Later, the same reversible process could be repeated by employing simple



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Figure 6. Reversible formation of a surface metallaoxetane.

**Scheme 22. Nickelaoxetane Intermediates in the CO<sub>2</sub> Fixation with Epoxides**



ethylene oxide under the formation of an unsubstituted surface argentaoxetane as intermediate on Ag(111) (Figure 6).<sup>130</sup>

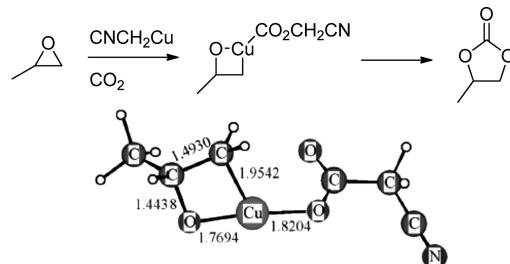
A similar structure was found by the same group in the reaction of *tert*-butyl nitrite on Pt(111). DFT calculations and high-resolution electron energy loss (HREEL) spectra gave the best fit for the four-membered platinumaoxetane as intermediate during the thermal activation of the nitrite to form *tert*-butanol and dehydrogenation products thereof.<sup>131</sup>

**2.2.3. CO<sub>2</sub> Fixation with Epoxides.** A metallaoxetane intermediate had been suggested by De Pasquale in 1973. In the fixation of CO<sub>2</sub> with epoxides to give cyclic carbonates<sup>132</sup> under Ni catalysis, the first step was proposed to be oxidative addition of the Ni(0) catalyst to one of the C—O bonds of the epoxide, which yields the intermediate nickelaoxetane **82** (Scheme 22). Subsequent CO<sub>2</sub> insertion afforded metallacycle **83**, from which Ni was reductively eliminated and the carbonate **84** formed.<sup>11</sup> Similar reaction pathways have been suggested in later adaptions of this reaction with Cu<sup>133</sup> and Pt catalysts,<sup>134</sup> and the Cu and Ni systems have been compared in a microwave study regarding their stereoselectivity.<sup>1,135</sup>

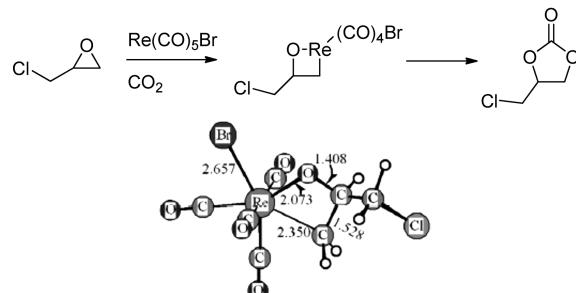
A number of other transition metal catalysts have been employed to facilitate this reaction: Cr,<sup>136,137</sup> Ni,<sup>138</sup> Re,<sup>139</sup> Zn,<sup>140,141</sup> Zn, Cu and Co,<sup>142</sup> Co and Cr,<sup>143</sup> and mixed Ru/Mn.<sup>144</sup> While in many cases the transition metal was merely serving as Lewis acid to activate the epoxide, Jiang et al. invoked the formation of a metallaoxetane. In analogy to De Pasquale's proposal,<sup>11</sup> they proposed oxidative addition of a Re(CO)<sub>5</sub>Br catalyst to the less hindered C—O bond of the epoxide followed by CO<sub>2</sub> insertion into the Re—O bond and reductive elimination of the metal to give the cyclic carbonate.<sup>139,144</sup>

Recent DFT studies by Guo et al. of the transformation catalyzed by Saegusa's copper cyanomethyl system<sup>133</sup> and Jiang's Re(CO)<sub>5</sub>Br system<sup>139</sup> gave theoretical support for the

**Scheme 23. Metallaoxetanes in the CO<sub>2</sub> Fixation with Epoxides—Calculated Structures**



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intermediacy of a cupraoxetane<sup>145</sup> and a rhenaoxetane,<sup>146</sup> respectively, by comparison with the energetic profiles of possible alternative pathways (Scheme 23).

### 2.3. C—C Bond Forming Reactions

**2.3.1. Reductive Coupling.** Jamison and co-workers reported the Ni-catalyzed reductive coupling of alkynes and epoxides. In the proposed reaction mechanism, nickelaoxetane **86** appears after oxidative addition of the Ni(0) catalyst (**85**) to the epoxide.<sup>147</sup> Similar insertions have been reported for Ni and other group 10 metals before.<sup>11,134,138,148,149</sup> The tethered alkyne then undergoes migratory insertion into the Ni—C bond to yield the six-membered oxametallacycle **87**, containing a bridgehead olefin. Jamison reasoned that the comparably long Ni—O and Ni—C bonds should release ring strain to an extent that the “anti-Bredt” double bond can be accommodated. Upon reaction with triethylborane, the Ni—O bond is cleaved (**88**) and Ni is eliminated through β-H elimination and subsequent reductive elimination (**89**) (Scheme 24).

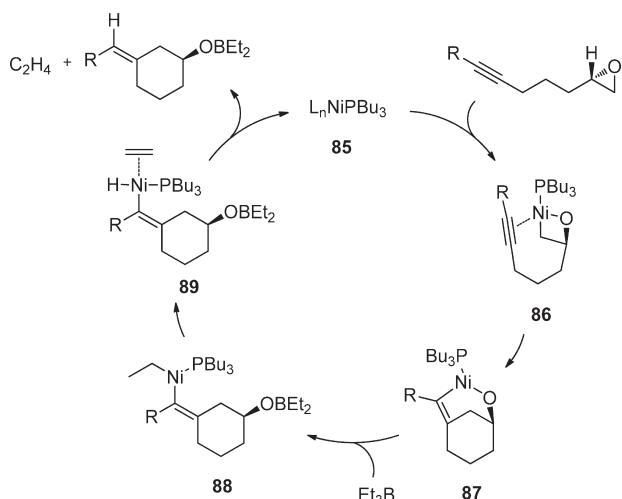
**2.3.2. Metallaoxetanes as Metathesis Precursors.** Metallaoxetanes have been proposed as intermediates in olefin metathesis reactions as precursors of the propagating metalla carbene species.<sup>150</sup> Beauchamp and co-workers hypothesized the formation of nickelaoxetane **90** in the reaction of gaseous Ni<sup>+</sup> with ethylene oxide in an ion beam apparatus.<sup>151</sup> A [2 + 2] cycloreversion yielded nickel carbene **91** and formaldehyde. The carbene was then able to undergo cross metathesis with perfluoroethylene CF<sub>2</sub>=CF<sub>2</sub> (Scheme 25).

Rooney and co-workers observed a significant increase of reaction rates in the ring-opening metathesis polymerization (ROMP) of norbornene with various ruthenium complexes (**92**) in the presence of molecular oxygen.<sup>152</sup> At the same time, epoxidation products **94** were found. When the ruthenium complex was oxidized in a preceding step (**95**) and then used in the reaction under exclusion of air, the same rate acceleration

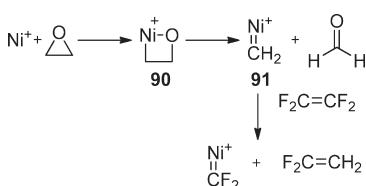
was noted as when the epoxide was used as substrate. These observations led the authors to propose that, after oxidation of the Ru complex, the formation of the transient ruthenaoxetane **93** took place, which underwent ring-opening to give the metal carbene species **96**, which promoted ROMP (Scheme 26).

Ab-initio calculations by Rappé and Goddard supported such a proposal.<sup>14</sup> Several years later, Rooney and Gilheany reported that OsO<sub>4</sub> catalyzed ROMP of norbornene when heated to 60 °C for 3 days in a sealed tube.<sup>153</sup> When a stoichiometric mixture of norbornene and OsO<sub>4</sub> was reacted at room temperature, the expected osmiumdioxolane was formed along with a small amount of polymerization product. This reactivity requires the formation of metal carbenes at some place in the reaction

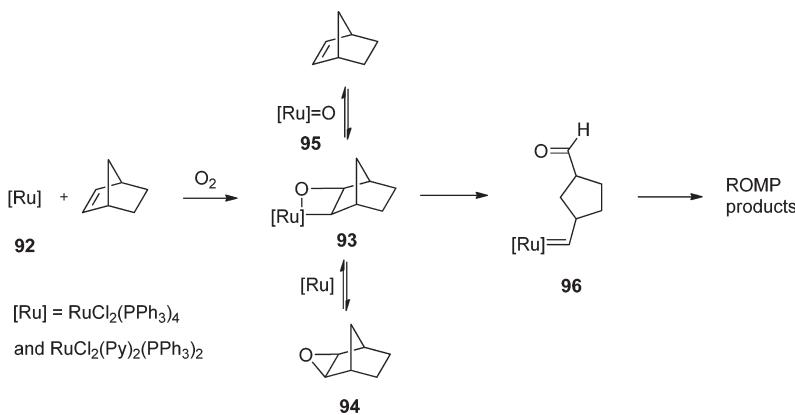
**Scheme 24.** Proposed Nickelaoxetane Intermediate in Reductive Coupling of Alkynes and Epoxides



**Scheme 25.** Gas-Phase Formation of a Nickel Carbene Species from a Nickelaoxetane



**Scheme 26.** ROMP via a Ruthenaoxetane



mechanism, and the authors concluded that these would be formed directly from an intermediate osmaoxetane. Interestingly, these results were not included in the discussion of the mechanism of OsO<sub>4</sub> catalyzed dihydroxylation of olefins (section 2.1.2).

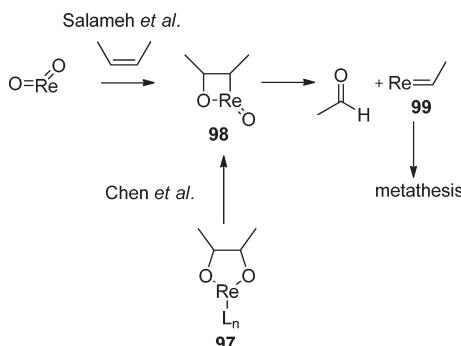
Mechanistic investigations of heterogeneous metathesis catalysts have been performed by Salameh et al.<sup>154</sup> Their studies of the Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst system revealed that olefins without allylic C—H bonds could be readily employed in the reaction. A previously discussed mechanism suggested the necessity of allylic C—H bonds for the formation of the propagating metal carbene through a π-allyl intermediate.<sup>155</sup> Through their findings, Salameh et al. proposed that the carbene species is rather formed through a “pseudo-Wittig” reaction, i.e. the formation and opening of a metallaoxetane. This, along with the reports by Chen that rhodium-alkylidene **99** species can be formed from the metalladioxolane **97** by rearrangement to a metallaoxetane,<sup>94a,c,156</sup> gave support to the intermediacy of rhenaoxetane **98** in this transformation (Scheme 27).

Further theoretical support for the involvement of metallaoxetanes in heterogeneous metathesis came from the Bao group.<sup>157</sup> DFT studies of Mo/β-zeolite catalyst systems were used to corroborate a mechanism in which the olefinic substrate performs a [2 + 2] cycloaddition with a metal-oxo ligand in a first endothermic step. In a second step, the active metal carbene species is formed by decomposition of the metallaoxetane to the metal alkylidene and a carbonyl.

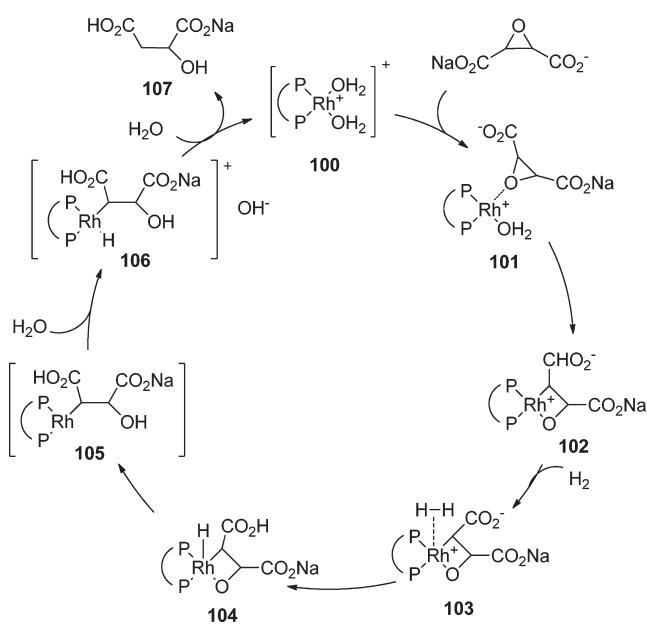
#### 2.4. Other Reactions

Bakos et al. reported the asymmetric hydrogenolysis of epoxides with a rhodium catalyst, employing chiral sulfonated

**Scheme 27.** Rhenaoxetane Intermediates Decompose to Metathesis Promoting Re Carbene Species



**Scheme 28. Proposed Rhodaoxetane in the Hydrogenolysis of Epoxides**



phosphines as ligands.<sup>158</sup> In a biphasic system, the authors performed high pressure NMR studies of a stoichiometric reaction mixture. According to their proposal, after the formation of the chiral phosphine-rhodium-diaqua complex **100**, the epoxide substrate (*cis*-epoxysuccinate) exchanged with one H<sub>2</sub>O ligand and coordinated via the epoxide oxygen (**101**). Subsequent oxidative addition of the metal to one C—O bond gave rise to rhodaoxetane **102** (Scheme 28). The spectral data collected via <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>31</sup>P detected <sup>103</sup>Rh-NMR spectroscopy indicated the formation of four diastereomers that likely formed a square-pyramidal structure, which they ascribed to a metallaoxetane species with a bidentate phosphine and a carboxy group in the apical position.<sup>158</sup> Molecular hydrogen coordination (**103**) and activation (**104**) set the stage for O—H reductive elimination under Rh—O bond cleavage to produce complex **105**. This was converted back to **100** by sequential oxidative addition to water (**106**) and reductive elimination of the ring-opened product **107** in the presence of excess solvent.

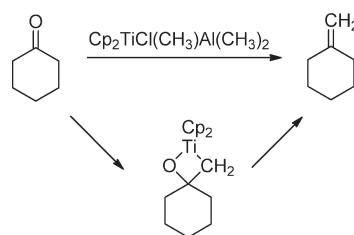
### 3. ISOLATED METALLAOXETANES

#### 3.1. Group 4 Metallaoxetanes

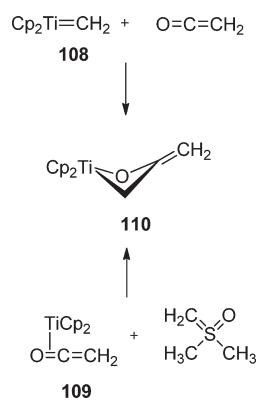
The Tebbe olefination of carbonyl groups is a classic organometallic transformation<sup>159</sup> where the intermediacy of a metallaoxetane was postulated (Scheme 29).<sup>1</sup>

Stimulated by the studies toward a better understanding of the Tebbe reaction mechanism,<sup>159–161</sup> several groups set out to prepare and analyze titanaoxetanes, which were the proposed intermediates. Grubbs and co-workers were the first to report the preparation of such a species (**110**) from the reaction of a titanium carbene complex **108** with ketene as well as from a titanium ketene complex **109** with dimethylsulfonium methylide (Scheme 30). They based the structural assignment on NMR spectroscopic studies. In the low temperature <sup>1</sup>H NMR spectrum, the resonances of the ring protons as well as the protons on the Cp ligand were inequivalent. Consequently, the authors

**Scheme 29. Tebbe Olefination**



**Scheme 30. Preparation of a Titanaoxetane via Two Different Pathways**



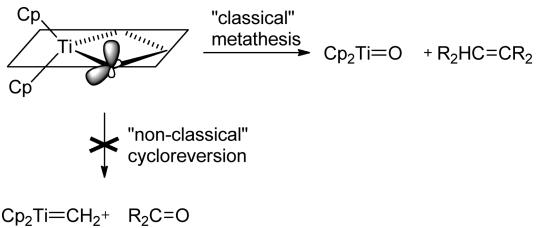
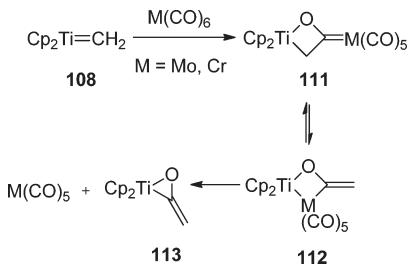
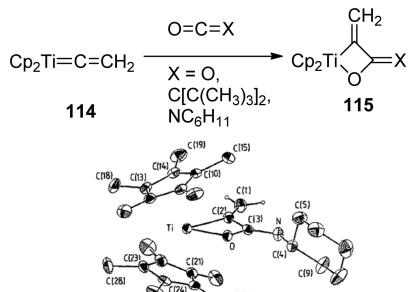
concluded the symmetry of the complex was disturbed due to puckering of the titanaoxetane ring.<sup>162</sup>

Bimetallic titanaoxetane complexes, such as **111**, were also prepared via a reaction of titanium carbenes **108** with Mo and Cr hexacarbonyl compounds.<sup>163</sup> These complexes were found to rearrange to (bis-metalla)oxetanes **112** and reductively eliminate Mo or Cr to give a titanaoxirane **113** (Scheme 31).

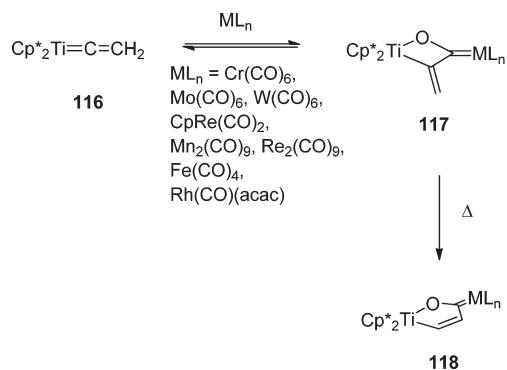
In 1993, Beckhaus et al. succeeded in isolating titanaoxetanes **115**, with two exocyclic double bonds formed from the reaction of Cp<sup>\*</sup>Ti vinylidene **114** with CO<sub>2</sub>, ketenes, and isocyanates (Scheme 32).<sup>164</sup> The crystal structure of the isocyanate product revealed a twisted conformation of the oxametallacycle with bond lengths of Ti—C = 2.121 Å and Ti—O = 1.983 Å while the diphenylketene product was essentially planar. The Ti—C (2.119 Å) and Ti—O (1.966 Å) bond lengths of the diphenylketene product are comparable with those of the isocyanate product.<sup>165</sup>

The resulting complex was thermally stable up to 150 °C but underwent [2 + 2] metathesis in the mass spectrometer in a “classical” Tebbe-like fashion to yield a metal oxide and an alkene.<sup>166</sup> Similar to the reports of Grubbs, the Beckhaus group also prepared bimetallic titanaoxetane complexes with exocyclic C=M double bonds **117** from a wide variety of transition metal carbonyl substrates.<sup>167</sup> These compounds underwent a “non-classical” [2 + 2] cycloreversion of the oxetane in which the Ti-vinylidene **116** and the corresponding metal carbonyl species were re-formed. Under heating, these compounds underwent a rearrangement in which the exocyclic methylene at the 3 position was incorporated under ring-expansion to five-membered oxatitanacycles **118** (Scheme 33).<sup>166,168</sup>

Böhme and Beckhaus also undertook theoretical studies confirming that planarity of the titanaoxetanes is the energetically

**Scheme 31. Bimetallic Titanaoxetane Complexes****Figure 7.** Lone pair orientation allows strong M—O interactions.**Scheme 32. Titanaoxetanes with Two Exocyclic Double Bonds**

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**Scheme 33. Formation of Bimetallic Titanaoxetanes and Ring Extension through Rearrangement**

preferred conformation and that exodouble bonds in the 4 position stabilize the ring toward cycloreversion and metathesis. A precoordination of the carbonyl compound and the metal center preceded the cycloaddition.<sup>169</sup> Similar results had been published earlier by Schiøtt and Jørgensen based on frontier orbital interaction studies. In this study, it was also shown that the formally forbidden  $2\pi + 2\pi$  cycloaddition could be made allowed by the involvement of a third high lying electron pair located on the methylene carbon atom.<sup>160</sup> Böhme and Beckhaus also provided a theoretical explanation for the classical metathesis of titanaoxetanes to give a titanium oxide and an alkene or allene. Due to the two energetically low lone pairs on oxygen in

and perpendicular to the ring plane, strong interactions between the oxygen and the metal center are present (Figure 7). This leads to metathesis rather than cycloreversion or electrocyclic ring-opening.<sup>169a</sup>

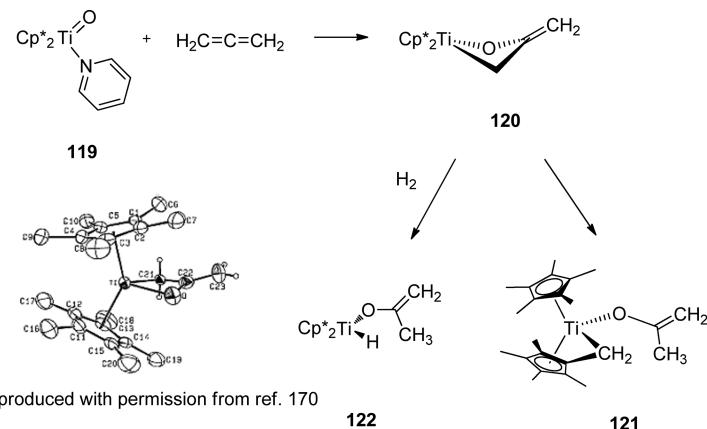
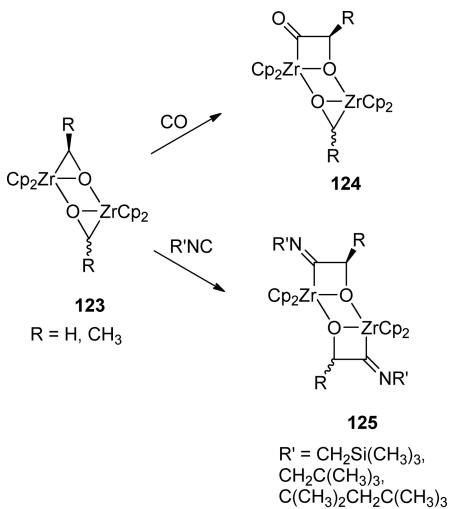
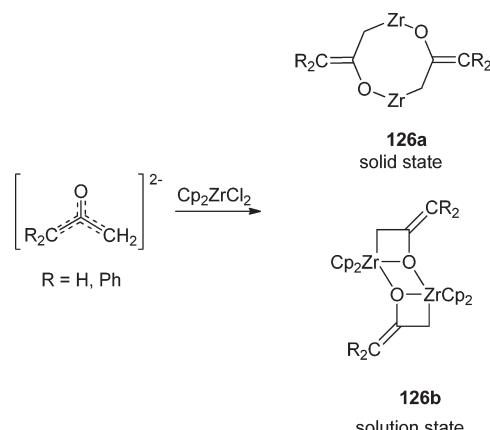
Another remarkable method of preparation of titanaoxetanes was reported by Andersen and co-workers.<sup>170</sup> They described the formation of titanaoxetane **120** from  $Cp^*2Ti(O)pyr$  (**119**) and allene, the first synthesis of such a structure from a metal oxide and an olefin. In the extensive discussion of the [3 + 2] vs [2 + 2] addition mechanism of metal oxo compounds with alkenes in regard to olefin epoxidation and dihydroxylation, such a pathway had been widely considered as energetically too demanding (section 2.1.2). The authors described the titanaoxetane as puckered with shortened Ti—C (2.074 Å) and elongated Ti—O (1.992 Å) bonds based on the crystal structure when compared to the complexes isolated by Beckhaus.<sup>164</sup> The increased Ti—O bond length is in accordance with Jørgensen's calculations of a weakening of that bond in the case of ring puckering.<sup>160</sup> Classical Tebbe-like metathesis was not observed, but upon heating, the titanaoxetane slowly cyclometalated a  $Cp^*$  methyl group under Ti—C bond cleavage and formed **121**. The exposure to 1 atm of  $H_2$  again led to cleavage of the Ti—C bond with the formation of the hydrido titanium enolate **122** (Scheme 34).

Erker and co-workers found that ( $\eta^2$ -aldehyde)zirconocenes **123** underwent a one carbon insertion into the Zr—C bond when exposed to carbon monoxide or isocyanides to give dinuclear zirconaoxetanes of the type **124** and **125**.<sup>171</sup> The solid state structure of the trimethylsilylmethyl isocyanide insertion product revealed Zr—O and Zr—C distances of 2.194 Å and 2.374 Å, respectively (Scheme 35). Investigations with the chiral ( $\eta^2$ -acetaldhyde)zirconocene *cis/trans*-**123** showed that the diastereometric ratio was predominantly retained in this reaction, which indicates that the complexes remained dinuclear during the insertion event.<sup>171b</sup>

Seyfert et al. reacted the dianions of methylketones with group 4 metal halides, anticipating the formation of the respective metallaoxetanes similar to the dinuclear complexes Erker and co-workers had found. The resulting Zr-product could be isolated and crystallized. Instead of metallaoxetane formation, mass spectrometry and X-ray analysis revealed an eight-membered dimeric structure **126a**.<sup>172</sup> In solution, the authors speculated that the metallaoxetanes **126b** should be the predominant species, based on NMR spectral data that was analogous to the reports by Grubbs for the preparation of related titanaoxetanes.<sup>162</sup> Vapor pressure osmometry resulted in a mass in accordance with a monomer for the Zr and Hf products (Scheme 36).

### 3.2. Group 5 Metallaoxetanes

During their studies on ene-diamido  $Cp'$  niobium(V) complexes, Galindo et al. observed that the dimethyl complex **127**

**Scheme 34.** Titanaoxetane via [2 + 2] Addition of a Metal Oxide and an Olefin**Scheme 35.** One Carbon Insertion into a Zr—C Bond Yields Dinuclear Zirconaoxetanes**Scheme 36.** Solid State and Solution State Structures of Oxazirconacycles

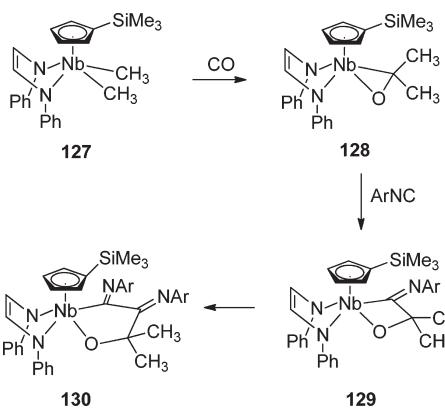
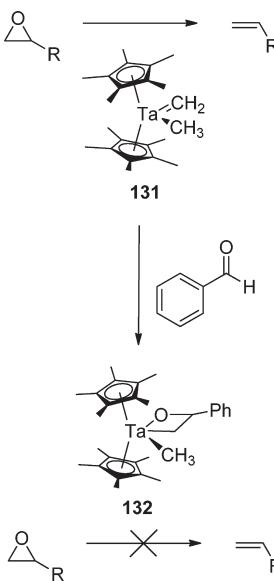
formed oxaniobacyclopropane (**128**) when exposed to 1 atm of CO.<sup>173</sup> This three-membered oxametallacycle inserted 1 equiv of isocyanide into the metal–carbon bond, yielding a niobaoxetane **129** with an exocyclic double bond in the 3-position. Addition of another equivalent of the isocyanide led to a second Nb–C insertion and gave a five-membered oxametallacycle **130** (Scheme 37). The authors could not present crystallographic data for the proposed species but assigned the structures by NMR spectroscopy and by analogy with similar tantalum and zirconium complexes.<sup>174,175</sup>

In an effort to elucidate whether the mechanism of transition metal catalyzed deoxygenation of epoxides involved

metallaioxetane intermediates, Bercaw and co-workers prepared moderately stable tantalaoxetanes by [2 + 2] cycloaddition of tantalum carbenes and aldehydes.<sup>176</sup> The crystal structure of the product from the reaction of  $\text{Cp}^*\text{Ta}(\text{=CH}_2)\text{CH}_3$  with benzaldehyde showed a slightly puckered ring and bond lengths of  $\text{Ta}-\text{C} = 2.236 \text{ \AA}$  and  $\text{Ta}-\text{O} = 2.053 \text{ \AA}$ . However, while the parent carbene **131** was able to catalyze the deoxygenation of epoxides successfully, the derived tantalaoxetane **132** failed to promote this reaction (Scheme 38). During monitoring of the reaction progress, no intermediates could be detected. The authors concluded thus that this deoxygenation does not proceed via a stepwise metallaioxetane mechanism but rather a concerted oxygen abstraction<sup>176</sup> in spite of extended Hückel calculations, which identified the concerted oxygen abstraction mechanism as a nonactivated process in contrast to the stepwise mechanism via a tantalaoxetane.<sup>177</sup>

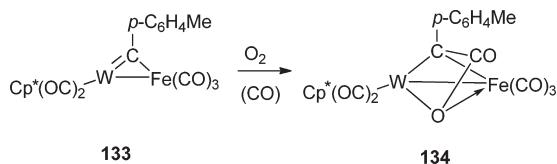
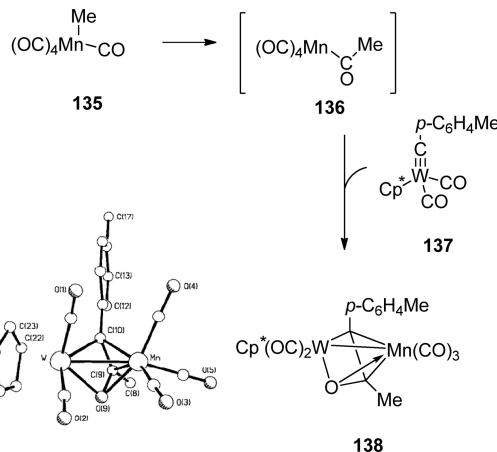
### 3.3. Group 6 Metallaioxetanes

Stone and co-workers reported the isolation of a mixed bimetallic W/Fe complex **134** with a bridging ligand that formally constituted a tungstenaoxetane. The complex was readily prepared by treating the electronically unsaturated dimetal

**Scheme 37. Niobaoxetane****Scheme 38. Tantalaoxetane Is Not Involved in Epoxide Deoxygenation**

complex  $[\text{FeW}(\mu\text{-C}(p\text{-C}_6\text{H}_4\text{Me}))(\text{CO})_5(\text{Cp}^*)]$  (133) with  $\text{O}_2$ . The oxetane oxygen was ligating the Fe center through a dative bond while the alkylidene carbon established a  $\sigma$ -bond with the second metal center. The mechanism of the formation was not further elucidated but must include a coupling of the alkylidene, O, and CO groups (Scheme 39).<sup>178</sup>

In a later report, the same group described the formation of another bridged tungstenoxetane, 138, by reaction of the alkylidynetungsten complex 137 with  $[\text{Mn}(\text{Me})(\text{CO})_5]$  (135). Again, the ring oxygen is involved in a dative bond to the second metal center (Mn) while in this case both metallaoxetane carbon atoms form  $\sigma$ -bonds with Mn. During the formation of 138, the authors propose a transient unsaturated species 136, which is generated through migration of the Mn bound methyl group to a carbonyl ligand. The tungsten–carbon triple bond can subsequently coordinate to 136 and through carbon–carbon bond formation followed by loss of CO lead to the observed product (Scheme 40).<sup>179</sup>

**Scheme 39. Bridging Bimetallic Tungstenoxetane****Scheme 40. Formation of a Bridging Tungstenoxetane**

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Metallaoxetanes were also postulated to be intermediates in the formation of metathesis-active carbene species (section 2.3.2). Schrock and co-workers prepared tungsten- and molybdaoxetanes 141 through [2 + 2] cycloadditions of aldehydes 140 with the appropriate metal–alkylidenes 139.<sup>180</sup> These underwent metathetical ring-opening and formed coupled products 142 and a metal–oxo species 143 (Scheme 41). A molybdaoxetane could be isolated and a solid state structure obtained through X-ray crystallography, showing a slightly puckered ring with  $\text{Mo}-\text{O} = 2.00 \text{ \AA}$  and  $\text{Mo}-\text{C} = 2.20 \text{ \AA}$  that shows significant resemblance of related tungstenacyclobutanes. Therefore, Schrock and co-workers concluded that the metallaoxetanes are structurally and possibly mechanistically closely related to their all-carbon metallacyclobutane counterparts.

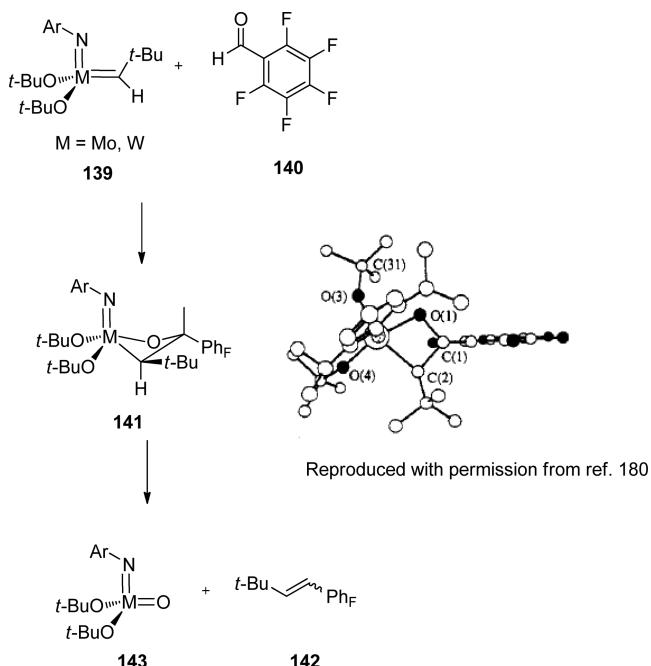
In 1993 Sundermeyer et al. presented the synthesis of a number of metallaoxetanes, among them the first stable chromaoxetane.<sup>181</sup> The reaction of Cr, Mo, and W carbenes 144 with diphenylketene did not give rise to the expected [2 + 2] cycloadduct 145, though. Instead, an internal rearrangement occurred and yielded isomeric metallaoxetanes 146, which were isolated and spectroscopically analyzed. The molybdaoxetane could be crystallized, and the solid state structure revealed a notably puckered ring. Selected bond lengths are  $\text{Mo}-\text{C} = 2.277 \text{ \AA}$  and  $\text{Mo}-\text{O} = 2.162 \text{ \AA}$ . The formation of the oxetanes was proposed to happen through nucleophilic attack by the carbene on the central ketene carbon followed by rearrangement to a metal–oxygen bound species which ring closed to the metallaoxetane and isomerized to give the exo double bond. No

thermal [2 + 2] cycloreversion to the metal oxide and allene was observed (Scheme 42).<sup>181</sup>

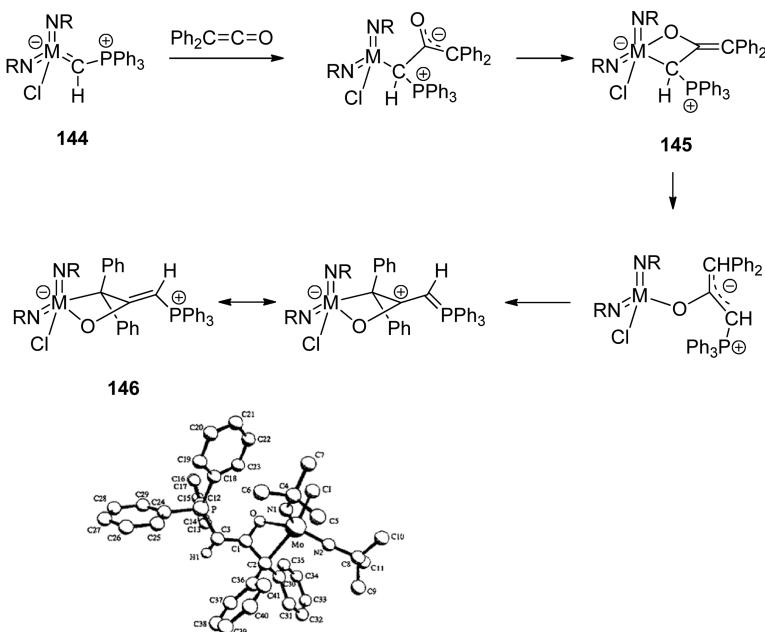
### 3.4. Group 8 Metallaoxetanes

Another class of metallaoxetanes was detected by Bergman and co-workers upon closer investigation of the highly reactive Ru-benzyne complex 147.<sup>182</sup> This complex reacted stoichiometrically with acetone to form a new

**Scheme 41.** Isolated Molybdaoxetanes and Tungstenaoxetanes



**Scheme 42.** First Stable Chromaoxetane



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oxaruthenacycle (153), in which a new bond between the Ru-coordinated phenyl and the acetone substrate has been formed. Although not proposed in the original paper, Ru-oxetane 150 was identified as a potential intermediate in subsequent studies.<sup>183</sup>

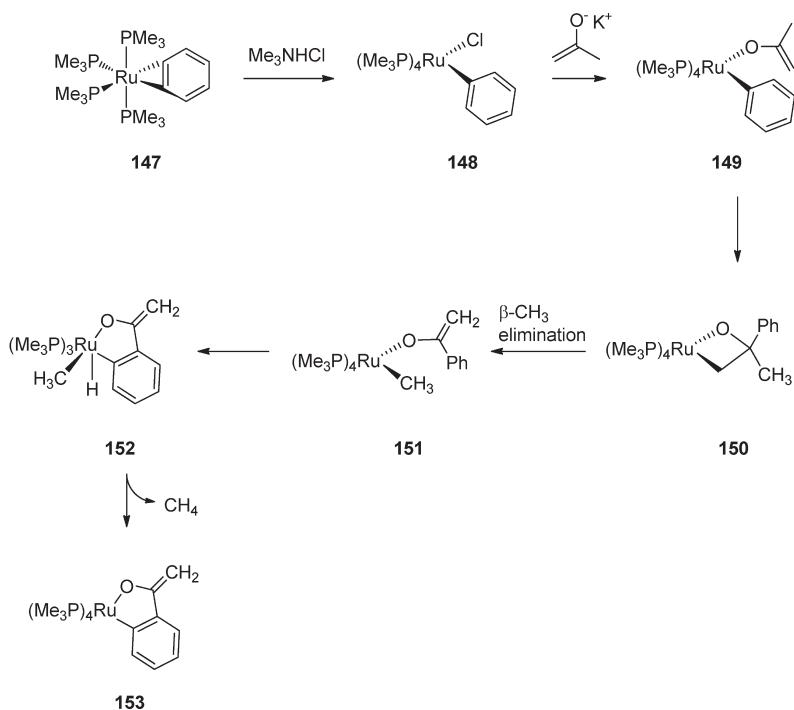
Treatment of Ru-benzyne complex 147 with Me<sub>3</sub>NHCl generated phenylchlororuthenium complex 148. Upon exposure of 148 to the potassium enolate of acetone, ruthenaoxetane 150 was formed via the O-bound metalla-enolate (149) as a transient intermediate. The mechanistically unusual formation of the metallaoxetane formally happens through migration of the Ru bound phenyl group to the central carbon of the enolate and subsequent ring closure.<sup>184</sup>

The reactivity of these metallaoxetanes is diverse and mechanistically unique.<sup>185</sup> Upon gentle heating,  $\beta$ -CH<sub>3</sub> elimination, for example, leads to cleavage of the Ru–C bond. Subsequent orthometalation of the migrated Ph group and C–H reductive elimination lead to the extrusion of methane and formation of the five-membered oxametallacycle 153, which conforms to the initial observations of the reactivity of the Ru-benzyne complex with acetone (Scheme 43).<sup>182</sup> In the course of this reaction, one new C–C bond was formed and one was cleaved.

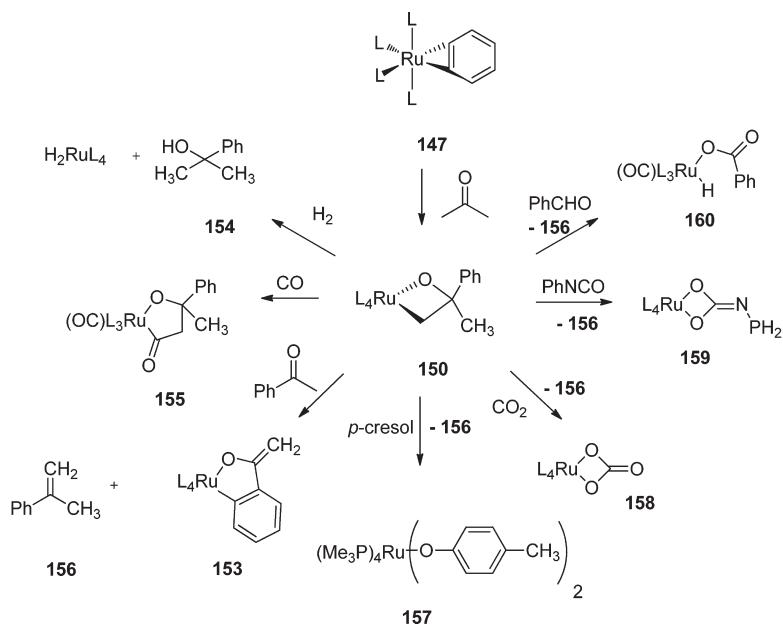
This rearrangement was only observed on ruthenaoxetanes with monodentate phosphine ligands and was inhibited by chelating ligands on the metal, suggesting that prior ligand dissociation was necessary for the  $\beta$ -CH<sub>3</sub> elimination to take place.

Treatment of ruthenaoxetane 150 with molecular hydrogen at room temperature cleanly afforded tertiary alcohol 154, the formal product of a nucleophilic attack of the phenyl group on the carbonyl of acetone, be it through a mechanistically novel pathway. Exposure to CO gave extended oxametallacycle 155. Interestingly, insertion into the Ru–C bond was observed exclusively. Similar to the reaction with acetone, the insertion was inhibited by chelating ligands, indicating that ligand dissociation and coordination of CO were elemental for the insertion step.

Scheme 43. Formation of a Ruthenaoxetane from a Ru-Benzene Complex



Scheme 44. Diverse Reactivity of Ruthenaoxetane 150

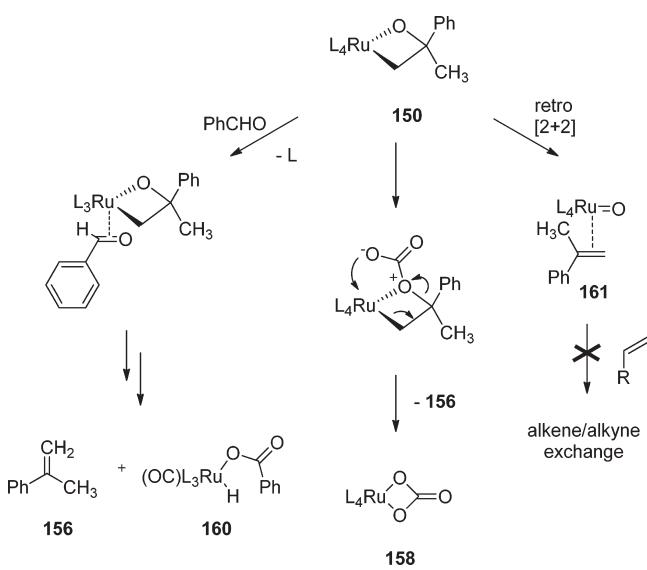


When proton (acetophenone, *p*-cresol) or carbon ( $\text{CO}_2$ , phenylisocyanate (PhNCO), benzaldehyde) electrophiles were employed, the extrusion of  $\alpha$ -methylstyrene (156) could be observed along with the formation of various cyclometalated (153, 158, 159) or open (157, 160) Ru complexes (Scheme 44).

The reactions of  $(\text{PM}_{\text{3}})_4\text{Ru}$ -oxetane and  $(\text{DMPE})_2\text{Ru}$ -oxetane with *p*-cresol and  $\text{CO}_2$  occurred at room temperature on the same time scale, suggesting that phosphine dissociation is not

part of the active mechanism but direct attack of the basic oxetane oxygen on the electrophile is followed by backbiting of the so generated oxide and concomitant extrusion of the methylstyrene (Scheme 45). The reaction with benzaldehyde, though, took significantly longer in the presence of chelating ligands; thus, a ligand dissociation step was proposed to be part of this mechanism. As the ruthenaoxetanes showed no reactivity toward alkenes and alkynes even at elevated temperatures, the authors disfavored

**Scheme 45. Mechanistic Considerations in the Reactivity of Ruthenaoxetane 150**



a mechanism that included the formation of a Ru-oxo species **161** (e.g., via a  $[2 + 2]$  cycloreversion). In this case, the  $\alpha$ -methylstyrene that is still coordinated to the metal center should—at least to some degree—exchange with other alkenes or alkynes, which is not observed.

In the same study, two further related structures were prepared and their reactivity investigated: ruthenaoxetane **163** was formed by reaction of the ruthenium acetate chloride complex  $[(\text{PMe}_3)_4\text{Ru}(\text{OAc})\text{Cl}]$ , **162** with the potassium enolate of 4,4-dimethyl-2-pentanone to give a structure with an exocyclic double bond.<sup>184</sup> Unlike the all-sp<sup>3</sup>-hybridized ruthenaoxetanes above, this structure could be crystallized and subjected to X-ray crystallography. The metallacycle portion is essentially planar and the Ru—O (2.146 Å) and Ru—C (2.158 Å) bond lengths almost identical.<sup>185</sup> The reactivity of this complex was different from that above. Reaction with *p*-cresol led to the formation of the ruthenium bis-cresolate complex **157**, identical to the case of the reaction with the ruthenaoxetanes above, but instead of *tert*-butyl allene as the organic product the free ketone 4,4-dimethyl-2-pentanone was produced. When the ruthenaoxetane was exposed to another equivalent of the parent 4,4-dimethyl-2-pentanone under heating, the di-*tert*-butyl acetylacetone complex **164** was formed, which was the result of a different C—C bond formation and subsequent cleavage process (Scheme 46). An exact mechanism for this transformation was not provided.

The other four-membered oxametallacyclic species reported was ruthenaoxetene **166**—the unsaturated analogue of a ruthenaoxetane. This was formed by extrusion of methane from the methyl enolate complex  $\text{Ru}(\text{PMe}_3)_4(\text{Me})(\text{OC}(\text{CH}_2)\text{CMe}_3)$ , **165** presumably via vinylic C—H activation.<sup>184</sup> It is noteworthy that the reactivity of this ruthenaoxetene was again different from that reported for the ruthenaoxetanes above. Similar to the reaction of *p*-cresol and ruthenaoxetane **163**, no butyne-formation occurred, but instead pinacolone, the parent ketone, was expelled under formation of the ruthenium bis-cresolate **157**. The same organic product was formed when **165** was reacted with molecular hydrogen at room temperature, while treatment with trimethylsilane led to formation of the silyl enol ether

analogue of pinacolone and Ru-phosphine species **167**, where one of the methyl groups of the  $\text{PMe}_3$  ligands was metalted (Scheme 47).

The formation of ruthenaoxetene **168** was reported by Chakravorty and co-workers as a product of the reaction of  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$  with equimolar amounts of 4-methyl-2,6-diformylphenol and *p*-toluidine.<sup>186</sup> As a potential reaction mechanism, they proposed decarbonylative orthometalation on one side of diformylphenol while the second carbonyl group formed the imine which was protonated and could establish a hydrogen bond to the metallaoxetane oxygen. In a crystal structure of the product, it became obvious that the metallacycle was planar and the bond lengths were Ru—O = 2.235 Å and Ru—C = 2.043 Å. The hydrogen bridge was also evident (Scheme 48).<sup>186</sup>

Later, the same authors described the insertion of various un-/monosubstituted alkynes into the Ru—C bond under formation of an expanded, six-membered oxametallacycle **169** (Scheme 49).<sup>187</sup> For the monosubstituted alkynes, the insertion was regioselective due to sterical hindrance from the  $\text{PPh}_3$  ligands.<sup>187a</sup> As a trend, they could observe faster insertion rates for electron-rich alkynes and electron-withdrawing substituents on the imine ligand, which they ascribed to a mechanism in which nucleophilic attack of the alkyne on the metal is the initiating step in the ring expansion.<sup>187b</sup>

Aneetha et al. reported related work with a wider variety of amines that lead to the same result of ruthenaoxetene formation, but no further reactivity studies were performed.<sup>188</sup>

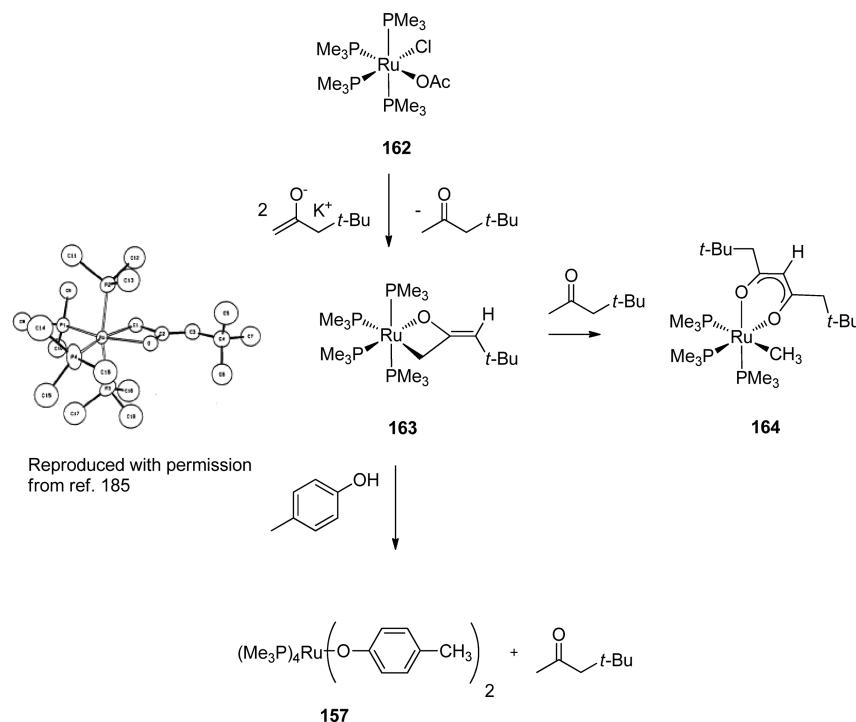
### 3.5. Group 9 Metallaaoxetanes

The exposure of simple epoxides to low-valent Ir and Rh complexes as  $\text{Ir}(\text{COE})(\text{PMe}_3)_3\text{Cl}$ <sup>189</sup> or  $\text{Rh}(\text{PMe}_3)_3\text{Cl}$ <sup>190</sup> leads to rearrangement of the epoxides to ketones.<sup>1</sup> In their initial reports, Milstein et al. had proposed sequential C—O oxidative addition, formation of a metallaoxetane,  $\beta$ -H elimination, and reductive elimination, although they could not isolate any intermediates. In a subsequent publication, Milstein reported the generation of rhodaoxetane (**172**) from the reaction of isobutylene oxide (**170**) and  $\text{Rh}(\text{PMe}_3)_3\text{Br}$  (**171**), which proved the feasibility of their proposal as well as the general possibility of oxidative addition of low valent late metal complexes to simple nonactivated epoxides.<sup>191</sup> This stood in contrast to earlier reports where strongly activated tri- and tetracyanoethylene oxides were employed as substrates to form metallaoxetanes through oxidative addition of Rh, Ir, Pd, and Pt complexes.<sup>148,149</sup> Rhodaoxetane **172** could also be prepared by treatment of halohydrin **173** (formed by C—Br oxidative addition) with base (Scheme 50). X-ray analysis revealed the four-membered ring to be effectively planar, with Rh—O and Rh—C bond lengths of 2.099 Å and 2.069 Å, respectively.<sup>192</sup> The preference for planarity was also supported by a theoretical study of the bonding interactions.<sup>191</sup>

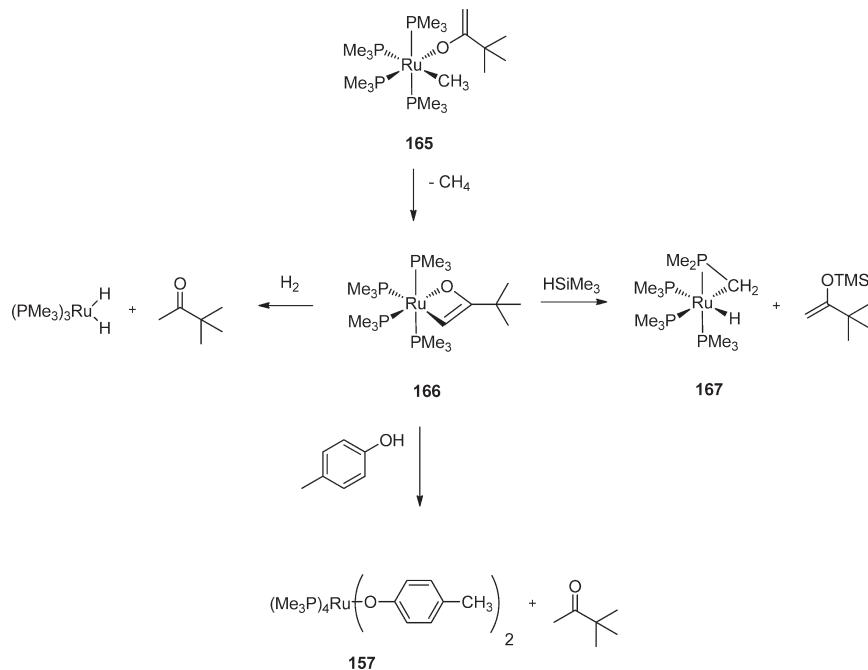
As the oxidative addition to an epoxide had been observed, a theoretical study of reductive elimination—the microscopic reverse—was performed to see whether formation of an epoxide from a metallaoxetane was feasible. The calculations led to the conclusion that the stability of the metallaoxetane was significantly higher than that of epoxide plus metal fragment, thus the observed direction of the reaction. Further calculations suggested that in the case of a  $[2 + 2]$  cycloreversion of the rhodaoxetane the formation of an alkene and a metal-oxo species is favored over the formation of a free carbonyl and a metal—alkylidene.<sup>191</sup>

In an attempt to elucidate the mechanism of heterogeneous  $\text{Ag}/\text{Al}_2\text{O}_3$  epoxidation of ethylene by molecular oxygen, Klemperer and Day investigated the oxidation of a  $\text{Ir}(\text{COD})(\text{P}_3\text{O}_9)$  complex by  $\text{O}_2$  as a model system.<sup>193</sup> Iridaoxetane **178**

Scheme 46. Crystalline Ruthenaoxetane



Scheme 47. Ruthenaoxetene



$[(C_8H_{12}O)Ir(P_3O_9)](TBA)_2$  and the  $\eta^3$ -allyl hydroxyl complex  $[(C_8H_{11}OH)Ir(P_3O_9)](TBA)_2$  (**179**) could be isolated. The former was crystallized and subjected to X-ray analysis. The solid state structure showed that one of the COD double bonds is still  $\pi$ -bound to the metal center while the other is oxidized to the oxametallacyclobutane. In a proposed mechanism of formation, dioxygen binds to **175** (the initial 18-electron Ir complex) in an

$\eta^1$ -fashion, which then forms the dioxo bridged bimetallic species **176**. Internal redox and insertion of one of the coordinated oxygen atoms into the M–C bond gives the iridaoxetane **178**, which in turn transforms into the final product by an intramolecular allyl hydrogen transfer to the oxetane oxygen.

Formation of the epoxide **180** as a result of reductive elimination from the metallaoxetane was not observed. Thus,

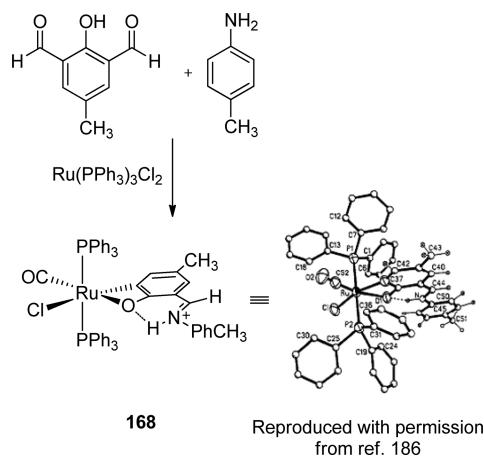
the authors concluded that the presence of a slightly acidic allylic hydrogen prevented this and rather led to the observed allyl-hydroxy species (Scheme 51).

In 1997 De Bruin et al. reported the oxidation of Rh-ethylene and Rh-COD complexes with aqueous  $H_2O_2$  to give the corresponding rhodaoxetanes.<sup>194</sup> The rhodaoxetane 182 derived from ethylene was the first stable unsubstituted 2-metallaoxetane reported (Scheme 52).

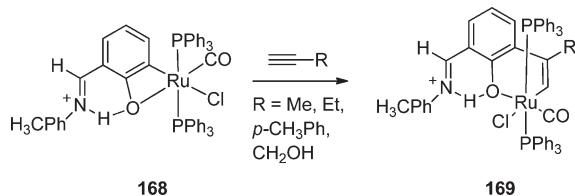
Iridium analogues of the described rhodaoxetanes have been prepared by  $O_2$  oxidation of the respective ethylene complexes.<sup>195</sup>

The mechanism of this metallaoxetane formation with hydrogen peroxide was investigated by DFT-calculations by Budzelaar et al.<sup>196</sup> After initial homolytic  $H_2O_2$  cleavage, a Rh(III)-hydroxo

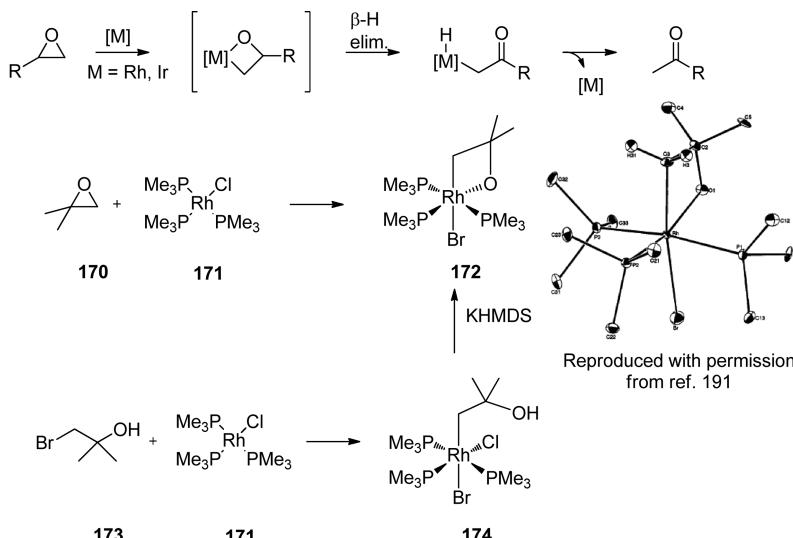
**Scheme 48.** Four-Membered Ru-Enolate



**Scheme 49.** Alkyne Insertion into Ru–C Bond



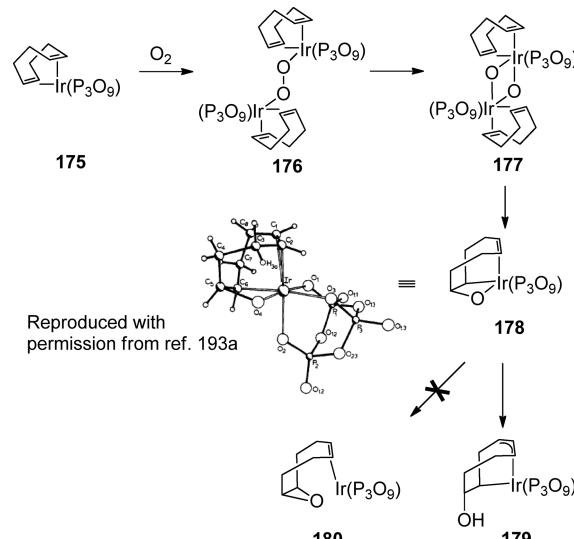
**Scheme 50.** Formation of a Substituted Rhodaoxetane through Oxidative Addition to an Epoxide



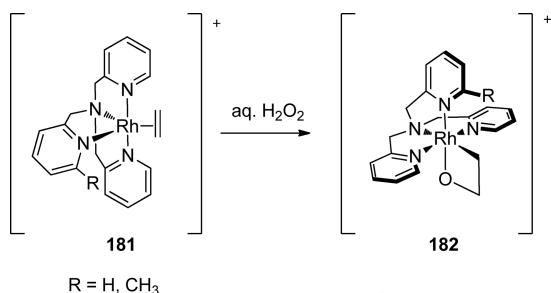
species (183) is formed oxidatively. Subsequent cyclization and deprotonation yields Rh(III)-oxetane 182 (Scheme 53). A solid state structure of the complex could be obtained through X-ray crystallography with almost identical bond lengths for Rh–O (2.000 Å) and Rh–C (2.070 Å).

Investigation of the reactivity of the unsubstituted rhodaoxetane revealed the nucleophilic nature of the oxetane oxygen. Thus, the reactivity of 182 toward many electrophiles was examined (Scheme 54). Under Brønsted acidic conditions, the proton activated the oxetane, promoting ring-opening. Depending on the choice of anion, a stable Rh(III) complex with coordinated anion could be formed (184). Similar reactivity was observed with methyl iodide (185). Acetonitrile was incorporated by attack of the oxetane oxygen on the electrophilic nitrile carbon. The extended six-membered metallacycle 186 was formed that rearranged at elevated temperatures to perform a net amination of the coordinated olefin (187).<sup>197</sup> A very slow incorporation of acetone was also observed. In this case the

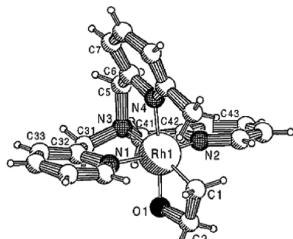
**Scheme 51.**  $O_2$  Oxidation of an Ir-COD Complex to an Iridaoxetane



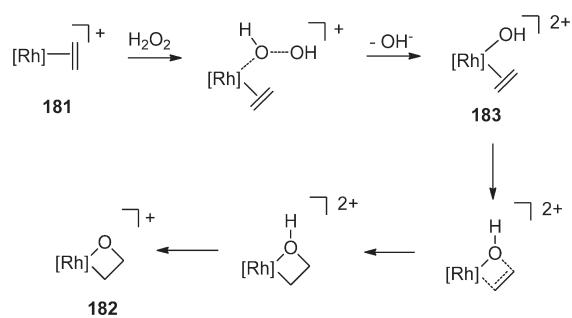
Scheme 52. First Isolable Unsubstituted Metallaoxetane



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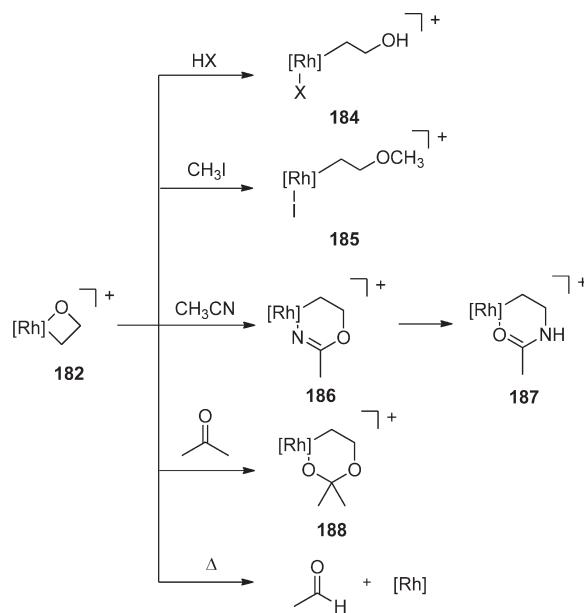
Scheme 53. Mechanism of Rhodaoxetane Formation



six-membered 4-metalla-1,3-dioxane **188** was the reaction product. Upon heating in DMSO,  $\beta$ -H elimination occurred and the generation of acetaldehyde was observed.<sup>198</sup>

Substitution of the tetradeятate TPA ligand to tridentate derivatives and the employment of a labile acetonitrile ligand further increased the reactivity of the rhodaoxetane **190**.<sup>199</sup> Acetaldehyde formation occurred through dissociation of the acetonitrile ligand and opening of a coordination site, which allowed for ligand rearrangement and  $\beta$ -H elimination at room temperature in  $\text{CD}_2\text{Cl}_2$  for all three TPA analogues (Me, Bu, and Bn-BPA). In the presence of ethylene, the BnBPA-Rh(I)-ethylene complex was re-formed. However, catalytic turnover could not be achieved, presumably because of decomposition or poisoning of the catalyst through competing reaction with  $\text{H}_2\text{O}_2$ . This competing reaction led to further oxidation of the rhodaoxetane to give the BnBPA-Rh(III)-formylmethyl hydroxyl species **191** (Scheme 55).

The Rh-COD complexes **192** were oxidized by  $\text{H}_2\text{O}_2$  in a similar way to give substituted rhodaoxetanes **193**. Both internal olefins were oxygenated by the same oxygen, resulting in a transannular ether formation.<sup>194,200</sup> Ether formation was proposed to occur through rhodaoxetane formation on one olefin and subsequent migratory insertion of the second double bond into the Rh-O bond. The resulting complexes were fairly stable in solution at room temperature, but with the addition of acid or upon heating, a new compound, a hydroxycyclooctenediyi

Scheme 54. Reactivity of Rhodaoxetane **182**

complex **194**, was formed. This structure contained an uncoordinated hydroxyl group and an  $\eta^3$ -allyl fragment while still having one Rh-C  $\sigma$ -bond (Scheme 56).

Interestingly, the cn- and BPA-Rh-COD complexes **192** could also be oxidized by  $\text{O}_2$  in the presence of a noncoordinating acid ( $\text{HBAr}^f$ ).<sup>200</sup> In comparison, the TPA-Rh-ethylene complex **181** formed a 3-rhoda-1,2-dioxolane **195** upon treatment with  $\text{O}_2$  under solvent-free conditions.<sup>201</sup> Such dioxolanes had been invoked earlier by Read to transfer one oxygen to  $\text{PPh}_3$  with the formation of triphenylphosphine oxide and rhodaoxetane **182** (Scheme 57).<sup>202</sup>

De Bruin also discussed the possibility of rhoda- and iridaoxetanes in oxygenation reactions employing paramagnetic Rh(II) and Ir(II) species. Oxygenation of open-shell Ir(II) ethylene species **196** with triplet oxygen led to the superoxo iridium(III) ethylene complex **197**, which could be trapped with 5,5-dimethyl-1-pyrroline N-oxide (DMPO). An intramolecular 1,2-insertion of the ethylene into the Ir superoxide fragment could then give rise to the iridaoxetane radical **198**. This species, in turn, could undergo Ir-O ring-opening under the influence of the solvent acetonitrile and ultimately furnish the observed formylmethyl-hydroxo product **200** (Scheme 58).<sup>203,204</sup>

Based on the TPA-rhodaoxetanes prepared by De Bruin, the Love group has performed further reactivity studies of these complexes. With the prospect of catalytic olefin carbohydroxylation, the rhodaoxetane was exposed to various alkanyl- and arylboronic acid reagents which led to transmetalation of the organic moiety to the Rh center under opening of the oxetane ring by Rh-O bond cleavage (**201**). This transformation could also be performed in a one-pot fashion with both the boronic acid and hydrogen peroxide present simultaneously. A subsequent reductive elimination step could close the proposed catalytic cycle and regenerate the Rh(I)-olefin catalyst while expelling the carbohydroxylated product (Scheme 59).<sup>205</sup>

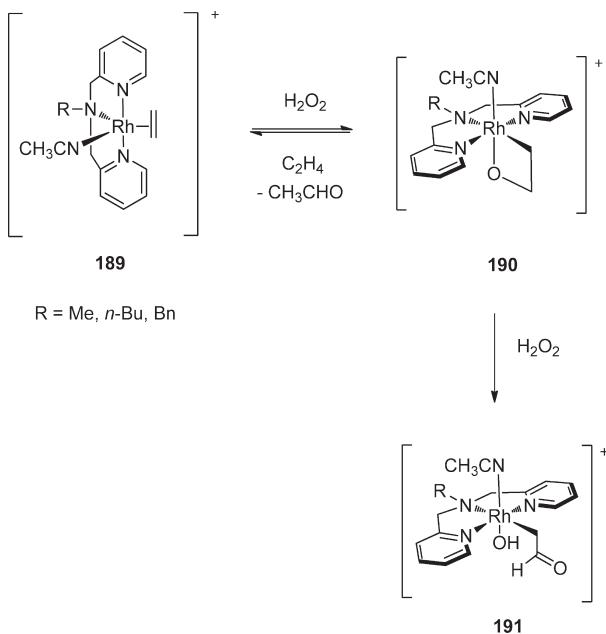
Related to De Bruin's work,<sup>194,200</sup> Flood and co-workers reported the stoichiometric preparation of a (COD)-iridaoxetane (**202**) by  $\text{H}_2\text{O}_2$  oxidation.<sup>206</sup> With  $\text{Cn}^*$  as ancillary ligand, the metallaoxetane could be isolated and spectroscopically analyzed, while in the case of a Cn ancillary ligand, the

metalla-oxetane could only be observed by *in situ* NMR at low temperatures. Similar to the (COD)-iridaoxetane reported by Klemperer and Day,<sup>193</sup> transformation of the metalla-oxetane into a hydroxyl allyl species **203** via internal allylic hydrogen transfer to the oxetane oxygen was observed (Scheme 60).

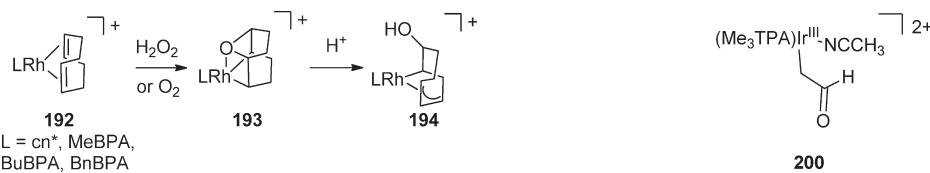
Employment of *tert*-butyl hydroperoxide led to the same result only at a slower rate while O<sub>2</sub> in MeOH produced the metalla-oxetane at a lower yield, presumably via *in situ* formation of H<sub>2</sub>O<sub>2</sub> in the protic solvent. Pyridine *N*-oxide, iodosobenzene, and O<sub>2</sub> in aprotic solvents gave no reaction.

Tejel and co-workers reported the aerobic oxidation of a diphenyltriazenide–Rh–COD complex **204** to a dimeric Rh-oxetane **205** under 100% O<sub>2</sub> incorporation.<sup>207</sup> The mechanism is proposed to involve coordination of O<sub>2</sub> to the monomeric Rh-complex, followed by activation by a second monomer to form the dinuclear rhodaoxetane.

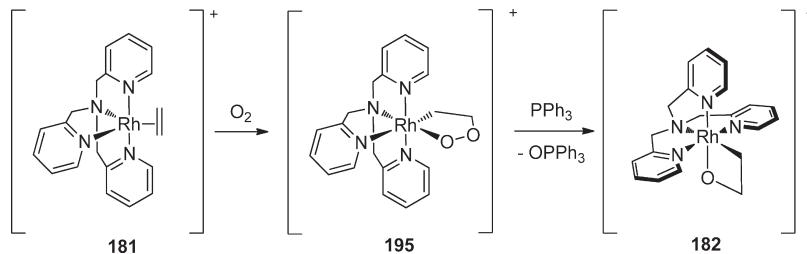
**Scheme 55. Tridentate Ligands Increase the Reactivity of Rhodaoxetane**



**Scheme 56. Rhodaoxetane from an Internal Alkene**



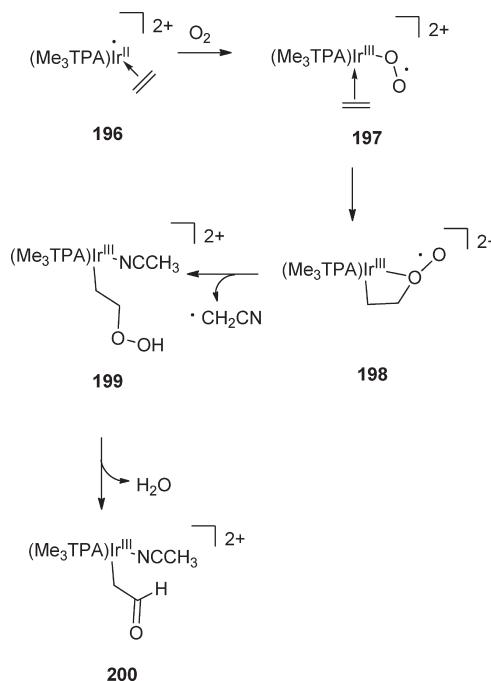
**Scheme 57. O<sub>2</sub> Oxidation Leads to Metalla-1,2-dioxolane**



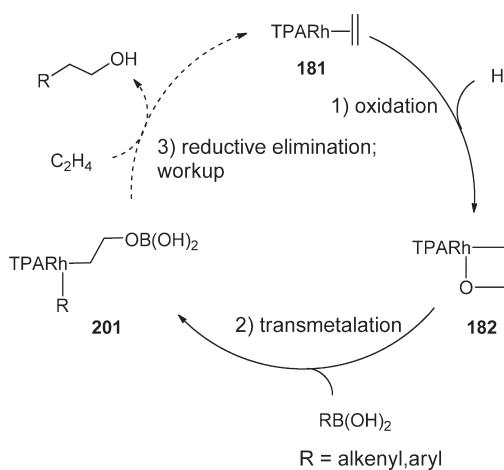
When the metalla-oxetane was treated with trimethylphosphane in benzene at 35 °C, transformation into the monomeric rhodaoxetane **206** and consequent quantitative formation of 4-cyclooctenone **207** was observed, yielding the oxidation of an internal alkene to a ketone as net-reaction.<sup>208</sup> The proposed mechanism for this transformation includes an initial cleavage of the dinuclear complex to a monomeric rhodaoxetane with two axial PMe<sub>3</sub> ligands. Subsequent  $\beta$ -H elimination from this complex was possible through decoordination of one diphenyltriazenide arm, which led to the Rh-hydride-enolate, from which in turn the oxidized cyclo-olefin could be O–H reductively eliminated. Tautomerization provided the ketone (Scheme 61).

It was also found that, if complex **205** is heated in the presence of carbon monoxide, two other products were found which had incorporated one CO molecule, carboxylic acid **210** and the bicyclic lactone **211**.<sup>209</sup> This transformation proceeded through an isomerization of **205** to the 16 electron hydroxallyl complex X and subsequent coupling of the CO group with C4. From this intermediate **209**,  $\beta$ -OH elimination and reductive C–O elimination were proposed to lead to the carboxylic acid product. Alternatively, nucleophilic attack of the hydroxyl group on the acyl followed by  $\beta$ -H elimination yielded the lactone (Scheme 62).

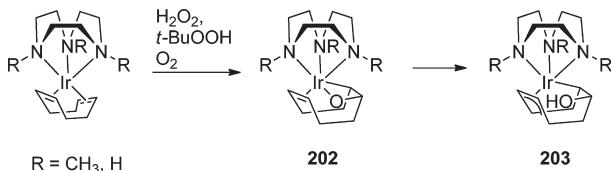
**Scheme 58. Iridaoxetanes as Putative Intermediates in Oxidation via Open Shell Species**



**Scheme 59.** Rhodaoxetane 181 as Potential Intermediate in a New Carbohydroxylation Protocol



**Scheme 60.** Formation of an Iridaoxetane



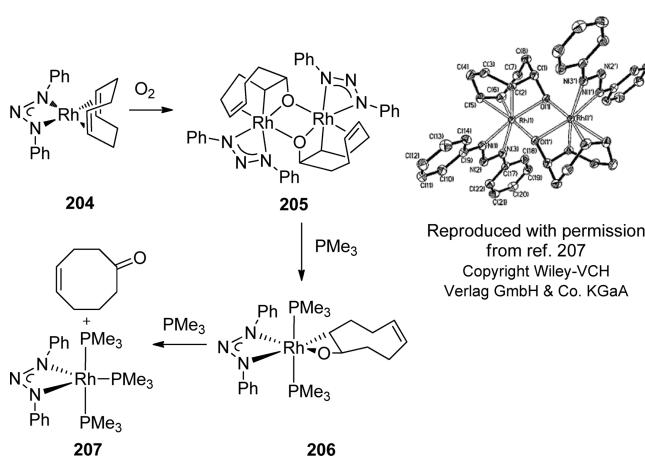
Several of the preceding Rh and Ir systems and their involvement in the oxidation of organic substrates have been reviewed in even greater detail recently.<sup>210</sup>

Blecke et al. studied the reactivity of an iridabenzene 212 toward substrates with unsaturation. When the iridabenzene was exposed to CO<sub>2</sub>, a [2 + 2] cycloaddition occurred. This broke the aromaticity of the metallabenzene and distorted it into a boat shape while forming the planar iridaoxetane 213, which was evident from the solid state structure of the complex (Scheme 63).<sup>211</sup>

During studies involving Wolff rearrangements on an iridacyclopentanone, Gómez et al. discovered the unexpected formation of iridacyclobutanone 214, which had been formed through migration of the transition metal rather than the organic moiety. The exocyclic double bond proved to be fairly electron rich and under ozonolysis conditions was cleaved to form iridaoxetane 215. The product could be isolated, and a solid state structure was determined (Scheme 64).<sup>212</sup>

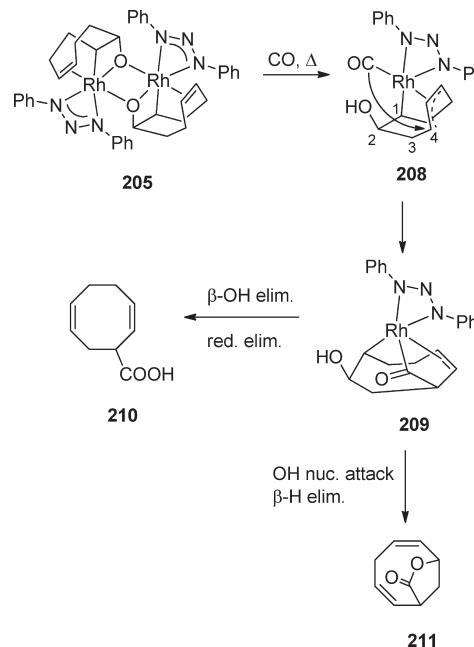
Recently, Schmidt et al. found in the asymmetric hydrogenation of itaconic acid with Rh phosphine catalysts that an increase in the substrate concentration led to a decrease in conversion. They observed the build-up of an organometallic species that did not further react to product and were able to isolate and identify rhodaoxetane 217 as this “dead-end” intermediate. For the deactivation pathway the authors proposed that through deprotonation and oxidative addition of the carboxylic acid functions the substrate is turned into a strong tridentate O, C=C, O chelate 216. A subsequent hydrometalation of the double bond leads to the stable rhoda(III)oxetane, which does not react any further (Scheme 65).<sup>213</sup>

**Scheme 61.** Oxidation of Olefins to Ketones via a Rhodaoxetane



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**Scheme 62.** Reaction of Rhodaoxetane 205 with CO

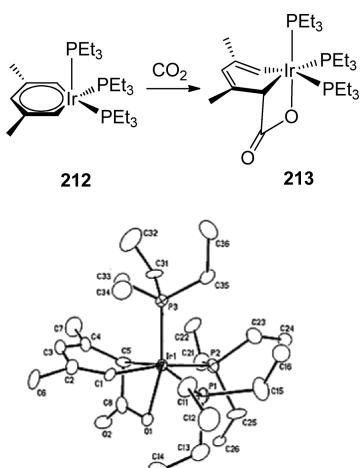


### 3.6. Group 10 Metallaoxetanes

A stable and isolable nickelaoxetane was prepared by Hillhouse and co-workers by a formal [2 + 2] cycloaddition of nickel carbene 218 and diphenylketene. The metallaoxetane product 219 could be obtained in crystalline form, and the Ni—O and Ni—C bond lengths were determined to be 1.8613 Å and 2.081 Å, respectively. In the same report, the authors proposed that the transient nickelaoxetane 220 might be formed as a first step during the incorporation of 2 equiv of CO<sub>2</sub>, followed by an insertion of the second equivalent into the Ni—C bond (Scheme 66).<sup>214</sup>

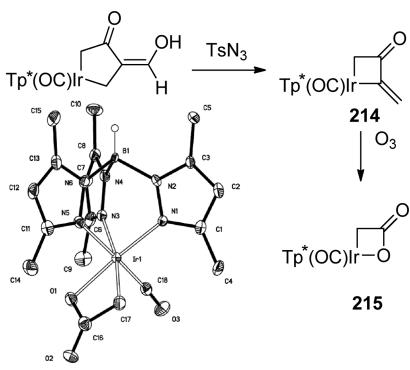
In 2003 Sharp and co-workers reported the oxidation of ethylene to acetaldehyde and reductive coupling of ethylene through a Pt(COD)oxo complex 222 and the formation of a platinaoxetane 224 by that same complex and norbornene (Scheme 67).<sup>215</sup> Based on the formation of the metallaoxetane

**Scheme 63.** Formation of an Iridaoxetane from an Iridabenzene



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**Scheme 64.** Ozonolysis of an Iridacyclobutanone with an Exocyclic Double Bond



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with norbornene, they suggested the intermediacy of a platinaoxetane in the ethylene oxidation, as well. The platinaoxetane 224 could be isolated and subjected to X-ray crystallography. The mechanism of the formation was proposed to involve the proton catalyzed formation of a Pt(II) hydroxo complex 223 that then undergoes coupling with the alkene.<sup>216</sup>

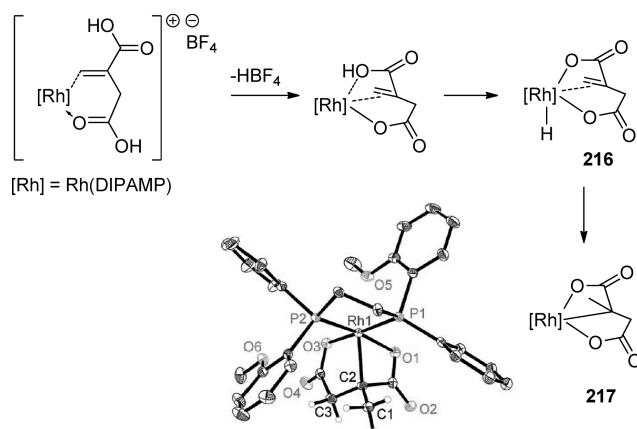
Later, the same group reported that exposure of these platinaoxetanes to Lewis acids (such as  $\text{BF}_3$ ) in the presence of other alkenes results in reversible alkene extrusion. This transformation proceeded through an alkene-coordinated metal-oxo species 226, exchange of the olefin, and reformation of the metallaioxetane 227 (Scheme 68).<sup>217</sup> In the presence of  $\text{BF}_3$  and traces of water, activation of the platinaoxetane through protons instead of the Lewis acid is also conceivable.<sup>216</sup>

Various ligand exchanges and coordination of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  gave access to a whole range of stable norbornene–Pt–oxetanes.<sup>218</sup>

The norbornene–COD–platinaoxetane 228 yielded Pt–O insertion products 229–232 when treated with CO, isocyanide and electron deficient alkenes and alkynes.<sup>219</sup>

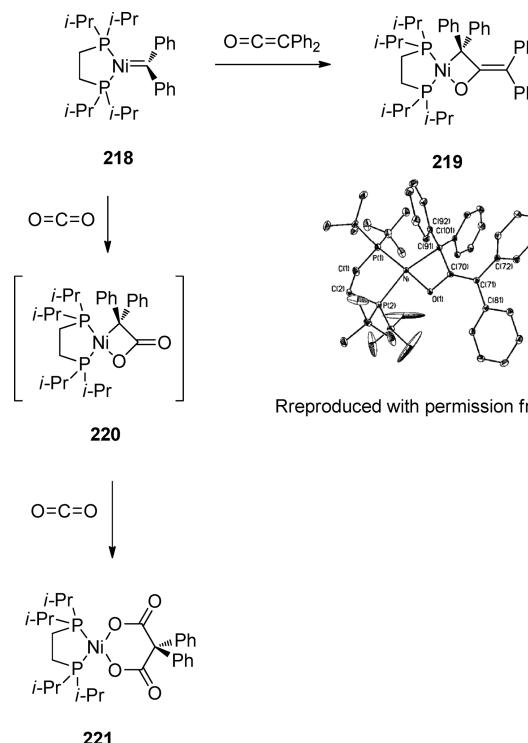
Systematic studies of the influence of various ancillary ligands, Lewis acids, carbon substituents, and oxidants on the reactivity of

**Scheme 65.** Rhodaoxetane through Formal Hydrometallation of a Double Bond



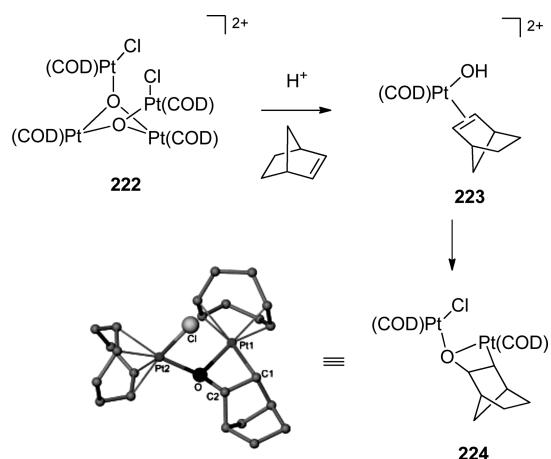
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**Scheme 66.** Nickelaoxetane from a Formal [2 + 2] Cycloaddition

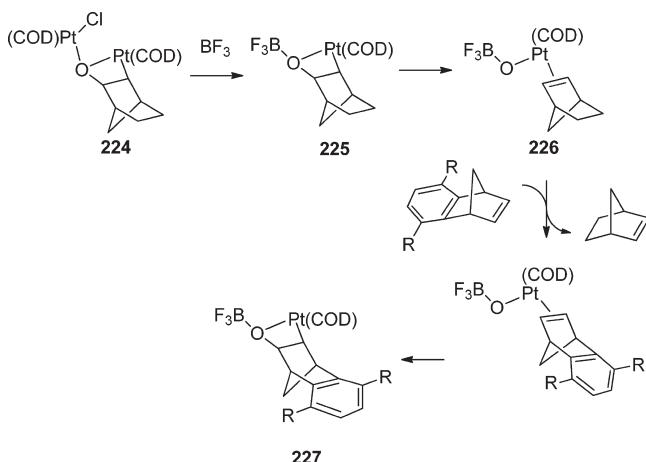
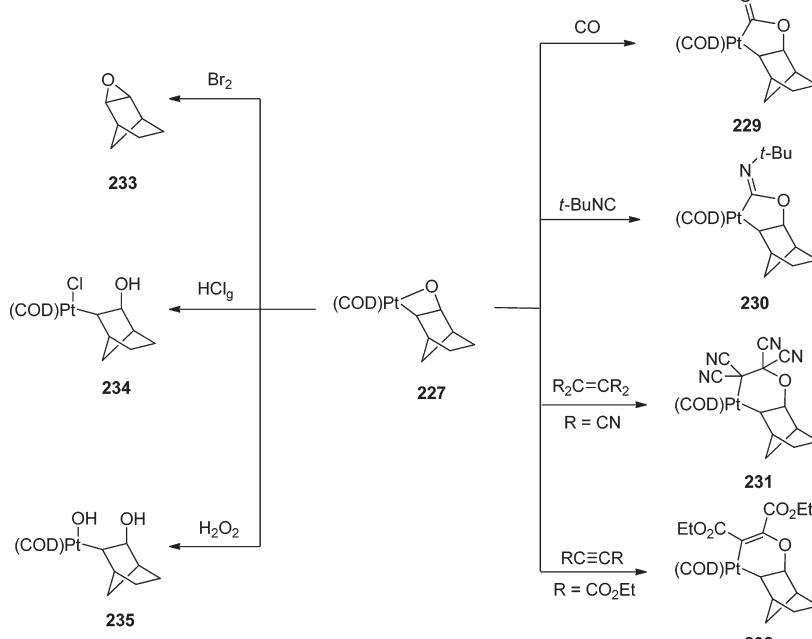


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platinaoxetane were performed.<sup>56</sup> These led to the observation of C–O reductive elimination in the presence of  $\text{Br}_2$  to give norbornene oxide 233 with COD as ancillary ligand and in the absence of Lewis acid. Epoxide formation is observed during heating to 60 °C also in the absence of  $\text{Br}_2$  when 227 was activated through coordination of 1 equiv of  $\text{Pt}(\text{COD})\text{Cl}$  to the oxetane oxygen. These findings constitute an epoxidation mechanism with the proven intermediacy of a metallaioxetane (see sections 2.1.1, 3.6, and 3.7).

**Scheme 67. Isolable Platinaoxetane from Norbornene**

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**Scheme 68. Reversible Alkene Extrusion from Platinaoxetanes****Scheme 69. Reactivity of Platinaoxetane 227**

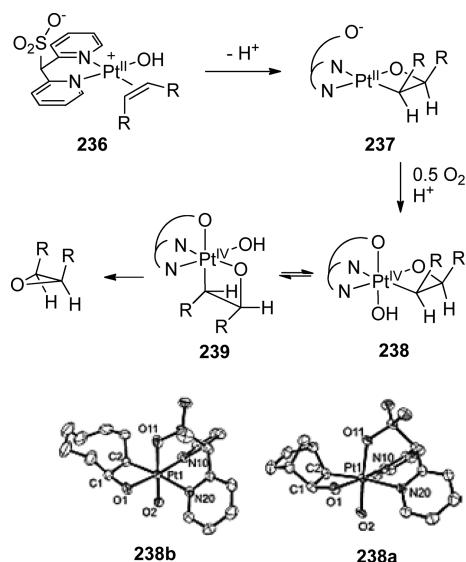
In the presence of  $\text{HCl(g)}$  or  $\text{H}_2\text{O}_2$ , the  $\text{Pt}-\text{O}$  bond was cleaved and the chloro (**234**) or hydroxo Pt species (**235**) with a  $\sigma$ -bound norbornol fragment was observed (Scheme 69). Although the latter compound is formally the product of simple  $\text{H}_2\text{O}$  addition, water alone did not effect hydrolysis. The authors suggested that hydrogen peroxide successfully hydrolyzed the platinaoxetane merely due to its slightly lower pH, which could initiate protonation of the oxetane oxygen.

Vedernikov and co-workers reported the preparation and isolation of a platinaoxetane with an anionic sulfonate ligand through aerobic oxidation of a  $\text{Pt}(\text{II})-\text{olefin}-\text{hydroxo}$  ( $\text{olefin} = \text{cis-cyclooctene, norbornene}$ ) complex **236** in water.<sup>220</sup> The X-ray structure revealed the strained character of the metallaoxetane. Indeed, upon heating in various solvents ( $\text{H}_2\text{O}$ ,  $\text{DMSO}$ ,  $\text{MeOH}$ ,  $\text{CD}_2\text{Cl}_2$ ) and even under solvent-free conditions,

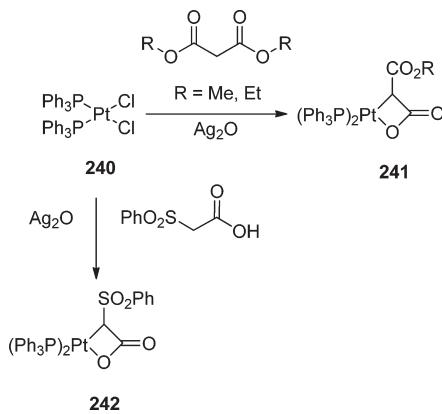
formation of the epoxide occurred via direct reductive elimination. As yet, the reported epoxidation oxidation is in a stoichiometric fashion, as attempts at rendering the reaction catalytic led to decomposition of the metal complex.

The formation of the metallaoxetane **239** occurs by hydroxyplatination of the coordinated olefin, followed by an intermediate formation of the square planar  $\text{Pt}(\text{II})$ -oxetane **237**. Upon exposure to  $\text{O}_2$ , complex **237** is oxidized to the octahedral  $\text{Pt}(\text{IV})$ -oxetane **238**.

Through experimental observations and DFT calculations, the authors suggested a rearrangement of the platinaoxetane complex **238** to the isomeric platinaoxetane **239** before reductive elimination of the epoxide takes place (Scheme 70). The complex formed from the more strained parent olefin norbornene **238a** was significantly more reactive than the cyclooctene complex **238b**.

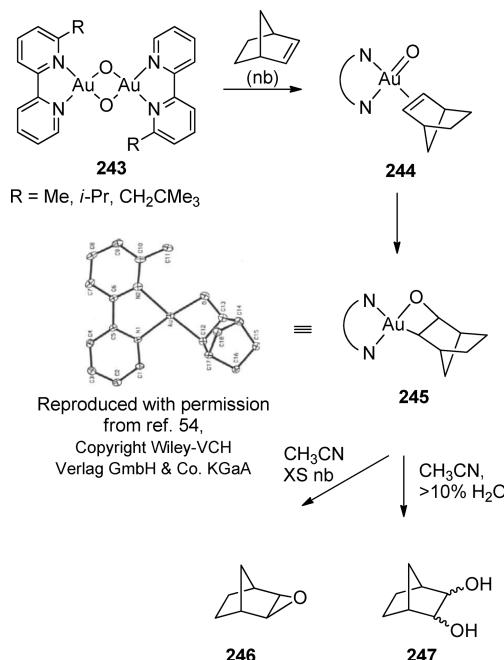
**Scheme 70.** Olefin Epoxidation via a Platinaoxetane

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**Scheme 71.** Formation of Platinaoxetanes from C—H Acidic Compounds

Polar solvents expedited the reaction, indicating a charged transition state for the elimination process. Furthermore, calculations supported the need of somewhat strained cycloolefins for the reductive elimination to occur, as the ethylene equivalent showed a high activation barrier for the elimination.

When *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (240) was heated with dialkyl malonate and silver oxide in dichloromethane, a new reaction product formed which displayed NMR-spectroscopic features, indicating the formation of a four-membered platinaoxetane 241 with an exocyclic C=O bond in the 3 position, formally a  $\beta$ -platinalactone.<sup>221</sup> <sup>31</sup>P and <sup>13</sup>C NMR characterizations showed inequivalent phosphines and carbonyl carbons, partly with markedly different Pt coupling. In the <sup>1</sup>H NMR spectrum, the Pt-CH resonance showed coupling with Pt and the methylene protons in the remaining ethyl ester chain were diastereotopic, indicating the formation of a chiral center, which is all in agreement with platinalactone formation. Although no X-ray quality crystals could be obtained, results from mass spectrometry and elemental

**Scheme 72.** Formation and Reactivity of the First Stable Auraoxetane

analysis all supported the presence of this species. When (phenylsulfonyl)acetic acid, PhSO<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, as another C—H acidic reagent was used, similar results were obtained and platinalactone complex 242 was produced (Scheme 71). The metallalactones were thermally stable and showed no reactivity toward alkylating agents such as methyl iodide.<sup>221</sup>

### 3.7. Group 11 Metallaoxetanes

The preparation and isolation of an auraoxetane from a dinuclear  $\mu$ -oxo-Au complex 243 and norbornene was reported by Cinelli et al. in 2005.<sup>54</sup> X-ray crystal structure analysis shows a square planar geometry with a minimal square pyramidal distortion. The Au—O bond length is 1.967 Å while the Au—C distance is slightly longer at 2.055 Å. Similar to the mechanism suggested by Sharp for the formation of platinaoxetanes,<sup>216</sup> the proposed mechanism for the formation of the auraoxetane consists of the cleavage of the dinuclear Au complex to form 244, a mononuclear Au-oxo species with the olefin coordinated. No evidence was provided for the Au=O double bond, but through a (formal) [2 + 2] cyclization with the olefin, it would yield the metallaoxetane 245.

Interestingly, with a large excess of norbornene (nb) in CH<sub>3</sub>CN, the formation of the corresponding epoxide 246 could be observed along with derivatives thereof such as various aldehydes. In the presence of >10% H<sub>2</sub>O in the solvent, cis and trans diols 247 were also formed (Scheme 72). Although no further mechanistic investigations about the formation of the metallaoxetane itself or the epoxide and diol products have been reported, further exploration of olefin dihydroxylation and epoxidation via auraoxetanes intermediates is desirable.

## 4. PREPARATION AND REACTIVITY OF METALLAOXETANES

Tables 1 and 2 present the preparation and reactivity of various metallaoxetanes. The tables are ordered first by the

**Table 1.** Metallaoxetane Preparation

<b>Insertion into epoxides</b>			
Metal	Comments	Section	References
V		2.2.1.	112
Cr	Computational	2.2.1.	120
Mo		2.2.1.	112, 113, 115
Mo	Computational	2.2.1.	120
W		2.2.1.	113, 114
Re		2.2.1.	126a, 127
		2.2.3.	139, 146
Fe	Computational Gas phase	2.2.1. 2.2.1. 2.2.1.	120 116 111, 117
Ru		2.2.1.	118
Ru		2.3.2.	152
Co	Computational	2.2.1.	120
Rh	Stepwise formation Metal surface/heterogeneous Biphasic system Crystal structure Electron poor epoxides only	2.2.1. 2.2.2. 2.4. 3.5. 3.5.	110 128 158 170, 222 148, 149, 223
Ir	Electron poor epoxides only	3.5. 3.5.	189 148, 149
Ni	Gas phase Computational	2.2.1. 2.2.1. 2.2.3. 2.3.1. 2.3.2.	119 120 11, 135 147 151 224-226
Pd	Electron poor epoxides only		224
Pt	Metal surface/heterogeneous	2.2.2. 2.2.3.	131 134
	Electron poor epoxides only	3.5.	148, 149, 224, 227, 228
Cu	Computational	2.2.1. 2.2.3.	120 133, 135, 145
Ag	Metal surface/heterogeneous	2.2.2.	52, 129, 130

<b>[2+2] addition of a metal carbene and carbonyl species</b>			
Metal	Comments	Section	References
Ti	Computational From ketene From metallo carbonyl species From Metallo-vinylidene From Metallo-vinylidene and metallo carbonyl species	3.1. 3.1. 3.1. 3.1. 3.1.	160, 169 162 163 164, 165 167
Ta	Crystal structure	3.2.	176
Cr	From metal carbene and ketene then rearrangement; crystal structure	3.3.	181
Mo	Crystal structure	3.3.	180
W	Crystal structure	3.3.	180
Ir	From iridabenzene	3.5.	211
Ni	From diphenylketene, crystal structure	3.6.	214

<b>[2+2] addition of a metal dioxo complex and olefin species</b>			
Metal	Comments	Section	References
Ti	From allene; crystal structure	3.1.	170
Cr	computational Gas phase	2.1.1. 2.1.1. 2.1.1.	14, 16, 24, 25 16, 17 12, 18, 19 34b, 45
Mo	heterogeneous catalyst system	2.3.2.	157
Mn		2.1.1.	37, 39, 40, 103
Re	Computational for methyltrioxy rhenium + ethylene Computational for LnRe=O + ketene Heterogenous catalyst system	2.1.1. 2.1.1. 2.3.2.	96-97 98 154

Table 1. Continued

Insertion into epoxides			
Metal	Comments	Section	References
V		2.2.1.	112
Cr	Computational	2.2.1.	120
Mo		2.2.1.	112, 113, 115
Mo	Computational	2.2.1.	120
W		2.2.1.	113, 114
Re		2.2.1.	126a, 127
		2.2.3.	139, 146
Fe	Computational	2.2.1.	120
	Gas phase	2.2.1.	116
		2.2.1.	111, 117
Ru		2.2.1.	118
Ru		2.3.2.	152
Co	Computational	2.2.1.	120
Rh	Stepwise formation	2.2.1.	110
	Metal surface/heterogeneous	2.2.2.	128
	Biphasic system	2.4.	158
	Crystal structure	3.5.	170, 222
	Electron poor epoxides only		148, 149, 223
Ir		3.5.	189
	Electron poor epoxides only	3.5.	148, 149
Ni	Gas phase	2.2.1.	119
	Computational	2.2.1.	120
		2.2.3.	11, 135
		2.3.1.	147
		2.3.2.	151
			224-226
Pd	Electron poor epoxides only		224
Pt	Metal surface/heterogeneous	2.2.2.	131
		2.2.3.	134
	Electron poor epoxides only	3.5.	148, 149, 224, 227, 228
Cu	Computational	2.2.1.	120
		2.2.3.	133, 135, 145
Ag	Metal surface/heterogeneous	2.2.2.	52, 129, 130
[2+2] addition of a metal carbene and carbonyl species			
Metal	Comments	Section	References
Ti	Computational	3.1.	160, 169
	From ketene	3.1.	162
	From metallo carbonyl species	3.1.	163
	From Metallo-vinylidene	3.1.	164, 165
	From Metallo-vinylidene and metallo carbonyl species	3.1.	167
Ta	Crystal structure	3.2.	176
Cr	From metal carbene and ketene then rearrangement; crystal structure	3.3.	181
Mo	Crystal structure	3.3.	180
W	Crystal structure	3.3.	180
Ir	From iridabenzene	3.5.	211
Ni	From diphenylketene, crystal structure	3.6.	214
[2+2] addition of a metal dioxo complex and olefin species			
Metal	Comments	Section	References
Ti	From allene; crystal structure	3.1.	170
Cr	computational	2.1.1.	14, 16, 24, 25
	Gas phase	2.1.1.	16, 17
		2.1.1.	12, 18, 19 34b, 45
Mo	heterogeneous catalyst system	2.3.2.	157
Mn		2.1.1.	37, 39, 40, 103
Re	Computational for methyltrioxy rhenium + ethylene	2.1.1.	96-97
	Computational for LnRe=O + ketene	2.1.1.	98
	Heterogenous catalyst system	2.3.2.	154

Table 1. Continued

Insertion into epoxides			
Metal	Comments	Section	References
V		2.2.1.	112
Cr	Computational	2.2.1.	120
Mo		2.2.1.	112, 113, 115
Mo	Computational	2.2.1.	120
W		2.2.1.	113, 114
Re		2.2.1.	126a, 127
		2.2.3.	139, 146
Fe	Computational	2.2.1.	120
	Gas phase	2.2.1.	116
		2.2.1.	111, 117
Ru		2.2.1.	118
Ru		2.3.2.	152
Co	Computational	2.2.1.	120
Rh	Stepwise formation	2.2.1.	110
	Metal surface/heterogeneous	2.2.2.	128
	Biphasic system	2.4.	158
	Crystal structure	3.5.	170, 222
	Electron poor epoxides only		148, 149, 223
Ir		3.5.	189
	Electron poor epoxides only	3.5.	148, 149
Ni	Gas phase	2.2.1.	119
	Computational	2.2.1.	120
		2.2.3.	11, 135
		2.3.1.	147
		2.3.2.	151
			224-226
Pd	Electron poor epoxides only		224
Pt	Metal surface/heterogeneous	2.2.2.	131
		2.2.3.	134
	Electron poor epoxides only	3.5.	148, 149, 224, 227, 228
Cu	Computational	2.2.1.	120
		2.2.3.	133, 135, 145
Ag	Metal surface/heterogeneous	2.2.2.	52, 129, 130
[2+2] addition of a metal carbene and carbonyl species			
Metal	Comments	Section	References
Ti	Computational	3.1.	160, 169
	From ketene	3.1.	162
	From metallo carbonyl species	3.1.	163
	From Metallo-vinylidene	3.1.	164, 165
	From Metallo-vinylidene and metallo carbonyl species	3.1.	167
Ta	Crystal structure	3.2.	176
Cr	From metal carbene and ketene then rearrangement; crystal structure	3.3.	181
Mo	Crystal structure	3.3.	180
W	Crystal structure	3.3.	180
Ir	From iridabenzene	3.5.	211
Ni	From diphenylketene, crystal structure	3.6.	214
[2+2] addition of a metal dioxo complex and olefin species			
Metal	Comments	Section	References
Ti	From allene; crystal structure	3.1.	170
Cr	computational	2.1.1.	14, 16, 24, 25
	Gas phase	2.1.1.	16, 17
		2.1.1.	12, 18, 19 34b, 45
Mo	heterogeneous catalyst system	2.3.2.	157
Mn		2.1.1.	37, 39, 40, 103
Re	Computational for methyltrioxy rhenium + ethylene	2.1.1.	96-97
	Computational for LnRe=O + ketene	2.1.1.	98
	Heterogenous catalyst system	2.3.2.	154

Table 2. Metallaoxetane Reactivity

C-O reductive elimination – epoxide formation			
Metal	Comments	Section	References
Cr	computational	2.1.1.	14, 25
	Gas phase	2.1.1.	16, 17, 24
		2.1.1.	18, 19, 34b, 37, 45, 135
Mn	via radical intermediate	2.1.1.	39, 103
		2.1.1.	40
Ru		2.1.1.	49, 50
Pt	from isolated metallaoxetane	2.1.4.	106
Ag	computational	3.6.	55, 56
	metal surface , heterogeneous	2.1.1.	53
Au	from isolated metallaoxetane	2.2.2.	129, 130
		3.7.	54
Retro [2+2] addition – carbonyl compound and metal carbene formation			
Metal	Comments	Section	References
Ti	gas phase, from isolated metallaoxetane	3.1.	166-168
Cr	computational	2.3.2.	14
Mo	computational	2.3.2.	14b, c
	heterogeneous $\beta$ -zeolite catalyst	2.3.2.	157
	from isolated metallaoxetane	3.3.	180
W	computational	2.3.2.	14c
	from isolated metallaoxetane	3.3.	180
Re	computational	2.1.2.	94c, 95
	gas phase	2.1.2.	94a, b
	mixed $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst	2.3.2.	150, 154
Fe	gas phase	2.1.4.	107, 108
Ru		2.3.2.	152
Os	stoichiometric amounts of metal	2.3.2.	153
Ni	gas phase	2.3.2.	151
Retro [2+2] addition – olefin and metal oxide formation			
Metal	Comments	Section	References
Ti		3.1.	159-161
	computational	3.1.	160, 169
	gas phase, from isolated metallaoxetane	3.1.	166
Cr	computational	2.2.1.	120
Mo	computational	2.2.1.	120
Re		2.1.2.	92
	computational	2.1.2.	93-95
	gas phase	2.1.2.	94a, b
		2.2.1.	125-127
Fe	gas phase	2.2.1.	116
	computational	2.2.1.	120
Ru		2.3.2.	152
Co	computational	2.2.1.	120
Rh	Driving force: re-aromatization of benzene	2.2.1.	110
	computational	3.5.	191
Ni	gas phase	2.2.1.	119
	computational	2.2.1.	120

Table 2. Continued

C-O reductive elimination – epoxide formation			
Metal	Comments	Section	References
Cr	computational	2.1.1.	14, 25
	Gas phase	2.1.1.	16, 17, 24
		2.1.1.	18, 19, 34b, 37, 45, 135
Mn	via radical intermediate	2.1.1.	39, 103
		2.1.1.	40
Ru		2.1.1.	49, 50
		2.3.2.	152
Pt	from isolated metallaoxetane	2.1.4.	106
Ag	computational	3.6.	55, 56
	metal surface , heterogeneous	2.1.1.	53
Au	from isolated metallaoxetane	2.2.2.	129, 130
		3.7.	54
Retro [2+2] addition – carbonyl compound and metal carbene formation			
Metal	Comments	Section	References
Ti	gas phase, from isolated metallaoxetane	3.1.	166-168
Cr	computational	2.3.2.	14
Mo	computational	2.3.2.	14b, c
	heterogeneous $\beta$ -zeolite catalyst	2.3.2.	157
W	from isolated metallaoxetane	3.3.	180
	computational	2.3.2.	14c
Re	from isolated metallaoxetane	3.3.	180
	computational	2.1.2.	94c, 95
Fe	gas phase	2.1.2.	94a, b
	mixed Re <sub>2</sub> O <sub>7</sub> /Al <sub>2</sub> O <sub>3</sub> catalyst	2.3.2.	150, 154
Ru	gas phase	2.1.4.	107, 108
Os		2.3.2.	152
	stoichiometric amounts of metal	2.3.2.	153
Ni	gas phase	2.3.2.	151
Retro [2+2] addition – olefin and metal oxide formation			
Metal	Comments	Section	References
Ti		3.1.	159-161
	computational	3.1.	160, 169
	gas phase, from isolated metallaoxetane	3.1.	166
Cr	computational	2.2.1.	120
Mo	computational	2.2.1.	120
Re		2.1.2.	92
	computational	2.1.2.	93-95
Fe	gas phase	2.1.2.	94a, b
	computational	2.2.1.	125-127
Ru		2.2.1.	116
	computational	2.2.1.	120
Co	computational	2.3.2.	152
Rh	Driving force: re-aromatization of benzene	2.2.1.	120
	computational	3.5.	110
Ni	gas phase	2.2.1.	191
	computational	2.2.1.	119
		2.2.1.	120

Table 2. Continued

C-O reductive elimination – epoxide formation			
Metal	Comments	Section	References
Cr	computational	2.1.1.	14, 25
	Gas phase	2.1.1.	16, 17, 24
		2.1.1.	18, 19, 34b, 37, 45, 135
Mn	via radical intermediate	2.1.1.	39, 103
		2.1.1.	40
Ru		2.1.1.	49, 50
Pt	from isolated metallaoxetane	2.1.4.	106
Ag	computational	3.6.	55, 56
	metal surface , heterogeneous	2.1.1.	53
Au	from isolated metallaoxetane	2.2.2.	129, 130
		3.7.	54
Retro [2+2] addition – carbonyl compound and metal carbene formation			
Metal	Comments	Section	References
Ti	gas phase, from isolated metallaoxetane	3.1.	166-168
Cr	computational	2.3.2.	14
Mo	computational	2.3.2.	14b, c
	heterogeneous $\beta$ -zeolite catalyst	2.3.2.	157
	from isolated metallaoxetane	3.3.	180
W	computational	2.3.2.	14c
	from isolated metallaoxetane	3.3.	180
Re	computational	2.1.2.	94c, 95
	gas phase	2.1.2.	94a, b
	mixed Re <sub>2</sub> O <sub>7</sub> /Al <sub>2</sub> O <sub>3</sub> catalyst	2.3.2.	150, 154
Fe	gas phase	2.1.4.	107, 108
Ru		2.3.2.	152
Os	stoichiometric amounts of metal	2.3.2.	153
Ni	gas phase	2.3.2.	151
Retro [2+2] addition – olefin and metal oxide formation			
Metal	Comments	Section	References
Ti		3.1.	159-161
	computational	3.1.	160, 169
	gas phase, from isolated metallaoxetane	3.1.	166
Cr	computational	2.2.1.	120
Mo	computational	2.2.1.	120
Re	computational	2.1.2.	92
	gas phase	2.1.2.	93-95
Fe	gas phase	2.2.1.	116
	computational	2.2.1.	120
Ru		2.3.2.	152
Co	computational	2.2.1.	120
Rh	Driving force: re-aromatization of benzene	2.2.1.	110
	computational	3.5.	191
Ni	gas phase	2.2.1.	119
	computational	2.2.1.	120

general way of preparation/reaction and then by metal, going in groups across the d-block elements.

## 5. DISCUSSION AND OUTLOOK

Metallaoxetanes have received increasing interest in recent years. Their involvement in catalytic transformations was proposed on many occasions, but experimental evidence was often scarce. The growing number of isolated metallaoxetanes again showed various reliable ways to access them synthetically and allowed for in-depth studies of their reactivity. With thorough product analysis studies and especially the evolution of ever more powerful computational methods, the intermediacy of these structures was corroborated for some reactions but disputed for others.

These multiple ways to prepare metallaoxetanes and the diverse reactivity thereof open the door to intentional and strategic design of new chemical transformations. If one would like to generate a certain structural motif that can be accessed through a metallaoxetane, many different ways might be available to generate this intermediate. In turn, if one accesses a metallaoxetane from a specific starting material (e.g., an olefin or an epoxide), a multitude of products is potentially available, depending on the conditions applied. Adjustment of the metal and the ligands employed could then lead to novel catalytic transformations or entirely new reactivity.

As section 4 illustrates, it is difficult to make generalized predictions as to how metallaoxetanes can be formed or how they react. It seems that many of the ways to form metallaoxetanes or how they react can be found with metals from throughout the whole d-block. For example, addition to epoxides as well as the microscopic reverse can be found with early, mid-, and late transition metals. However, [2 + 2] additions and retro-additions are more frequently found with early to mid-transition metals, whereas  $\beta$ -X elimination is almost exclusively happening from low-valent late transition metals.

We hope that this review inspires interest in the field of metallaoxetane-based reaction development. The solid groundwork laid by many chemists by careful experimental and computational investigations will undoubtedly assist others in designing new reactions. This will, in turn, elevate metallaoxetanes from much-debated intermediates into the realm of strategic reaction design with metallaoxetanes as the reaction centerpiece.

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Alexander Dauth studied Chemistry at the University of Vienna, where he received his master degree in 2006 in the field of natural product synthesis, working under Prof. Edda Gössinger. He then started his Ph.D. with Prof. Jennifer A. Love at The University of British Columbia in organometallic chemistry and methodology. His project focuses on the development of new catalytic reactions based on metallaoxetanes as intermediates.



Prof. Jennifer Love received her Ph.D. in 2000 under the direction of Prof. Paul Wender at Stanford University. She was an NIH postdoctoral fellow in the lab of Prof. Robert Grubbs at Caltech from 2000–2003. She joined the faculty of the University of British Columbia in 2003 and was promoted to Associate Professor in 2009. Her research interests include the mechanistic investigation of M–X bond reactivity and applications in organic synthesis.



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