# Rhenium-Catalyzed Dehydration and Deoxydehydration of Alcohols and Polyols: Opportunities for the Formation of Olefins from Biomass

Suresh Raju, Marc-Etienne Moret, and Robertus J. M. Klein Gebbink*

Organic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

ABSTRACT: In view of the depletion of petroleum oils, new synthetic routes for the sustainable production of chemicals, fuels, and energy from renewable biomass sources are currently widely investigated. In particular, nonedible sugars and polyols are promising starting materials to produce olefins by dehydration, deoxygenation, or deoxydehydration (DODH) of these poly vicinal alcohols. In this perspective, we highlight the recent evolution of rhenium-catalyzed dehydration and DODH of biomass-derived alcohols and polyols to obtain olefins. Improving over the classical acid-catalyzed dehydration reaction, rhenium-mediated systems are very selective and more active to provide high yields of olefin products, but dehydration alone cannot be used to fully defunctionalize sugars. This issue is addressed by a growing research effort in the field of Re-catalyzed DODH, which allows complete dehydroxylation to form olefins in high yield. Recent developments in this field include the development of new molecular rhenium catalysts, the application of cheaper and more available reductants, and a growing mechanistic understanding owing to both experimental and computational studies. Finally, recent efforts to move beyond rhenium toward cheaper metals (Mo, V) are discussed.

KEYWORDS: biomass, olefins, diols, polyols, rhenium, deoxygenation, dehydration, deoxydehydration
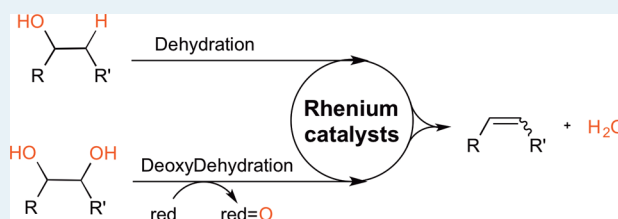
1. INTRODUCTION

The anticipated depletion of fossil hydrocarbon resources,[1] coupled with a gradual increase in cost, calls for the development of new supply chains for the chemical industry that rely on renewable feed stocks. The reduced, carbon-rich molecules that constitute the backbone of most commodity chemicals and pharmaceutical compounds should ideally be produced out of atmospheric carbon dioxide, which is not only abundant but also produced in excess by human activity relying on combustion as a source of energy. An attractive alternative to the challenging direct chemical reduction of carbon dioxide is to make use of the available biochemical machinery for the first reduction steps and use biomolecules such as sugars as a starting point for chemical synthesis.[2,3]

In contrast to the traditional hydrocarbon feedstock derived from fossil resources, the small molecules obtained from the degradation of biomass are typically oxygen-rich and hyper-functionalized: sugars contain approximately one oxygen atom per carbon atom. Thus, efficient use of biomass poses novel challenges to synthetic chemists: although traditional synthetic routes often involve the introduction of functionality on "naked" carbon backbones via C−H bond activation or hydrofunctionalization of olefins, we now need to defunction-alize oxygen-rich molecules. In essence, dehydroxylation reactions are required to convert sugars and sugar-derived polyol compounds into valuable chemicals.[4]

Perhaps the simplest approach to this problem would be acid-catalyzed dehydration reactions, but theses processes suffer from regio- and chemo-selectivity problems. In addition, the stoichiometric removal of all (or most) of the oxygen content of sugars in the form of water ultimately results in the production of elemental carbon (charring). To address this problem, a range of reductive deoxygenation methods[5,6] (e.g., hydrodeoxygenation,[7,8] hydrogenolysis,[9] decarbonylation,[10] decarboxylation,[11] or direct deoxygenation[12]) via heterogeneous[13,14] or homogeneous[15−18] catalysis are under investigation.

An appealing alternative approach consists in combining the two former reactions into a formal deoxydehydration (DODH[19]) sequence converting a vicinal diol into an olefin with release of one oxygen atom and one water molecule, a reaction that is the formal reverse of the well-known olefin dihydroxylation reaction (Scheme 1). Because late transition elements are not oxophilic enough to abstract oxygen atoms from most organic substrates while their early counterparts form metal−oxygen bonds that are too strong to be reductively cleaved in a catalytic cycle, elements in the middle of the transition series (e.g., V, Mo, W, Re) are attractive candidates for the development of catalytic DODH reactions of biomass-derived polyols. Among these, rhenium has rapidly emerged as the most promising metal,[20−22] presumably because of its large number of accessible oxidation states (−1 to +7) and its ability

Scheme 1. Schematic Representation of Rhenium-Catalyzed Deoxygenation, Dehydration, and Deoxydehydration Reactions
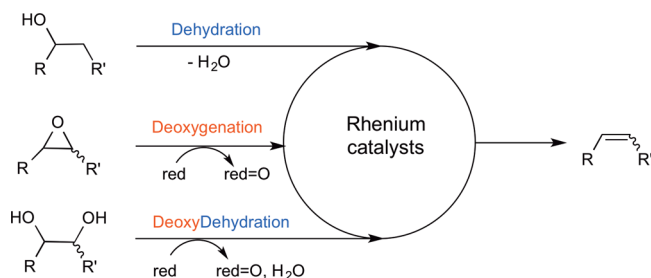

to form strong bonds to ancillary ligands that allows the tuning of its catalytic activity.[23,24] The rapid development of rhenium-based DODH catalysts builds upon the well-documented oxygen atom transfer (OAT) chemistry of rhenium oxo compounds,[25−28] many of which are known to mediate catalytic OAT to strong oxygen acceptors like triphenylphosphine from substrates such as organic sulfoxides,[29] pyridine *N*-oxides[30−38] and epoxides[39−43] to form the corresponding organic sulfides, pyridines and olefins, respectively. In this perspective, we cover the latest developments in the rhenium-catalyzed conversion of alcohols to olefins via dehydration (Section 2) and DODH (Section 3). In addition, emerging alternatives based on cheaper metals (Mo, V) are briefly discussed.

2. RHENIUM-CATALYZED DEHYDRATION

Acid- and base-catalyzed dehydration reactions of alcohols to render olefins are well-known organic reactions included in all standard organic chemistry textbooks,[44] and the acid-catalyzed reaction is a classical reaction for freshmen chemistry practical courses. For larger scale operations, these reactions come with many downsides related to, for example, waste management and overall reaction selectivity (i.e., uncontrolled reactions of different hydroxyl groups leading to multiple products including different oligomers and polymers). Alternative catalysts for these reactions that (partly) overcome these issues are mostly based on nontransition metal oxides and on cation-exchanged structured oxides including zeolites.[45] Several recent reports indicate the potential utility of both homogeneous and heterogeneous Re-catalysts for the dehydration of biomass-derived alcohols to olefins.

2.1. Homogeneous Catalysts. The use of homogeneous Re-based catalysts for alcohol dehydration was pioneered by Espenson and co-workers who pointed out the ability of methyltrioxorhenium (MTO) to catalyze a number of different dehydration reactions.[30] In their initial 1996 report, it was shown that some aromatic alcohols are smoothly converted to the corresponding ethers in high yields in 3 days at ambient conditions in dry benzene (Scheme 2). For a series of secondary benzylic alcohols, PhCH(OH)R, the conversion increases with the size of the R group (R = H, 36%; Me, 86%; Et, 89%; Ph, 100%). Electron-withdrawing substituents on the aromatic rings slow down the reactivity, whereas electron-donating substituents enhance the overall conversion to ethers. Aliphatic alcohols show lower conversions (<8%), whereas in combination with secondary benzylic alcohols, these give nonsymmetrical ethers in high yields (69−95%). Depending on the reactivity of aliphatic alcohols, mixtures of symmetric and nonsymmetric ethers are obtained in these reactions.

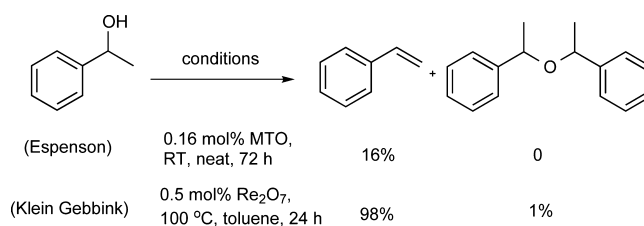**Scheme 2. MTO-Catalyzed Ether and Olefin Formation from 1-Phenylethanol**
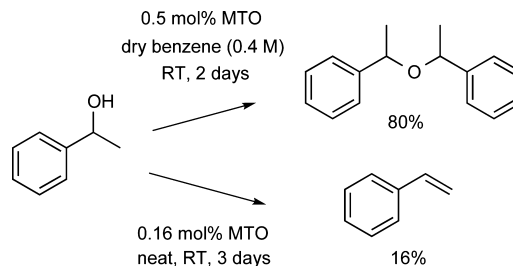
Smaller primary alcohols lead to ethers, whereas longer aliphatic alcohols (1-dodecanol or 1-undecanol) form olefins, albeit in low yields. The authors rationalize these observations by invoking a concerted ether formation process from a Re−dialkoxide species that would be more difficult for longer alcohols due to limited coordination space.

Using 0.2 mmol of MTO with a variety of neat alcohols (15 mL) results in formation of the corresponding olefins at room temperature over 3 days. For most alcohols, the yield of olefin is very low under these conditions. Olefin yields could be significantly improved (11−89%) with the use of 1 mol % loading of MTO for different cyclic and acyclic, secondary benzylic alcohols (0.2 M) in benzene as solvent.

The performance and scope of rhenium systems for the dehydration of alcohols—including biomass-derived ones—was further improved by Klein Gebbink and co-workers. The conversion of 1,2,3,4-tetrahydronaphthol to the corresponding olefin can be achieved by using 1 mol % of MTO within 0.5 h by adjusting the reaction temperature to 100 °C in technical grade toluene in air.[46] 1-Phenylethanol was converted to styrene with a number of different commercially available rhenium catalysts under these reaction conditions within 24 h (Scheme 3). The highest formation of styrene (98%) is

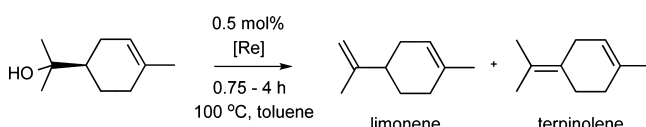**Scheme 3. Re-Catalyzed Dehydration of 1-Phenylethanol to Styrene and the Corresponding Ether**

	conditions		
(Espenson)	0.16 mol% MTO, RT, neat, 72 h	16%	0
(Klein Gebbink)	0.5 mol% Re₂O₇, 100 °C, toluene, 24 h	98%	1%

achieved with Re_2O_7 with only traces of ether being formed (1%). Compared to the typical use of sulfuric acid as the catalyst for this reaction (39% styrene and 5% ether yield, concurrent product oligo-/polymerization), these numbers show the enhanced reaction selectivity that can be obtained with the use of non-Brønsted acidic rhenium catalysts. In a later study by Klein Gebbink et al., ether formation was clearly observed as an intermediate step in the course of the reaction, eventually yielding the olefin in nearly quantitative yields.[47]

Different alkyl- and aryl-substituted benzylic alcohol substrates are converted to the corresponding olefins smoothly and in near quantitative yields using Re_2O_7. In addition, aliphatic tertiary and secondary allylic, as well as homoallylic alcohols are converted to give moderate to high olefin yields. The dehydration of aliphatic secondary and homoallylic

alcohols requires more forcing conditions to obtain high olefin yields (i.e., reactions have to be carried out at 150 °C in toluene).[48] At this elevated temperature, 3-octanol gives a mixture of octene isomers (77%), whereas the primary alcohol 1-octanol is transformed to 1-octanal (18%) as the main product with traces of octanoic acid and octyl octanoate out of 82% conversion in 24 h. These investigations provide the following reactivity order within one class of substrates: tertiary > secondary ≫ primary alcohols. Based on different alcohol substrates, the observed order of reactivity is allylic > aliphatic > homoallylic alcohols.

A series of bioderived terpene alcohols were additionally subjected to Re-catalyzed dehydration reactions.[48] In fact, a range of rhenium catalysts including low valent carbonyl compounds, mid-to-high valent oxo compounds, and Re_2O_7 are active for the dehydration of α-terpineol to terpenes, a notable exception being the inactivity of perrhenate salts. Re_2O_7 shows a good product selectivity toward limonene and terpinolene (65:35), while other rhenium catalysts as well as H_2SO_4 give 2–9% and 50% of other isomers (α-terpinene, γ-terpinene, and para-cymene), respectively (Scheme 4). For other terpene

Scheme 4. α-Terpineol Dehydration to Limonene and Terpinolene at 100 °C Using Different Re Catalysts


[Re]	initial rate (mmol/h)	limonene (%)	terpinolene (%)
Re_2O_7	6.3	65	35
$HReO_4$ (aq)	4.7	57	32
MTO	0.48	66	24
$ReIO_2(PPh_3)_2$	2	61	28
$ReOCl_3(PPh_3)_2$	0.84	61	31

alcohols, the Re_2O_7-catalyzed reaction yields the corresponding terpenes and isomers thereof, mostly with very good mass balance. In some cases (e.g., for (−)-borneol) more forcing conditions (higher temperature and longer reaction times) are required. The optimized reaction conditions were then applied to upgrade tea tree oil (from *Melaleuca alternifolia*), which is composed of nearly 50% of α-terpineol, together with a mixture of other terpenes. This showed the complete dehydration of α-terpineol to the mixture of limonene and terpinolene isomers already present in the oil with 92% total mass balance.

The partial solubility of Re_2O_7 in solvents containing small amounts of water, including technical grade toluene, in relation to the formation of $HReO_4$ in the presence of H_2O, raised questions about the homogeneous or heterogeneous nature of the Re_2O_7 catalyst. In a typical hot filtration test, both the filtrate and the residue (major Re part) showed further reactivity when new substrate was added, pointing out that soluble as well as insoluble Re species may take part in the reaction.[48] Finally, Re_2O_7 was compared to some of the commonly used solid acid catalysts (e.g., zeolites, alumina) in the dehydration of α-terpineol. This has shown that under the optimized reaction conditions for Re_2O_7 (i.e., toluene as the reaction solvent and mild reaction conditions <150 °C), this catalyst outperforms all of the solid acid catalysts tested in terms of activity as well as product selectivity.

The mechanism of the rhenium-catalyzed alcohol-to-olefin transformation has been investigated. Two plausible reaction pathways were envisioned early on by Espenson (Scheme 5), in

Scheme 5. Possible Dehydration Pathway Using MTO, Either Concerted (Top) or Ionic (Bottom) (Adapted from Ref 47)
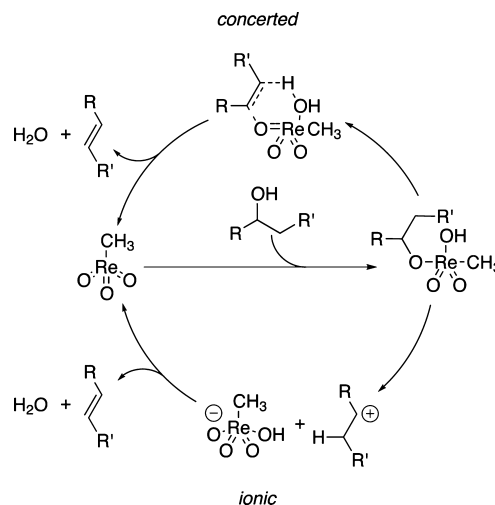

which the release of olefin from the transient Re–alkoxide species takes place in either a concerted (top) or an ionic pathway (bottom).[30] In general, primary aliphatic alcohols favor the concerted pathway, while aromatic alcohols favor the ionic pathway due to carbenium ion stabilization. To provide more insight in the mechanism of these rhenium-catalyzed alcohol dehydration reactions, Klein Gebbink et al. studied the conversion of 1-phenylethanol to styrene in more detail.[47] Because the structure and active site properties of Re_2O_7 are less defined, MTO was chosen as the catalyst in these studies. MTO itself gives a high styrene yield (89%) under the same reaction conditions as typically used with Re_2O_7.

It is important to note that water and oxygen are essential reaction components in these rhenium-catalyzed dehydrations. Only a small amount of styrene (6%) is obtained under air-free conditions, whereas in the absence of water, the reaction does not proceed at all. Water is proposed to facilitate the likely proton transfer steps, but the role of oxygen is less clear. It was envisioned to be involved in the reoxidation of inactive reduced species such as methyldioxorhenium (MDO). However, no evidence was found for the reduction of MTO by the alcohol or the formation of the corresponding ketone under catalytic conditions.

N-coordinating bases with sufficient base strength (i.e., conjugated acids' $pK_a > 4$) inhibit the dehydration reaction, albeit not because of coordination to MTO (i.e., no significant change of Re=O vibrations was observed for MTO in the presence of these bases), but likely by decreasing the proton activity in the reaction medium. Primary KIE values for $PhCD(OH)CH_3$ (1.28) and $PhCH(OH)CD_3$ (1.48) suggest that no α- or β-C–H bond is broken in the rate-determining step. On the basis of these experimental data, a fully concerted pathway to styrene formation was excluded. The MTO-catalyzed dehydration reaction was found to be first order in both substrate and catalyst, and the experimentally determined activation parameters ($\Delta H^{\ddagger} = 13.4$ kcal/mol, $\Delta S^{\ddagger} = -8.3$ J/mol·K) suggest an ordered rate-limiting transition state

Scheme 6. Proposed Alcohol-to-Olefin Dehydration Catalytic Cycle by DFT Calculations (Adapted from Ref 47)
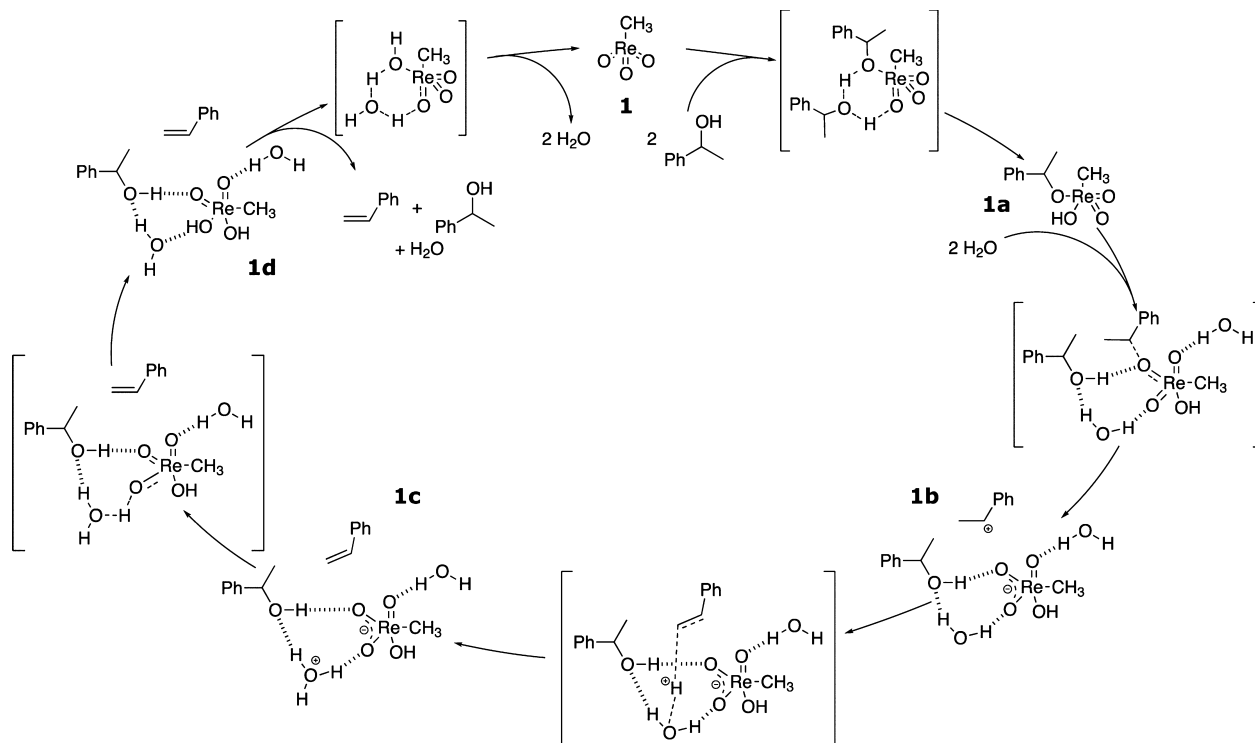

involving both substrate and catalyst. Carbon skeletal rearrangement and the reactivity order (tertiary > secondary ≫ primary alcohols) clearly indicate the involvement of carbenium species (i.e., the ionic pathway).

This is additionally supported by DFT calculations. The activation energy calculated for the concerted pathway is very high ($\Delta G^{\ddagger}$ = 33−40 kcal/mol) to release styrene from a MeReO$_2$(OH)(1-phenylethoxy) (**1a**) species. The lower-energy ionic pathway was found to proceed via an E1-type mechanism commonly known for Brønsted acid-catalyzed dehydration reactions. The proposed mechanistic cycle is shown in Scheme 6. The initial formation of **1a** is assisted by another alcohol molecule, followed by C−O cleavage to form a charge-separated species, which is facilitated by an additional alcohol and two water molecules. Subsequent proton transfer from the β-position of the carbenium ion to a water molecule and another proton transfer from the hydronium ion to the anionic rhenium species results in the formation of styrene and of MeReO$_2$(OH)$_2$ (**1d**) species. Finally, a water molecule assists the dehydration of **1d** back to MTO, which completes the cycle. It is noted that the mechanism involves five coordinated rhenium species throughout the cycle starting from four coordinated MTO. In addition, reaction steps that are assisted by "second-sphere" alcohol molecules may also be assisted by water molecules.

2.2. Heterogeneous Catalysts. In addition to the homogeneous systems discussed above, rhenium has also found use in solid–gas heterogeneous catalysis for the dehydration of short-chain alcohols. Wang et al. reported dehydration catalysts for the conversion of 2-butanol to butene isomers synthesized by solution-based atomic layer deposition of rhenia on mesoporous silica (SBA-15). In particular, they demonstrated that modifying the silica support with a layer of alumina alleviates the catalyst stability problems originating from the particularly weak interaction of rhenium oxide with

SiO$_2$.[49,50] They used unmodified ReO$_x$/SBA-15 and modified ReO$_x$/AlO$_x$/SBA-15 for the gas phase dehydration of 2-butanol to butene isomers (1-butene, *cis*- and *trans*-2-butene) at 90−105 °C in a continuous flow reactor (0.5% 2-butanol-He and 200 mL/min) (Scheme 7).[51] Under these conditions, the

Scheme 7. Dehydration of 2-Butanol over ReO$_x$/SBA-15 and ReO$_x$/AlO$_x$/SBA-15 Catalyst in a Continuous Flow Reactor (0.5% 2-Butanol-He and 200 mL/min)
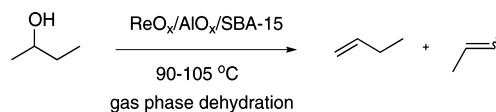
ReO$_x$/SBA-15 catalyst is very active and shows 100% conversion of 2-butanol during the first 120 min of operation at 105 °C, which drops to 24% after ∼220 min. At lower temperatures (90 °C), the conversion drops more significantly over time (11% after ∼230 min). It is likely that catalyst deactivation already started at the early stage of the reaction, but the presence of excess active sites maintained the high conversion of 2-butanol at 105 °C in the first 120 min.

In comparison, the alumina-modified SBA-15 catalyst ReO$_x$/AlO$_x$/SBA-15 provides a relatively high conversion of 2-butanol (67%) even after 220 min of operation, whereas at 90 °C, the initial activity is low (∼45%). Further characterization of the used and fresh catalysts by a number of different techniques (TEM, STEM, in situ UV−vis (DRS), and ^{27}Al MAS NMR) revealed a strong interaction of rhenia with the alumina phase. Apparently, this results in a decreased initial catalytic activity but leads to higher overall catalyst stability for the ReO$_x$/AlO$_x$/SBA-15 catalyst. Sublimation, sintering, and reduction of rhenia under the reaction conditions were found to be the main cause for catalyst deactivation.

**Scheme 8. Schematic Representation of Re-Catalyzed DODH**
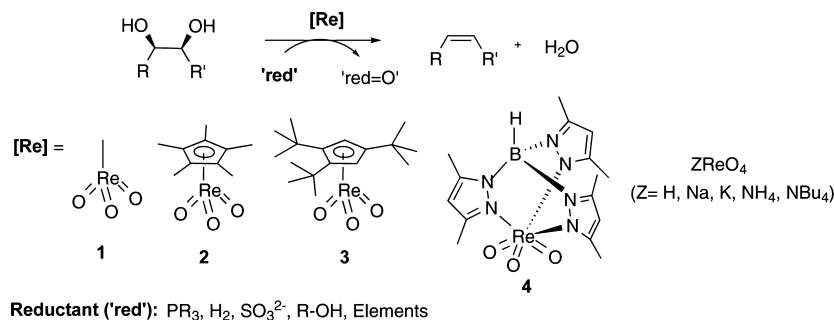
3. RHENIUM-CATALYZED DEOXYDEHYDRATION (DODH)

MTO's known ability to catalyze oxidative oxygen-atom transfer reactions suggests that the reverse reductive deoxygenation reactivity—in the form of dehydration and deoxygenation reactions—may be harnessed for the transformation of biomass into value-added chemicals.[2,52] Carried out individually on vicinal diols such as those found in the polyols that are readily available from biomass, dehydration, and deoxygenation would yield aliphatic ketones and alcohols, respectively. Combining them in a deoxydehydration (DODH) reaction sequence constitutes an attractive route to olefins from vicinal diols. This reaction formally yields hydrogen peroxide as the byproduct, but is typically carried out in the presence of a sacrificial reductant acting as oxygen acceptor and driving the reaction, producing water as the byproduct. In this way, the formation of water is inevitable in catalytic DODH reactions and the rational design of catalysts should accordingly consider water-stable catalysts. A common problem in the application of DODH to biomass-derived polyols is the competing dehydration pathway that generates a range of products from a single starting material. Thus, highly active catalysts able to selectively perform several consecutive DODH reactions are required.

In general, rhenium trioxo compounds such as MTO and perrhenate (Scheme 8) are attractive DODH catalysts that are easily handled under ambient conditions and display good air and moisture stability because of the high Re(VII) oxidation state. Next to MTO, ligands based on the Cp or Tp scaffold[19] afford catalytically active trioxorhenium compounds that can be tuned by substituent effects (Scheme 8). Initial studies commonly used PPh₃ as a clean oxygen-atom acceptor, but the use of cheaper reductants that are available on a large scale is crucial for the development of scalable processes for biomass transformation. Section 3.1 describes the evolution of molecular trioxorhenium compounds as DODH catalysts mainly with PPh₃ as the reductant, and Section 3.2 covers MTO and perrhenate-catalyzed DODH processes with a focus on the investigation of a variety of reductants (Scheme 8). In addition, the recent development of supported Re-based DODH catalysts is discussed in Section 3.3, while Section 3.4 highlights recent efforts to replace rhenium itself by cheaper, more abundant metals.

3.1. Cp- and Tp-Based Oxo-Rhenium-Catalyzed DODH.[19]
Replacing the two-electron donor methyl group in MTO by a six-electron donor Cp-ligand can be thought to decrease the Lewis acidity of rhenium which consequently decreases the Re=O bond strength in order to facilitate the catalytic activity. In addition, this allows for fine-tuning of the

ligand environment around the metal, which may turn out to be beneficial for the development of catalytic DODH reactions under mild reaction conditions. Initial studies revealed the ability of the Cp*-ligand[19] to stabilize the high valent Re(VII) oxo compound Cp*ReO₃ (**2**), which can undergo oxo-transfer reactions. Herrmann et al. have studied in detail the synthesis and reactivity of Cp*ReO₃, which resulted in a number of well-characterized Cp*-based oxo rhenium compounds.[23,53−55] In particular, these pioneering studies provided a stoichiometric reaction cycle for the deoxydehydration of vicinal diols: Cp*ReO₃ (**2**) can be reduced to the Re(V)oxo dimer **2A** and the reaction of glycol with either **2A** or Cp*ReOCl₂ produces Re(V)oxo(glycolato) **2B**. The retro-cyclization of **2B** to produce ethylene takes place at 150 °C under neat conditions or in refluxing toluene (Scheme 9).[56] Later, Gable

Scheme 9. Stoichiometric Reactions of Cp*ReO₃ Analogues
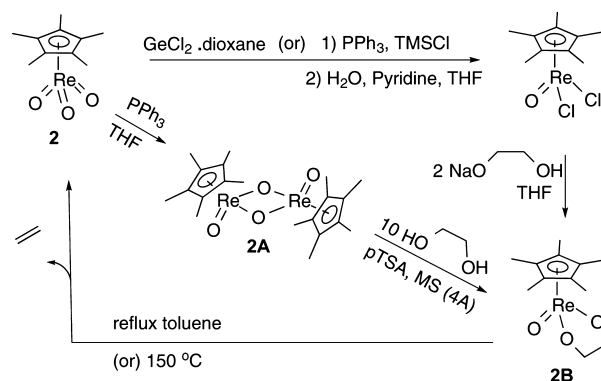
reported the one-pot synthesis of glycolate **2B** (and its derivatives) directly from Cp*ReO₃ and studied the thermochemistry of these complexes in detail both by experimental and computational methods.[57]

Inspired by the extensive work of Gable on reductive deoxygenation and retro-cyclization of **2B** to **2**, Andrews et al. developed a catalytic DODH reaction using **2** with triphenylphosphine as the stoichiometric reductant in 1996.[58] Initially, a turnover number (TON) of 55 per rhenium was demonstrated by using less than 2 mol % of **2** for the quantitative conversion of 1-phenyl-1,2-ethanediol to styrene in chlorobenzene at 90 °C (Scheme 10). Next to the conversion of the 1-phenyl-1,2-ethanediol substrate, the Cp*ReO₃/PPh₃ DODH system was the first ever reported Re catalyst to convert biomass-derived polyols to obtain the corresponding deoxygenated olefin products. Glycerol, a byproduct from biodiesel production,[52] gives 67% of allyl alcohol (TON = 67) with 100% selectivity in chlorobenzene at 125 °C with this

Scheme 10. Cp*ReO$_3$-Catalyzed DODH To Form Olefins by Using PPh$_3$ as Reductant
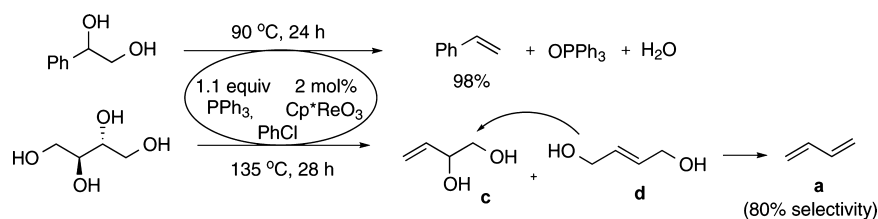
Scheme 11. (a) Proposed Cp*ReO$_3$-Catalyzed DODH Mechanism Using PPh$_3$; (b) Proposed Catalyst Decomposition Pathway
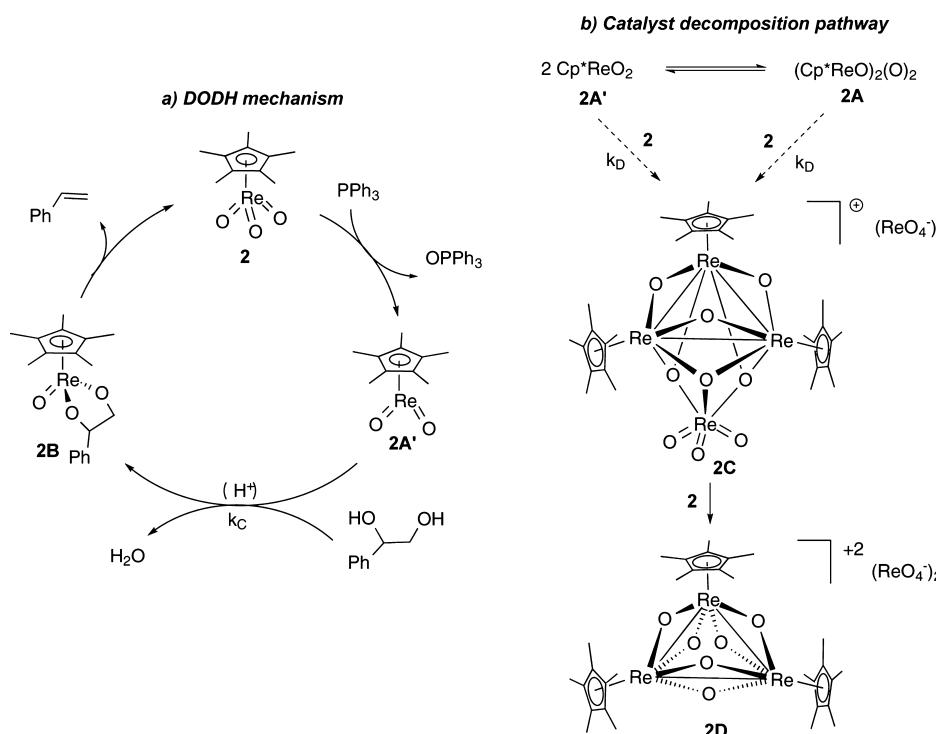
system under nonhomogeneous conditions, whereas the reaction in a homogeneous *N*-methylpyrrolidinone (NMP) solution results in only 28 TON. Also, erythritol is converted using PPh$_3$ (1.1 equiv) to 1,3-butadiene (**a**) (80% selectivity, TON = 25), an important monomer for the polymer industry, via the intermediate formation of 3-butene-1,2-diol (**c**) and *cis*-2-butene-1,4-diol (**d**). In control experiments, clean formation of butadiene was observed from **c**, whereas **d** is isomerized to **c** (in the first 2.5 h) first and then gives butadiene. These observations represent the first report of what was later coined as a 1,4-DODH via rhenium-mediated isomerization (vide infra).

The proposed mechanism involves the initial reduction of **2** to Cp*ReO$_2$ (**2A′**) by PPh$_3$, followed by diol condensation with **2A′** resulting in **2B**, which finally extrudes the olefin product to retrieve **2** in the catalytic cycle. Detailed kinetic studies of 1-phenyl-1,2-ethanediol conversion to styrene were carried out to probe the reaction mechanism (Scheme 11a). Polar solvents give low TONs, mainly due to catalyst decomposition to a purple compound that was initially thought to be an over-reduced Re(III) species but was later identified by Gable et al. as the mixed-valent monocationic tetranuclear cluster **2C**.[42] The formation of **2C** was shown to be faster in THF than in benzene by a factor 2. In addition, the relative rate of diol condensation (k_C) over **2C** formation (k_D) was found to be higher in benzene ($k_C/k_D \approx 60$ vs $k_C/k_D \approx 2$ in THF). On

the other hand, additives like *para*-toluenesulfonic acid (pTSA) in THF increase the yield of styrene (91%) by accelerating the condensation reaction (k_C). The overall reaction rate turned out being independent of the concentrations of 1-phenyl-1,2-ethanediol and PPh$_3$, with the extrusion of styrene from the glycolate intermediate **2B** being rate-limiting.

Later, some insight into catalyst decomposition pathways was gained by Gable et al., who established the identity of **2C**, which forms by the comproportionation of **2** and **2A**. In the presence of different oxygen transfer reagents (DMSO or **2**), compound **2C** can be oxidized to the green dicationic trinuclear cluster **2D**. Deposition of insoluble purple/green ionic clusters was seen as the cause of fast catalyst deactivation (Scheme 11b). Because catalyst decomposition is initiated by the dimerization equilibrium of LReO$_2$, alterations of the ligand on rhenium could lead to a shift in the equilibrium toward LReO$_2$ and consequently to an increase in catalytic performance.[59]

The range of Cp-based DODH catalysts was expanded by Klein Gebbink et al., who reported on the use of 1,2,4-tris(*tert*-butyl)cyclopentadienyl trioxo-rhenium (Cp^{ttt}ReO$_3$, **3**) for DODH reactions.[60] The Cp^{ttt}-ligand[19] is about as electron-donating as the Cp*-ligand,[61,62] but bulkier. This was anticipated to stabilize Re catalysts by avoiding degradation to multinuclear rhenium species. At 2 mol % loading, Cp^{ttt}ReO$_3$ converts 1,2-octanediol to 1-octene (95%) at 180 °C in

chlorobenzene within 12 h with PPh$_3$ as the reductant, with reactions carried out in closed reaction vessels (Scheme 12).

Scheme 12. Cp^{ttt}ReO$_3$ (3)-Catalyzed DODH of Vicinal Diols to Olefins
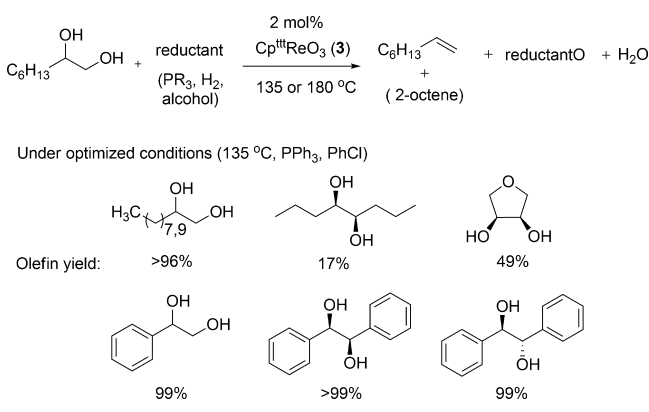
Lowering of the catalyst loading down to 0.05% in this case allows for TON per rhenium of 1400 to be reached in this reaction, which showed the improved stability and catalytic performance of Cp^{ttt}ReO$_3$. The reaction profile shows the clean formation of 1-octene with only small amounts of 2-octene isomers (6%, *trans/cis* = 1:1) being formed, which can be reduced to trace amounts (2% at 135 °C) or even fully eliminated at lower reaction temperatures. In contrast to the lower reactivity of **2** in THF solution, **3** gives full substrate conversion to 84% 1-octene in this solvent (with 7.6%, 2-octene isomers, *trans/cis* ≈ 1:2). An increased activity at higher reaction temperature (180 °C vs reflux temperature) was also observed with other phosphine reductants like PCy$_3$ (94%) and P(C$_6$F$_5$)$_3$ (47%). Additionally, the use of alternative reductants (3-pentanol or H$_2$) in combination with **3** gives moderate yields of octenes and octane, respectively. Na$_2$SO$_3$ hampers the catalytic activity to low yields of 1-octene (5%) in 24 h, whereas without the addition of any reductant 50% of 1-octene is obtained by the disproportionation of diol (Section 3.3.3A). These observations illustrate that the catalytic DODH reaction can be carried out with a number of different reductants, including the diol itself.

Studies of the scope of the reaction revealed that, under optimized conditions (2 mol % catalyst, 1.1 equiv PPh$_3$, 135 °C, PhCl), terminal aliphatic (C8, C10, C12) and aromatic (styrene) diols are cleanly converted by **3** to the corresponding olefins in excellent yields. Reactions take place with full retention of diol configuration: *cis*- or *trans*-stibene are selectively and quantitatively formed from (*R,S*)- or (*R,R*)-1,2-diphenyl-1,2-ethanediol, respectively. Aliphatic (4*S*,5*S*)-octane-4,5-diol and (3*S*,4*S*)-tetrahydrofuran-3,4-diol provide lower yields of olefin (17−49%). Preliminary results on the conversion of biomass-derived polyols showed the versatile use of **3** in DODH reactions. High yields of allyl alcohol (91%) can be obtained selectively from glycerol, whereas the heterogeneous reaction mixture of erythritol in chlorobenzene results in a mixture of butenediols and butadiene, with the latter being the major product. Homogeneous reaction mixtures in pyridine result in improved product yields at 60% erythritol conversion, 42% of products are obtained with 71% selectivity to 1,3-butadiene. Moreover, following the protocol by Toste et al.[63] (vide infra) using 3-octanol as the reductant at 170 °C yields

67% 1,3-butadiene with 7% 2,5-dihydrofuran (**b**) as a side product at full substrate conversion.

In line with the concept of increased steric requirements for the development of improved DODH catalysts, Gable has studied the hydridotris(3,5-dimethylpyrazolyl)borate complex Tp*ReO$_3$ (**4**). Tp* provides a very congested environment around the Re-trioxo moiety (cone angle of Tp* = 255°) and has electron-donating properties that are similar to Cp* (anionic 6e$^−$ donor).[64] Nevertheless, **4** in combination with PPh$_3$ needs 4 days to complete the conversion of 1-phenyl-1,2-ethanediol to styrene (5 mol % **4**, 1.1 equiv PPh$_3$ at 100 °C in toluene-d$_8$). In addition, the presence/formation of water slows down catalytic turnover due to the hydrolysis of Tp*Re(V)-diolate (**4B**). Based on detailed kinetic studies and theoretical calculations on **2B** and **4B**, Gable proposed the olefin extrusion step to proceed via a metallaoxetane intermediate. Moreover, the activation barrier for rate-limiting olefin extrusion was found to be slightly higher (2−4 kcal/mol) for the Tp* complex than for the Cp*-complex. (i.e., for ethylene extrusion $\Delta H^{\ddagger}$ = 28 and 32 kcal/mol for **2** and **4**, respectively).[65−67] The proposed three-step mechanism of DODH mediated by Tp*ReO$_3$/PPh$_3$ parallels that of the Cp*ReO$_3$/PPh$_3$ system.

Catalytic DODH of polyols to the corresponding olefins was also found to proceed with **4** albeit to a lesser extent than with the Cp-based systems. Using typical reaction conditions (5 mol % **4**, 1.1 equiv PPh$_3$ at 121 °C in toluene-d$_8$ for 24 h), 40% conversion of erythritol is achieved toward a mixture of butadiene (**a**), 3-butene-1,2-diol (**c**), and *cis*-2-butene-1,4-diol (**d**) in a ratio of **a**/**c**/**d** = 1.6/7.2/1, whereas threitol conversion proceeds to an even lower extent but without the formation of **d** (21%, **a**/**c**/**d** = 1/1.4/0). The anticipated high activation energy for extrusion of the *trans*-2,3-diolate or the isomerization of **d** to **c** seems to hamper further conversion under the reaction conditions.[68,69] It is noted that *cis*- and *trans*-butenediols (**c**, **d**) were formed as the side products in different (polar/apolar) solvents, whereas 2,5-dihydrofuran (**b**) only was formed as the side product in 3-octanol.

In summary, building on the pioneering work of Cook and Andrews[58] on DODH mediated by Cp*ReO$_3$, a small number of Cp- and Tp-based oxo-rhenium compounds have been shown to act as catalysts for this reaction. Trioxorhenium compounds supported by organic ligands[23,24] offer a unique opportunity for the systematic improvement of DODH catalysts by ligand design. Based on our current understanding of the reaction mechanism, a key aspect in further studies is the incorporation of steric protection to avoid Re cluster formation while maintaining—or, better, lowering—the activation barrier for the rate-limiting olefin extrusion.[59]

3.2. MTO-Catalyzed DODH. Next to Cp- and Tp-based catalysts, readily available compounds such as MTO and perrhenate are good candidates for the development of practical, scalable processes. Hence, there has recently been a surge of research on their application to DODH reaction. In particular, these simple catalysts have been used as benchmark systems to broaden the scope of the reaction in terms of the stoichiometric reductant, moving from triphenylphosphine to more available and environmentally benign compounds. The following section covers recent developments in this area.

3.2.1. MTO/H$_2$ System. The first report on the use of MTO for catalytic DODH reactions focuses on the use of molecular hydrogen as the reducing agent, which at forehand seems the most practical and cheap reductant for these reactions. In this report, Abu-Omar et al. studied the transformation of epoxides

and diols to olefins using 5−10 mol % MTO as the catalyst under medium hydrogen pressures (5−20 bar).[70] Under these reaction conditions, *cis*-1,2-cyclohexanediol is converted to cyclohexene in 60% yield and a small amount of fully reduced cyclohexane (3%), with the remaining substrate being a mixture of 1,2-cyclohexanediols (*trans/cis* = 4). *Trans*-cyclohexanediol, on the other hand, was found not to be reactive at all. For erythritol, charring occurs under these reaction conditions. Anhydroerythritol, the dehydrative cyclization product of erythritol, provides some 2,5-dihydrofuran (25%) with a small amount of THF (5%) at 34 bar H_2 in dioxane. In addition, epoxides are conveniently deoxygenated to high yields of olefins by the MTO/H_2 system. In THF, 1-hexane oxide can be deoxygenated to 1-hexene (95%) at 5.5 bar H_2 pressure within 8 h. At an increased H_2 pressure of 21 bar, *n*-hexane (96%) is obtained in 8 h, whereas a mixture of 1-hexene (76%) and hexane (18%) is obtained after 4 h of reaction time. These observations clearly demonstrate that MTO in combination with H_2 gives access to an effective DODH catalyst as well as to an effective, albeit slow hydrogenation catalyst.

The reaction profile for the deoxygenation of styrene oxide was studied in detail: it initially shows the formation of 1-phenyl-1,2-ethanediol (due to the presence of water) in addition to styrene. Close to depletion of styrene oxide (at 80% conversion in 3 h), the formed 1-phenyl-1,2-ethanediol also starts to transform to styrene (80% in 5 h), which is completely reduced to ethylbenzene at an extended reaction time of 16 h (Scheme 13, Figure 1).

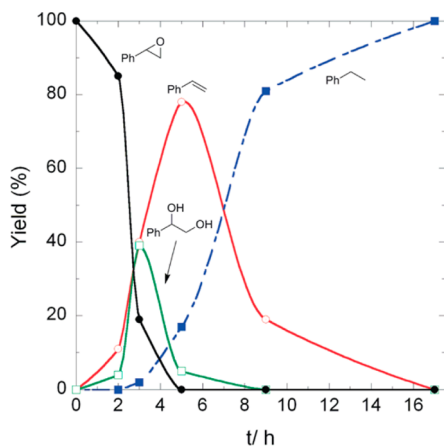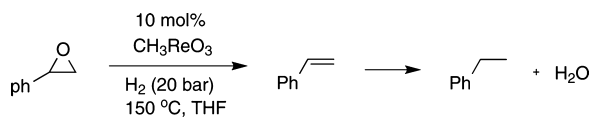**Scheme 13. MTO/H_2 System for Deoxygenation of Styrene Oxide**

Figure 1. Reaction profile of MTO-catalyzed styrene oxide deoxygenation under hydrogen pressure (20 bar) at 150 °C in THF (picture adapted from ref 70).

The reaction mechanism was proposed to involve the initial reduction of MTO to MDO by hydrogen, followed by coordination of the epoxide or diol substrate to form a Re(V)diolate (**1C**), which converts in the same epoxide adduct **1B**, and final extrusion of the olefin product via the metallaoxetane intermediate (**1B′**) (Scheme 14).

Scheme 14. Postulated Mechanism for MTO Reduction by H_2

L_n = solvent molecule
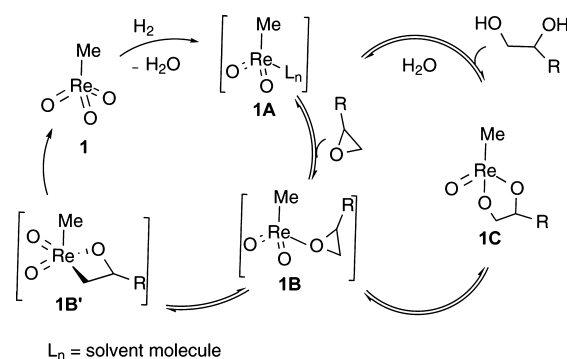
Later, Bi et al.[71] evaluated this proposed reaction pathway by means of DFT calculations. According to these calculations, addition of hydrogen to MTO happens via a [2 + 3] rather than a [2 + 2] cycloaddition pathway (i.e., H−H + O=Re=O). However, the direct addition of H_2 to MTO is endothermic ($\Delta H^{\ddagger}$ = 43.5 kcal/mol), and also the addition of H_2 to epoxide- or THF-coordinated MTO through a [2 + 3] cycloaddition is found to be unfavorable ($\Delta H^{\ddagger}$ = 41−42 kcal/mol). Therefore, the pathway via the reduction of MTO by H_2 as proposed by Abu-Omar was ruled out on the basis of these calculations. Instead, the reduction step was proposed to be the formation of the Re(V)(OH)(alkoxo) species **1E** by reaction of dihydrogen with Re(VII)diolate **1D**. The latter can be formed either by a [2σ−2π] cycloaddition of an MTO-coordinated epoxide or by reaction of 1-phenylethane-1,2-diol with MTO. H_2 addition to **1D** then happens via a [2 + 3] cycloaddition pathway to obtain **1E**, which is stabilized by a dative bond of the β-hydroxyl group of the alkoxo fragment. Subsequent proton transfer takes place from this axial β-hydroxyl group to the equatorial hydroxo ligand. Release of the olefin product via a concerted elimination pathway from the resulting Re(V)diolate(aquo) adduct **1F** is favored over elimination from the corresponding water free Re(V)diolate (**1C**) species (Scheme 15).

The experimentally observed formation of diol from the epoxide substrate and its subsequent transformation are explained by a fast equilibrium between Re(VII)diolate **1D** and the diol in the presence of water. Because addition of H_2 to **1D** is slow, the competitive reaction with water cleaves the five-

**Scheme 15. DFT-Calculated Mechanism of MTO-Catalyzed Deoxygenation of Epoxide Using H_2 as the Reductant**
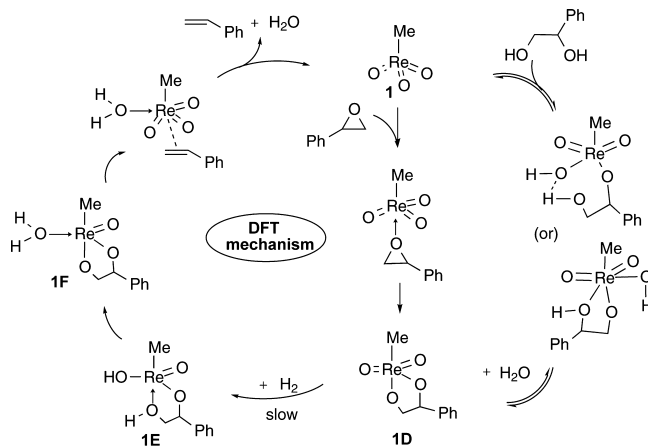
membered diolate ring in **1D** to form MTO and the diol (Scheme 15).

3.2.2. ZReO$_{3,4}$/Sulfite DODH System. Inorganic sulfites and bisulfites are relatively cheap and accessible, easy to store and use, and the inorganic sulfate byproduct by means of easy separation makes a sulfite-driven catalytic DODH system attractive. The group of Nicholas reported detailed investigations on the use of sulfites as the reductant for DODH reactions catalyzed by MTO and perrhenates (ZReO$_4$).[72,73] Reactions carried out in benzene at 150 °C take relatively long (4 h to 4 days) to completely convert diol substrates, and yields for the corresponding olefins are moderate with minor quantities of etheric dehydration products. Even though sulfites are soluble only in polar and hydroxyl solvents, the use of such solvents results in as little as 10−15% or no substrate conversion, which was attributed to the inhibition of MTO by solvent coordination. The conversion of 1-phenyl-1,2-ethanediol to styrene (23−71%) was optimized in benzene (0.2 M substrate) with different oxo-rhenium catalysts (8−10 mol % of MTO, NaReO$_4$, NH$_4$ReO$_4$, Bu$_4$NReO$_4$, or Re$_2$O$_7$) in combination with 1.5 equiv of Na$_2$SO$_3$ at 150 °C. MTO and Bu$_4$NReO$_4$ give the best catalytic performances among these catalysts and further studies on the conversion of aliphatic diols (1,2-octanediol, 1,2-decanediol, and 1,2-dodecanediol) were, accordingly, carried out with these two catalysts. Aliphatic diols were found to be less reactive compared to 1-phenyl-1,2-ethanediol, requiring longer reaction times with moderate product yields (e.g., 1,2-octanediol needs 7 days to obtain 38% 1-octene at 95% conversion). Though there were no significant improvements in product yields, addition of 15-crown-5 in benzene lowered the reaction time considerably (from 40 to 21 h for 1,2-octanediol conversion). Both MTO and Bu$_4$NReO$_4$ provide high olefin yields (60−89%) for aliphatic diols in the benzene/15-crown-5 system at 150 °C in 45−110 h. Due to the Lewis acidic nature of MTO, different pyridine-based *N*-donors retard the catalytic reactions (similarly to what is observed for Re-catalyzed dehydration reactions) by the known pathway of adduct formation.[74,75] *Cis*-cyclohexanediol is converted into cyclohexene in modest yields (18 and 25% for MTO and Bu$_4$NReO$_4$, respectively), whereas the *trans*-isomer does not react as earlier noted for MTO/H$_2$. Nonetheless, a considerable amount of *cis*- to *trans*-diol isomerization was observed under the reaction conditions. In case of the acyclic substrate (+)-diethyl L-tartrate, retention of configuration to form the *trans*-product diethyl fumarate was observed at a moderate yield (35%).

Treatment of erythritol results in butadiene (**a**) as the major product, together with the minor products 2,5-dihydrofuran (**b**) and 2-butene-1,4-diol (**d**). In this case product yields are higher for Bu$_4$NReO$_4$ (**a**/**b**/**d** = 27/6/5) than for MTO (**a**/**b**/**d** = 14/2/5). The product selectivity was explained by the fast initial formation of 3-butene-1,2-diol (**c**) followed by subsequent butadiene formation. On the other hand, initial DODH of the internal vicinal diol to produce 2-butene-1,4-diol (**d**) seems to proceed slowly, which explains the small amounts of 2,5-dihydrofuran (**b**) side product by dehydrative cyclization (Scheme 16). The isomerization of **d** to **c** that occurs in the Cp*ReO$_3$/PPh$_3$ system is not observed with MTO or Bu$_4$NReO$_4$ in combination with Na$_2$SO$_3$.

Treatment of glycerol with Na$_2$SO$_3$ and 10% NaReO$_4$ at 150−160 °C in a distillation setup forms 15% allyl alcohol together with a dark viscous residue. But, under neat conditions

Scheme 16. Schematic Representation of Erythritol Reactivity for Sulfite-Driven DODH
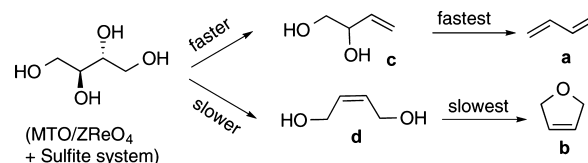

(no solvent) in a closed reaction tube, 60% 1-octene can be obtained from 1,2-octanediol within 20 h.

From the outcome of all these studies, the effect of the cations associated with perrhenates (Z$^+$ReO$_4^-$) on catalysis is not clearly understood. The reactivity in epoxide deoxygenations with Na$_2$SO$_3$ as the reductant illustrates this notion best. In the deoxygenation of styrene oxide and cyclohexane oxide (at 150 °C in benzene), NH$_4$ReO$_4$ gives low olefin yields, 20% and 15%, respectively, whereas NaReO$_4$ is not at all active in these reactions.

The mechanism of the MTO/Na$_2$SO$_3$-catalyzed DODH was initially proposed to involve a pivotal Re(V)diolate intermediate (**1C**), which can be either formed via initial glycol condensation with MTO followed by reduction of the resulting Re(VII)diolate (**1D**) with sulfite or vice versa via reduction followed by condensation. Room-temperature equilibrium formation of **1D** was earlier known to occur by diol condensation with MTO. In their mechanistic study, Nicholas and co-workers investigated the MTO/sulfite system by means of in situ ^{1}H NMR spectroscopy, using the more soluble (Bu$_4$N)$_2$SO$_3$ as the reductant. **1D** reacts readily at RT with PPh$_3$ (<10 min) but slowly with (Bu$_4$N)$_2$SO$_3$ (24 h) to produce a reduced Re(V)diolate **1C** in an oligomerization equilibrium with the dimer **1C′** and/or its isomers. Thermolysis of this mixture at 60−100 °C releases styrene in the proposed rate-limiting reaction (Scheme 17).

Scheme 17. Proposed Mechanism for MTO/Sulfite DODH System
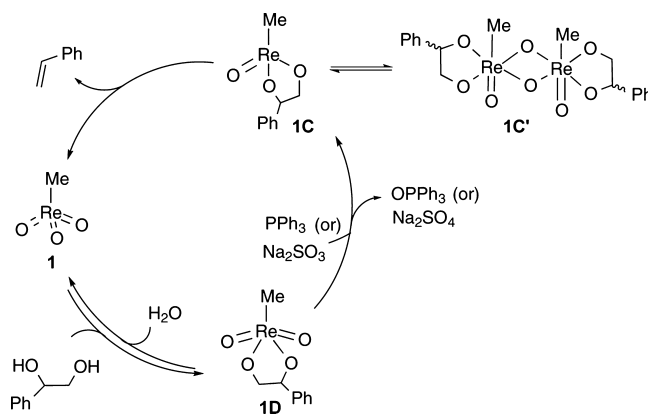
Another recent report from the same group uses DFT calculations to further investigate the reaction pathways of DODH mediated by the MTO/Na$_2$SO$_3$ system,[76] identifying a lower energy pathway in which a rhenium sulfate complex is the active species: attack of sulfite (NaSO$_3^-$) at a Re═O bond of MTO forms MeRe(V)O$_2$(OSO$_3$Na)$^-$ (**1G**) as the first step of the reaction. The Re−O−SO$_3$ bond stays intact throughout the calculated DODH cycle. Accordingly, these studies predict initial monosulfite coordination to MTO, followed by glycol

Scheme 18. DFT-Calculated DODH Pathways for MTO/Na₂SO₃ System (Adapted from Ref 76)
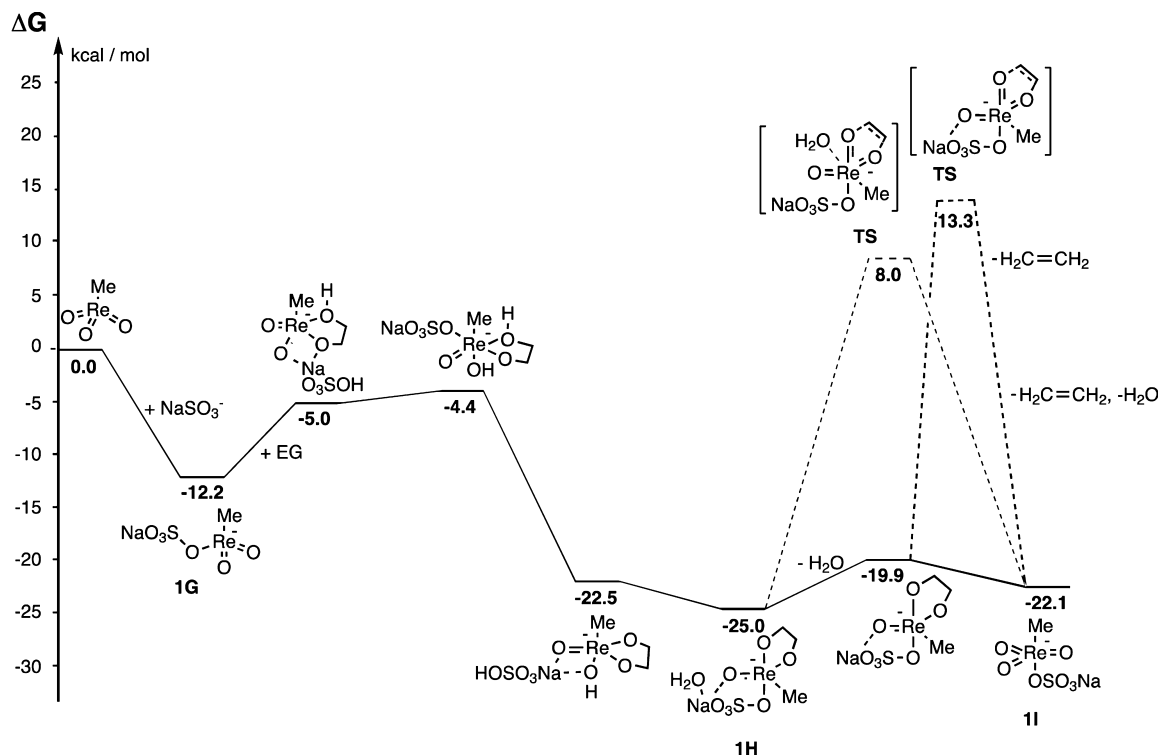
condensation to form Re(V)diolate(OSO₃Na)(H₂O)⁻ (**1H**) and subsequent fragmentation of **1H** to release the olefin product and MTO(OSO₃Na) ⁻ (**1I**). The olefin extrusion step in this sequence is rate-limiting ($\Delta G^{\ddagger}$ = 33 kcal/mol). Finally, NaSO₄⁻ is released from **1I** to regenerate MTO (Scheme 18).

3.2.3. Alcohol Reductants in Re-Catalyzed DODH. The use of alcohols as reductant has been studied in detail by a number of different research teams. Starting from the diol disproportionation reaction, followed by DODH with alcohol as external reductant, the corresponding mechanistic proposals are critically reviewed in the following sections.

3.2.3A. Disproportionation Reactions. In 2010, Bergman and Ellman reported on the use of low-valent rhenium carbonyl compounds (Re₂(CO)₁₀, BrRe(CO)₅) to obtain olefins without an external reductant from a variety of vicinal diols.[77] This phenomenon can be explained by disproportionation reactions in which the diol is both the oxidant and the reductant. Oxidation of the diol by two or four electrons would result in the respective formation of either hydroxyketone or diketone byproducts associated with maximum olefin yields of 50% or 67%, respectively (Scheme 19). Arguably, depending on the reactivity of the formed hydroxyketone, further consecutive hydrogen transfer can take place from the former or the latter. These reactive ketone products are generally difficult to
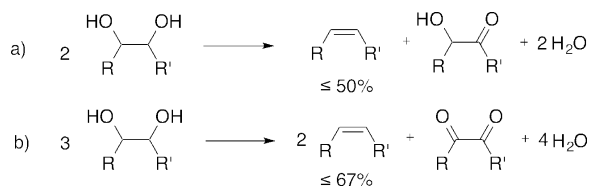
quantify due to further uncontrolled reactions like aldol condensation and oligomerization/polymerization under the reaction conditions. Therefore, the chemoselectivity for the overall yield (ranging 50−67%) is rather difficult to estimate. In most of the cases, the olefin yield is less than 50%, which suggests that the diol is a more efficient reductant than the hydroxyketone.

The conversion of 4,5-octanediol to 4-octene (50%) and 1,2-tetradecanediol to 1-tetradecene (48−52%) were obtained in the presence of Re₂(CO)₁₀ (2.5 mol %) at 180 °C under air in 3.5 h. The formation of diketone compounds was evidenced by NMR and GC−MS, but these products could not be quantified because of further decomposition. Other observations include that the reaction proceeds above 170 °C in an air atmosphere in the presence of Re₂(CO)₁₀ (2.5 mol %), whereas the reaction does not work under air-free (N₂ atm) conditions. This observation parallels a similar observation on the role of oxygen on rhenium-catalyzed dehydration reactions (section 2).[47]

In 2011, Fernandes et al. observed the formation of styrene from 1-phenyl-1,2-ethanediol in moderate yields using oxo-rhenium catalysts (ReIO₂(PPh₃)₂, ReOCl₃(PPh₃)₂, and Re₂O₇) as part of their study on Re-catalyzed epoxide deoxygenation.[40] Using 10 mol % of catalyst, different aryl-substituted epoxides were deoxygenated (refluxing in toluene under air for 15 min−2 h) to olefins (30−78%) without adding any external reductants. Access to internal reductants is brought about by ring opening of styrene oxide to 1-phenyl-1,2-ethanediol during the course of reaction, as was also observed for the MTO/H₂ system (vide supra).

Following the initial observations on the disproportionation of diols by Bergman and Ellman, Abu-Omar et al. have employed 2 mol % MTO to convert *cis*-cyclohexanediol to cyclohexene (61%) and the corresponding oxidized diketone products (Scheme 20b.) With MTO (2 mol %) as the catalyst,

Scheme 19. Possible Disproportionation Reactions of Diols to Olefins

Scheme 20. Catalytic Disproportionation of Vicinal Diols to Olefins
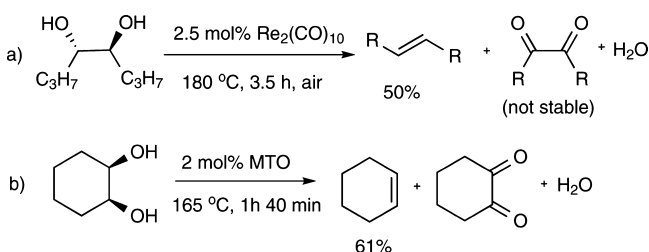
disproportionation of glycerol to allyl alcohol was also accomplished through reactive distillation. Dihydroxy acetone, the initial oxidation product, is quite reactive and was found to transform into polymeric products under the reaction conditions, which made the quantification of primary oxidation products impossible. The volatile products correspond to an overall yield of 37% of olefinic products and the ratio for allyl alcohol/propanal/acrolein = 1:0.22:0.15 (Scheme 21). Interestingly, NH_4ReO_4 (5 mol %) gives a comparable product yield (40%), while other perrhenate catalysts $NaReO_4$ and $KReO_4$ result in very low yields under the reaction conditions. Addition of an equimolar amount of NH_4Cl or HCl to $NaReO_4$ increases the overall yield in volatile products to 46−48%. No significant effects of additives on reactions carried out with MTO were observed, while the addition of NaCl or KCl to NH_4ReO_4 reduces the catalyst's productivity or does not affect it, respectively.

Later d'Alessandro et al. expanded the scope of glycerol conversion under a flow of bubbling N_2, air, or H_2 to collect the volatile products in an ice-cooled water trap.[78] Disproportionation of neat glycerol at 140 °C (8−16 h) under H_2 bubbling results in a maximum yield of allyl alcohol of 34% and 32%, when 2 mol % of ReO_3 or MTO are employed as the catalyst, respectively. At higher temperature (170 °C), the selectivity of allyl alcohol (ReO_3 (30%) and MTO (25%)) goes down due to minor amounts of acrolein, diallyl ether, and allyl formate side product formation. Other catalysts such as NH_4ReO_4 and $Cp*ReO_3$ give traces of allyl alcohol at 140 °C and 5−21% at 170 °C. In all cases, air/N_2 bubbling results in a lower selectivity to allyl alcohol than H_2 bubbling. The addition of alcohol as reductant/solvent significantly improves the yield for 2,5-dimethyl-3-pentanol (ReO_3, MTO = 91, 87%) and 1-hexanol (ReO_3, MTO = 70, 22%) at 140 °C under H_2 bubbling, whereas relatively low yields are obtained under air bubbling (2,5-dimethyl-3-pentanol: ReO_3, MTO = 64, 61%; 1-hexanol: ReO_3, MTO = 20, 28%). Other tested solvents with MTO at 170 °C result in significant amounts of acrolein product in addition to allyl alcohol; allyl alcohol/acrolein (yield

%) = 25/7 (2-octanol), 31/26 (1,3-propanediol), and 7/7 (sulpholane). Because complete demethylation of MTO was observed in NMR during the induction period (<1 h), the polymeric rhenium oxide (ReO_3) or poly-MTO[19] are suggested to be involved in catalysis. The overall combined observations that diols may serve as their own reductant in what is a formal disproportionation reaction and that higher boiling secondary alcohols can be used as sacrificial reductants in Re-catalyzed DODH reactions have spurred the interest in the further development of this catalytic chemistry for the DODH of diols and of bioderived polyols.

3.2.3B. Catalytic DODH with MTO/Alcohol Systems. During the investigation of the $Re_2(CO)_{10}$-catalyzed disproportionation of diols (vide supra),[77] Bergman and Ellman have found that adding an excess (9−13 equiv) of a higher chain secondary alcohol (e.g., 3-octanol, 2-octanol, or 3-nonanol) as an external reductant enhances the overall reactivity to obtain excellent olefin yields (>80%) within 4 h. The presence of a Brønsted acid (pTSA or H_2SO_4) in combination with 3-octanol allows for the reaction to proceed at a lower temperature (~155 °C), lower catalyst loading (1%), and shorter reaction times (1.5 h). These reactions were postulated to proceed via air oxidation of the starting rhenium carbonyls to rhenium oxo compounds, among which may in fact be the real catalyst for the reactions. Once again, olefin formation is observed for the *cis*-isomer of 1,2-cyclohexanediol (72%), while the *trans*-isomer stays untouched with $BrRe(CO)_5$/3-octanol at 170 °C. Applying $Re_2(CO)_{10}$/3-octanol/pTSA (12 h at 160 °C) to erythritol results in 62% of 2,5-dihydrofuran (**b**) but no butadiene (Scheme 22). The reaction pathway is assumed to

Scheme 22. Conversion of Erythritol to 2,5-Dihydrofuran Using $Re_2(CO)_{10}$/3-Octanol
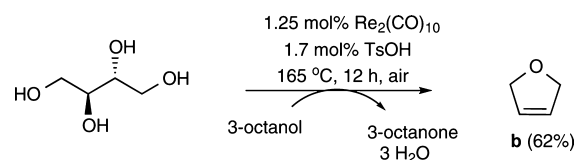

involve the initial acid-catalyzed cyclodehydration of erythritol to 1,4-anhydroerythritol, followed by DODH to form **b**. The significant enhancement in catalytic performance by the addition of acid is proposed to originate from facilitated olefin extrusion through protonation of the rhenium diolate intermediate. Also, Nicholas et al. tested Bu_4NReO_4 (10 mol % at 150 °C in benzene) with alcohols as reductant for the conversion of 1-phenyl-1,2-ethanediol to styrene.[73] The use of 2,4-dimethyl-3-pentanol results in 55% styrene in 4 h, whereas

Scheme 21. MTO-Catalyzed Disproportionation of Glycerol to Volatile Products
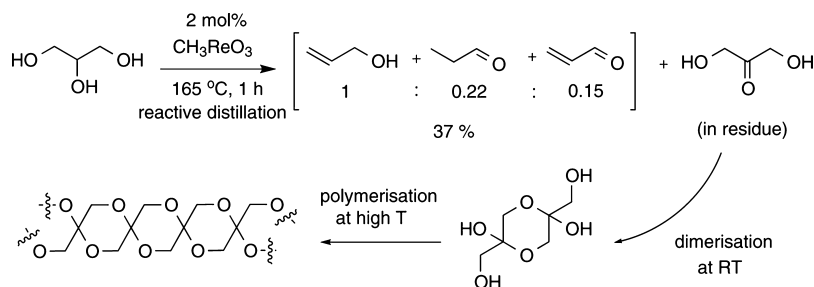
n-butanol does not result in any product formation at all even after 22 h.

In 2012, Toste and co-workers reported on the use of MTO in a number of different DODH reactions in which an excess (10 equiv) of a secondary alcohol is used as the reductant as well as solvent, with reactions being carried out in a closed vessel at temperatures above 170 °C.[63] 3-Octanol or 3-pentanol were found to be the best reductants among a series of tested alcohols for anhydroerythritol conversion to 2,5-dihydrofuran (**b**). In addition to the expected 3-octanone/3-pentanone resulting from oxidative dehydrogenation, octene/pentene isomers are formed next to the desired DODH product as the result of dehydration reactions. With this system, a series of different sugar-derived polyols can be converted to the corresponding olefins and polyenes (Scheme 23). Glycerol is

Scheme 23. MTO-Catalyzed DODH of Biomass-Derived Polyols to Olefins using *sec*-Alcohols as Reductants
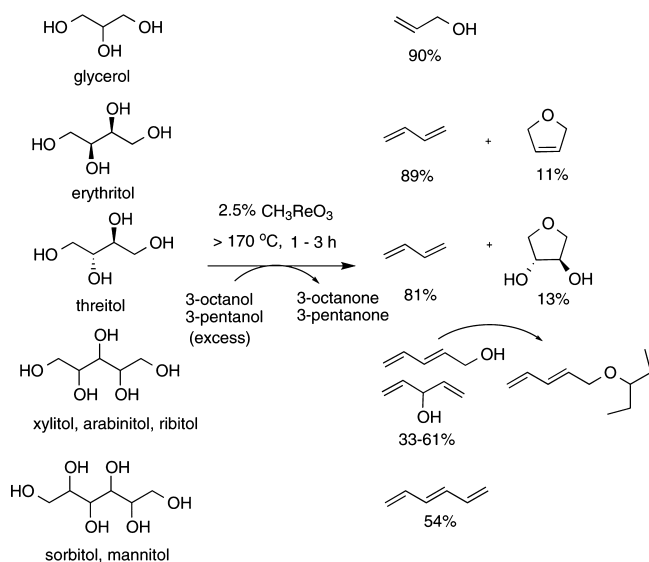

selectively converted to allyl alcohol (90%) with the MTO/3-octanol system, and 1,3-butadiene was obtained from the corresponding tetritol. Both C$_4$-polyol isomers can be used to obtain butadiene in excellent yields, i.e., 89 and 81% butadiene yield is obtained at full conversion from erythritol and threitol, respectively. Next to butadiene, 11% of 2,5-dihydrofuran (**b**) is formed from erythritol, which is the result of a sequential DODH to form 2-butene-1,4-diol (**d**) followed by dehydration or vice versa (vide infra). On the other hand, the dehydrated product from threitol, anhydrothreitol, is formed as a reaction product in 13% yield, because the *trans*-orientation of the hydroxyl groups in cyclic anhydroerythritol prevents facile extrusion of an olefin product from the corresponding rhenium-diolate intermediate (vide infra).[68]

In a similar way, at a six times lower concentration of polyol in 3-pentanol (0.05 M instead of 0.3 M) different isomers of C$_5$-polyols (xylitol (61%), D-arabinitol (43%) and ribitol (33%)) can be converted with the MTO/3-pentanol system into pentadienol isomers, which are transformed to etheric compounds by reaction with the excess of alcohol reductant. (*E*)-1,3,5-Hexatriene, an interesting polymer precursor,[79] can be obtained in 54% yield as the only observed product from both D-conformers of C$_6$-polyols (D-sorbitol and D-mannitol).

Nearly at the same time, independent work from the group of Abu-Omar also demonstrated the use of MTO (2 mol %) in combination with a slight excess of 3-octanol (1.5 equiv) for the conversion of glycerol into volatile products (52%), mainly resulting in allyl alcohol, and minor amounts of acrolein and propanal (observed relative ratio 1:0.07:0.02).[80] In this case, reactions were performed at 165 °C in a distillation setup, and all volatile products were collected within 1 h. This study also showed that other alcohols such as 1-heptanol, 1-cyclohexanol, 1,3- and 1,2-propanediol can be utilized as the sacrificial reductant. Under the same reaction conditions with 3-octanol as reductant, NH$_4$ReO$_4$ (5 mol %) was also found to be a good catalyst to obtain 74% of C$_3$-volatile products from glycerol in a ratio of 1:0.02:0.01 (allyl alcohol/acrolein/propanal). On the other hand, the conversion of erythritol via reactive distillation in combination with a primary alcohol (1-heptanol) as the reductant does not result in butadiene formation, but instead mainly produces 2,5-dihydrofuran (**b**) and a minor amount of crotonaldehyde (**e**) (58%, **b:e** = 1:0.28). Reacting threitol under these conditions only results in 7% of crotonaldehyde (Scheme 24).

Scheme 24. MTO-Catalyzed Erythritol Conversion Using 1-Heptanol by Reactive Distillation
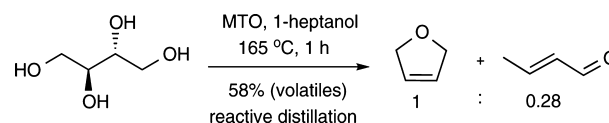
Toste et al. have applied the above-mentioned MTO/*sec*-alcohol DODH system to a number of other bioderived substrates, thereby showing the synthetic potential of this catalytic system. Reaction of the cyclic C$_6$-polyol inositol results in a mixture of benzene and phenol through three consecutive DODH reactions, and two consecutive DODH reactions and one dehydration reaction, respectively (Scheme 25).[63] Different

Scheme 25. MTO-Catalyzed DODH To Produce Aromatics and Furans from Inositol and Sugars
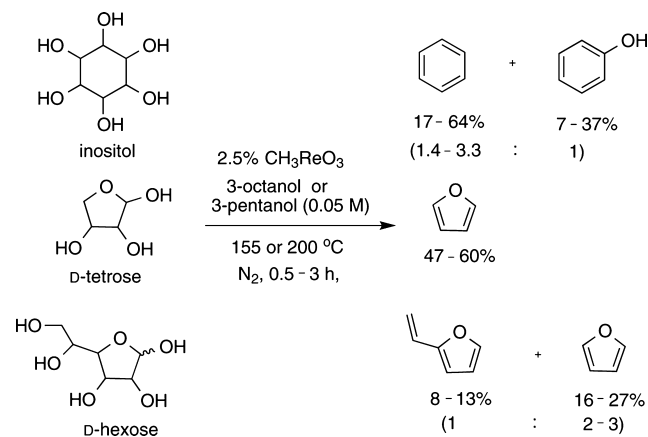
isomers of inositol give moderate to excellent overall yields (24−96%) of a mixture of benzene (17−64%) and phenol (7−32%) after 30 min at 200 °C. The ratio of benzene to phenol varies from 1.4 to 3.3 depending on the isomer of inositol used in this reaction.

Sugars are another interesting substrate class because these constitute a major part of biomass feedstocks and can be

obtained rather straightforwardly. D-configured tetrose and hexose can be completely deoxygenated with the MTO/*sec*-alcohol system to obtain furan derivatives, again through a combination of DODH and dehydration reaction steps. D-Erythrose and D-threose provide 60 and 47% of the corresponding furan, whereas different isomers of D-hexose give a mixture of furan (16−27%) and vinyl furan (8−13%). Although the vinyl furan is the anticipated product in these reactions, retro-aldol pathways can lead to a furan compound (Scheme 25).

In general, DODH reactions require a 1,2-configured diol moiety to take place. Moreover, the specific stereoconfiguration is crucial in cyclic vicinal diols as shown by several examples of difference in reactivity of the *cis*- and *trans*-1,2-cyclohexanediol isomers. As shown for the conversion of erythritol to 1,3-butadiene, 2-butene-1,4-diol (**d**) is formed as one of the intermediate products. This 1,4-diol may undergo a dehydrative cyclization reaction to form 2,5-dihydrofuran (**b**), which is a typical side product for many catalytic DODH systems. Nonetheless, reaction profile analysis for a number of catalysts has shown that the 1,4-diol is not *per se* a dead-end of the reaction sequence and may be taken further to form the desired diene.

Though Cp*ReO$_3$-catalyzed isomerization of 2-butene-1,4-diol (**d**) to 3-butene-1,2-diol (**c**) was earlier observed under DODH reaction conditions,[58] a recent study from the Toste group has addressed this issue further through an investigation of so-called 1,4-DODH and 1,6-DODH reactions (Scheme 26).[69] MTO and other oxo-rhenium catalysts are known to

Scheme 26. MTO-Catalyzed [1,4]- and [1,6]-DODH To Produce Olefins
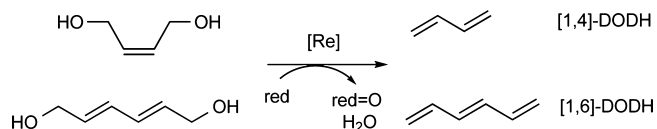
catalyze the [1,3]−OH shift of allylic alcohols,[81−85] which makes this rhenium-mediated isomerization reaction in tandem with DODH reactions a powerful synthetic tool for biomass valorization. Both *cis*- and *trans*-2-butene-1,4-diol give 1,3-butadiene (70%) as the main product within 30 min at 170 °C, using 2.5 mol % MTO in 3-pentanol. Similar reactivity is observed for substituted and cyclic 1,4-diols, as well as for *cis,cis*-muconic alcohol which afforded (*E*)-1,3,5-hexatriene (1,6-DODH). Under similar reaction conditions, (*Z*)-4-methoxy-2-butene-1-ol does not give butadiene, which shows the requirement of two OH groups.

A plausible mechanism for the rhenium-mediated [1,3]−OH shift of allylic alcohols includes the coordination of the alcohol to MTO to form alkoxy(hydroxy)rhenium species via proton transfer to a Re-oxo fragment, followed by concerted proton exchange, as shown in Scheme 27 for 2-butene-1,4-diol. All steps involved in this isomerization reaction are considered to be in equilibrium.

In the same report, Toste et al. elaborated on the use of DODH reactions to synthesize interesting chemical scaffolds/building blocks starting from biomass-derived polyol compounds. As an example, mucic acid was used to produce muconic acid, which is a widely used precursor for adipic acid and other industrially important products like terephthalic acid and 1,6-hexanediol. Muconic acid can be obtained in 43% yield

Scheme 27. MTO-Mediated Isomerization of Butenediols
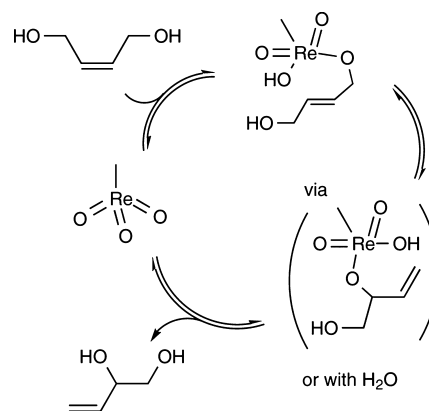

with a small amount of diester side product (14%) using the MTO/3-pentanol system. Alternatively, the use of perrhenic acid in combination with *n*-butanol enables both DODH and esterification reactions to obtain dibutyl muconate (62%), which can be further hydrogenated using Pd/C to obtain dibutyl adipate in a simple one-pot two-step procedure (Scheme 28). Another recent report by the group of Su and Zhang expands this reaction further to obtain nearly quantitative yields (99%) of adipic acid esters (mixture of monoester and diester) by using 5 mol % MTO/3-pentanol at lower reaction temperatures (120 °C).[86] Mucic acid is first converted to the monoester followed by the diester in 24 h, resulting in 99% yield for this mixture of ester compounds. It is a very selective, yet slower reaction than at 180 °C (67% in 20 h for MTO/3-octanol) under flowing N$_2$, whereas faster rates occur with air flow (96% in 24 h) and much faster reaction rates by using a water separator reaction set up (99% in 8 h). Following the reaction profile starting from diethylmucate with 3-pentanol provided evidence that ester group exchange occurs before the DODH reaction sequence proceeds.

The use of an alcohol as both solvent and sacrificial reductant facilitates DODH reactions in a number of ways (i.e., higher solubility of polyols at high temperature, assisting the initial reduction of precatalyst). In addition to the advantageous solubility of polyol substrates in alcohols, the ketones that are formed in the dehydrogenative oxidation may be reduced back to the alcohols stage (e.g., via hydrogenation with H$_2$) in order to recycle the reductant. In such cases, a proper separation protocol of ketone compounds is essential. In this respect, Nicholas et al. reported on the use of benzyl alcohol as the stoichiometric reductant for DODH reactions in combination with NH$_4$ReO$_4$ (2.5−10 mol %) as the catalyst.[96] Reactions were carried out in different aromatic solvents to evaluate a number of substituted benzyl alcohol as reductants, which showed that neutral to moderately electron-rich benzyl alcohols seem best suited for this purpose. The combination of NH$_4$ReO$_4$ and benzyl alcohol was shown to give consistent product yield for diethyl fumarate (80−85%) from (+)-diethyl tartrate, for six recycling experiments (after an initial drop of 15%), by following a so-called "react−cool−recharge" procedure in a batch reaction (i.e., quantitatively precipitated NH$_4$ReO$_4$ at RT is charged again) (Scheme 29).

The product separation is demonstrated conveniently by using NaHSO$_3$ that forms an adduct with benzaldehyde (oxidized product of reductant), which is followed by filtration and solvent evaporation resulting the olefin product. Treating

Scheme 28. DODH of Mucic Acid to Muconic Acid and Adipic Acid Esters
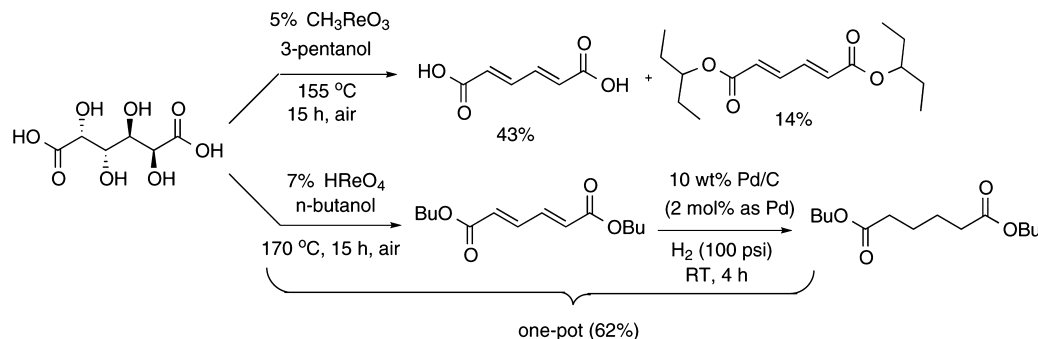
**Scheme 29. NH4ReO4/Benzyl-Alcohol-Catalyzed DODH of (+)-Diethyl L-Tartrate to Diethyl Fumarate**
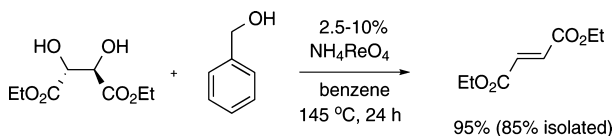
the benzaldehyde adduct with NaHCO3 in ethyl acetate then releases benzaldehyde (Scheme 30).

Srivastava et al. reported a similar DODH reaction by using 10% MTO with 5-nonanol (<2 equiv) as reductant in benzene solvent at 90 °C in 24 h.[97] 1-Phenyl-1,2-ethanediol (97%) and styrene oxide (99%) are conveniently transformed to styrene, whereas aliphatic diols and epoxide give low to moderate olefin yields even at high temperature (140−150 °C): 1,2-hexanediol (10%), cis-cyclohexanediol (15%), 1,2-tetradecaenediol (50%), 1-hexaneoxide (17%), and cyclohexaneoxide (54%).

3.2.3C. Mechanism of DODH in the MTO/Alcohol System. The interest in oxo-rhenium-catalyzed DODH (and transfer hydrogenation) reactions with alcohols as the sacrificial reductant has led to a number of experimental and computational studies on the mechanism of these reactions. These studies outline a number of possible reaction pathways, various high-valent rhenium intermediates that are likely to play an active role, and different overall energy barriers for the DODH reaction. The DODH reaction sequence is generally thought to follow the steps proposed by Andrews for the Cp*ReO3-catalyzed reactions with phosphine reductants and involves: (a) reductive deoxygenation of the starting Re-trioxo species to a Re(V)dioxo intermediate, (b) diol condensation to form a

Re(V)diolate with release of water, and (c) oxidative extrusion of the olefin product from the Re(V)diolate intermediate with formation of the Re-trioxo species to complete the catalytic cycle. In the mechanism proposed by Toste et al. for the MTO/sec-alcohol system, the alcohol would reduce MTO to MDO, which was confirmed by trapping MDO by an alkyne to result in a stable MDO-alkyne species (Scheme 31). The energy barrier of this activation step seems high, as alcohol reduction of MTO to MDO happens only at temperatures above 150 °C.

Scheme 31. Alkyne-Trapped MDO Intermediate Formation from 3-Pentanol and MTO
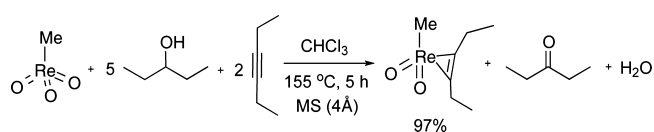

With this information in hand, Toste et al. postulated the mechanism shown in Scheme 32, which involves a slow formation of MDO from the alcohol coordinated MeReO2(OH)(OCHR2) species, a fast condensation of MDO with the diol leading to Re(V)diolate (**1C**), followed by the final extrusion of the olefin product from **1C**, which was also considered as rate-contributing.[69]

This mechanism is in stark contrast with the mechanism proposed by Abu-Omar et al. for the disproportionation of glycerol on the basis of a first-order dependence of the reaction rate both on glycerol and MTO and of a kinetic isotope effect of 2.4 found for the DODH of d_5-glycerol(OH)$_3$ indicative of a rate-limiting C−H bond breakage, which involves a Re(VII)

Scheme 30. Product Separation Process for NH4ReO4/Benzyl Alcohol System (Adapted from Ref 22)
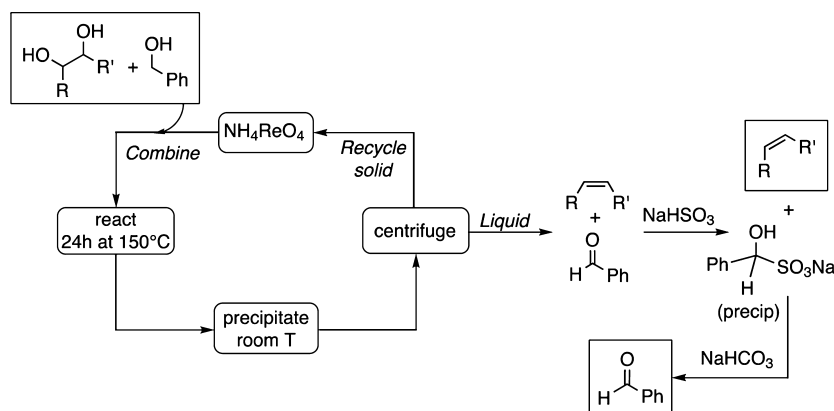
**Scheme 32. Proposed DODH Mechanism Involving MDO as the Active Species**
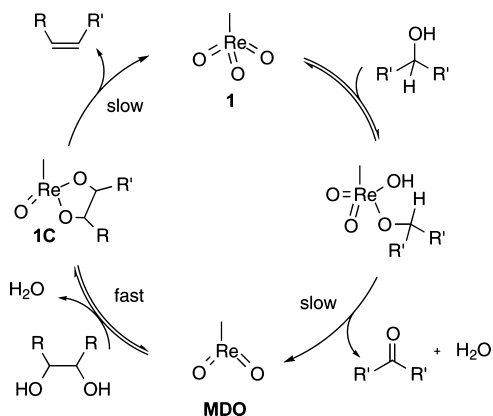
diolate as the active species and follows the (b) → (a) → (c) sequence (i.e., condensation → reduction → extrusion).[80] Later, these two DODH reaction pathways were evaluated by DFT calculations by Wang et al.[68]

The calculations show that the reaction is overall thermodynamically favorable (ΔG = −25.6 kcal/mol). The activation barriers corresponding to the (a) → (b) (reduction → condensation) and the (b) → (a) (condensation → reduction) pathways were calculated to be $\Delta G^{\ddagger}$ = 45.2 and 53 kcal/mol, respectively. However, a lower free enthalpy of activation ($\Delta G^{\ddagger}$ = 39.2 kcal/mol) was calculated for an alternative pathway that does not involve MDO but its

hydrated counterpart MeReO(OH)$_2$ (MODH),[19] which forms by transfer hydrogenation of MTO by the alcohol. The C−O bond breakage to release the ketone and the reduced MODH species is the rate-limiting step. Initial formation of the alkoxy(hydroxyl)rhenium(VII) species is assisted by another alcohol molecule for H-transfer, followed by MODH formation which reacts with glycol to obtain the Re(V)diolate intermediate. Moreover, again another alcohol molecule assists the glycol condensation reaction. Eventually, olefin is released from Re(V)diolate via a concerted extrusion pathway (Scheme 33). The absence of DODH reactivity for cyclic *trans*-diols is explained from the calculated inaccessible energy barrier ($\Delta G^{\ddagger}$ = 69.9 kcal/mol) for olefin extrusion under DODH reaction conditions.

Su, Zhang, and co-workers also used DFT calculations to provide more insights into the MTO/alcohol system, mainly for mucic acid conversion to muconic acid. Their DFT calculations also suggest the formation MODH (7.8 kcal/mol) as the active species rather than MDO (19.4 kcal/mol), which require activation barriers of $\Delta G^{\ddagger}$ = 39.6 and 47.5 kcal/mol, respectively.[86] Initial DODH of mucic acid proceeds with MODH species involving the α/β-hydroxyl groups rather than the α/γ-positions, with relative free enthalpies of activation of $\Delta G^{\ddagger}$ = 21.2 and 29.5 kcal/mol, respectively. The consecutive second DODH is much easier than the first DODH to produce the end product muconic acid, with relative free enthalpy of activation ($\Delta G^{\ddagger}$) of 17.6 and 21.2 kcal/mol, respectively. From all the DFT calculations for different MTO/reductant DODH systems, reduction of Re(VII) to Re(V) is found rate-limiting: $\Delta G^{\ddagger}$ = 34.1 and 39.2 kcal/mol for MTO/H$_2$ and MTO/
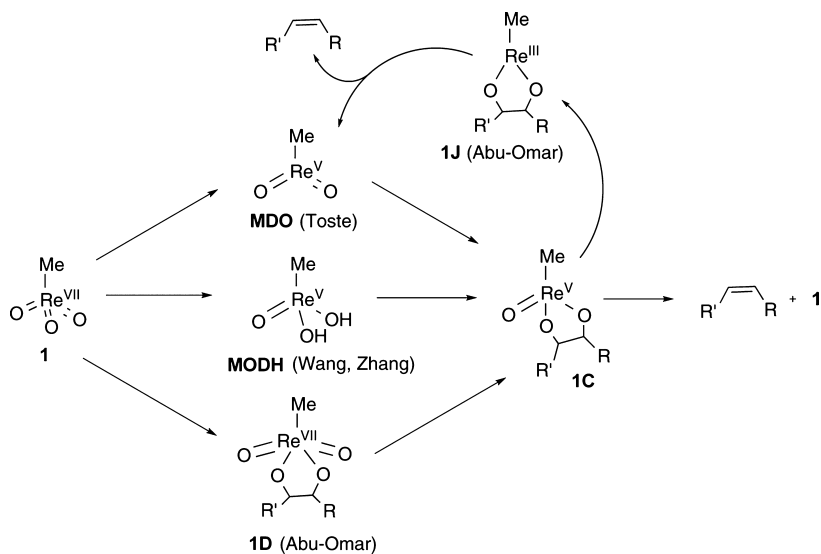
Scheme 33. DFT-Calculated DODH Mechanistic Pathway for MTO/3-Octanol via an MODH Intermediate
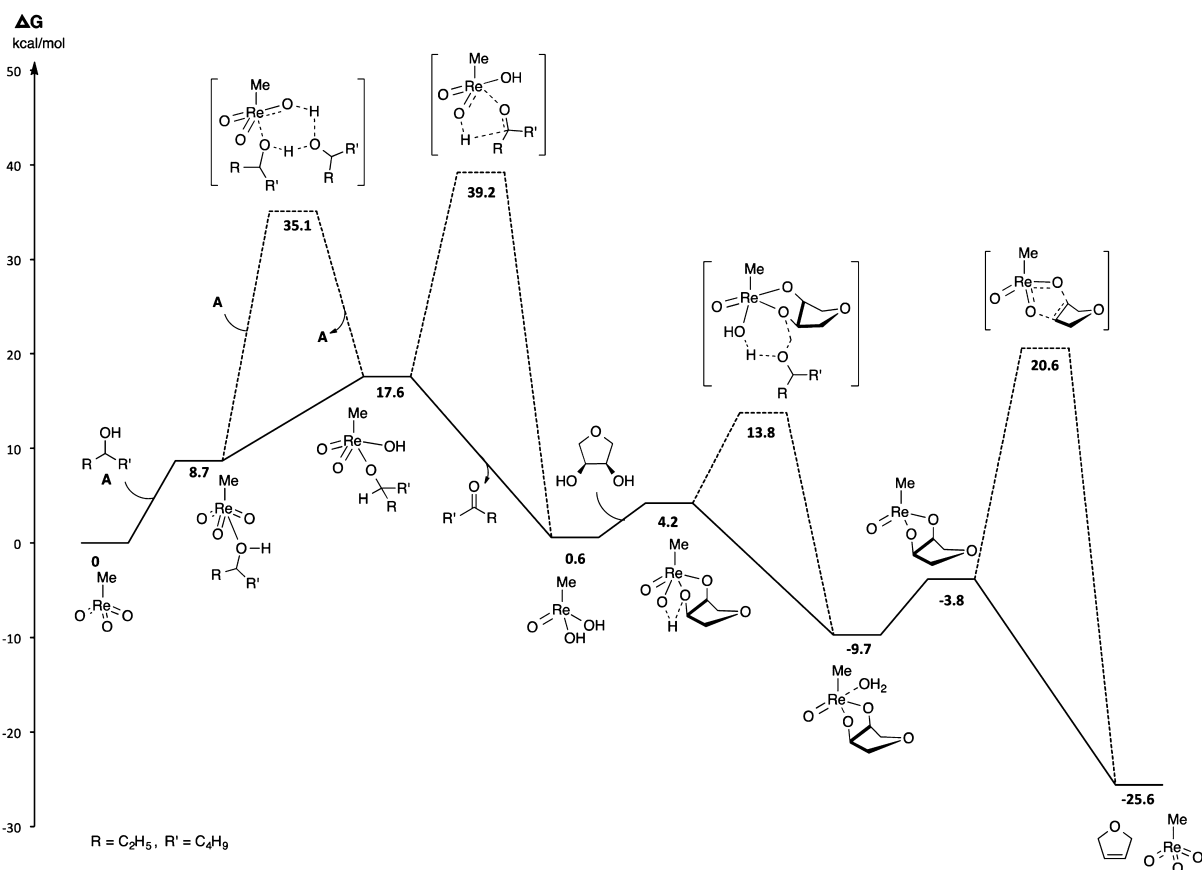
Scheme 34. MDO-Catalyzed DODH via Re(III)Diolate Species
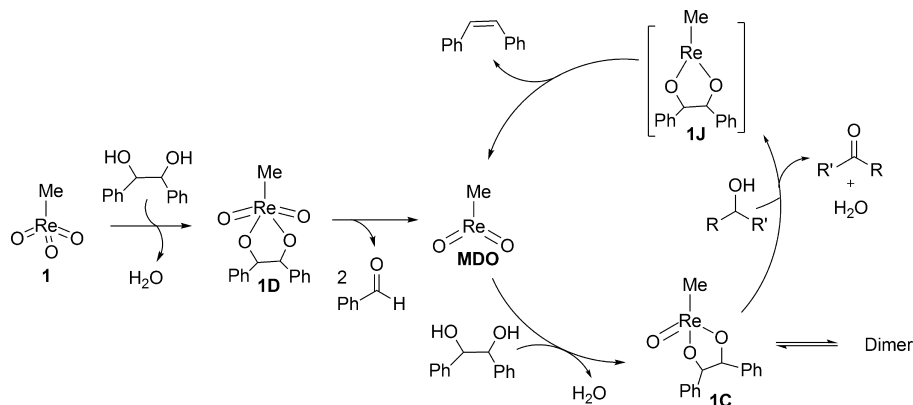
Scheme 35. Combined Different Mechanistic Proposal for MTO/Alcohol DODH System

alcohol, respectively, whereas for the MTO/sulfite system final olefin extrusion ($\Delta G^{\ddagger}$ = 33 kcal/mol) is rate-limiting.

Later, Abu-Omar et al. proposed an alternative DODH pathway for the conversion of hydrobenzoin to stilbene with MTO or MDO·L$_2$ (L = PCy$_3$, PPh$_3$) as the catalysts and 3-octanol as the reductant at 140 °C.[87] There is an induction period (10 min) for stilbene formation starting from MTO, whereas immediate reaction occurs by using the Re(V)-complexes MDO·L$_2$. Formation of benzaldehyde is observed when heating the Re(VII)diolate (**1D**) at 140 °C in a separate experiment, without the formation of styrene. The actual catalysis therefore is proposed to proceed through MDO, MTO not taking part in the catalytic cycle. Additionally, kinetic data show a half-order rate dependence on [Re], which is explained by the dimeric form of MDO. A small primary kinetic isotope effect of 1.4 found with 3-D-octanol suggest the rate-limiting reduction of **1C**, and from the obtained thermodynamic activation parameters ($\Delta H^{\ddagger}$ = 16 ± 3 kcal/mol, $\Delta S^{\ddagger}$ = −154 ± 33 J/mol·K), the large activation entropy supports the bimolecular transition state. On the basis of these data, the mechanism was proposed to involve a monomer−dimer equilibrium for the reduction of Re(V)diolate (**1C**) by the alcohol reductant to form a putative Re(III)diolate (**1J**), which eventually releases stilbene and retrieves MDO to continue the main catalytic cycle (Scheme 34). For the moment, no

additional experimental evidence corroborates the involvement of a Re(III)diolate species.

The different mechanistic proposals for the MTO/alcohol DODH system are summarized in Scheme 35. All of them invoke a reduced rhenium diolate compound as the olefin-releasing species, but a number of questions are not definitely resolved yet. Toste and co-workers demonstrated that alcohols are competent to reduce MTO to Re(V) species by trapping the known alkyne adduct of MDO, whereas the DFT calculations by Wang as well as Zhang groups predict a lower-energy pathway to MODH as an intermediate ($\Delta G^{\ddagger}$ = 6−8 kcal/mol lower than MDO). The recent and intriguing proposal by Abu-Omar that a more reduced Re(III)diolate may be involved introduces an additional layer of potential complexity.

It is worth noting that the different mechanistic proposals are not necessarily mutually exclusive; that is, several pathways may be accessible as a function of the substrate and conditions. In particular, both the diol condensation with MTO to form **1D** and the reduction of MTO to MDO are known to be accessible and one or the other may be favored depending on the reaction conditions (concentration, proticity of the medium, and so forth). In addition, the presence of hydrophilic alcohols/diols and the formation of water during the reaction complicate the system by giving access to a large number of potentially

interconverting hydroxide/alkoxide species. Mixed Re(V)- and Re(VI)-diolates are also accessible under catalytic conditions. Narrowing down the range of possible pathway will likely require isolation and/or careful characterization of reduced oxo-rhenium species (e.g., MDO, MODH) and diolate species (Re^{III} to Re^{VII}) in order to study their individual reactivity and lend experimental support to the computational models.

3.2.4. Elemental Reductants for Re-Catalyzed DODH. Nicholas et al. have very recently reported the use of elements such as Zn, Fe, Mn, and C (2 equiv) as reductants in combination with NH_4ReO_4 (10 mol %) at 150 °C in benzene (24 h) to convert 1,2-decanediol to 1-decene (34−69%).[88] Advantageously, these elemental reductants and their corresponding oxidized products do not dissolve in the reaction mixture leading to easy separation of olefins. Increasing 1-decene yield was obtained upon increasing the amount of Zn (56% for 1.1 equiv and 68% for 2 equiv), whereas the presence of air leads to low yield (8% with 1.1 equiv Zn) due to competing air oxidation of Zn. Other nonaliphatic diols such as 1-phenyl-1,2-ethanediol (46%), (+)-diethyl L-tartrate (68−84%), and batyl alcohol (51%) can also be converted to the corresponding olefins in moderate to high yields with different combinations of elemental reductants (Scheme 36).

Scheme 36. Elemental Reductants in Combination with Oxo-Rhenium Catalysts for DODH Reactions
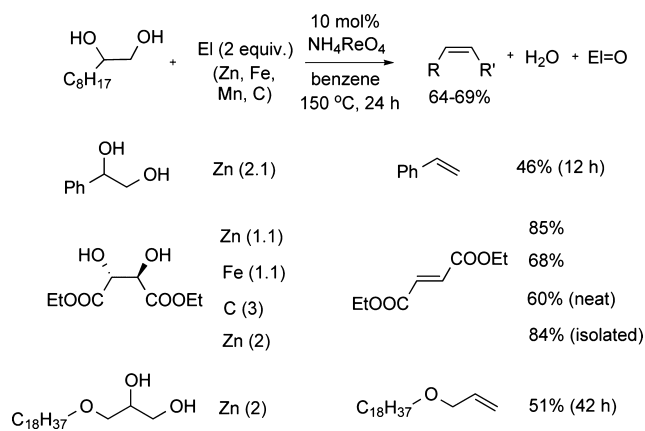
Zinc (2 equiv) in combination with the cationic rhenium(V) salts $[Py_4ReO_2]^+$ Cl$^-$ or PF$_6^-$, results in 90 or 67% 1-decene yield, respectively. The stoichiometric reaction of $[Py_4ReO_2]^+$ Cl$^-$ (**5**) with 1,2-decanediol (1.6 equiv) at 150 °C in 16 h results in 1-decene (0.98 equiv; 98% with respect to Re) and no other organic products (i.e., aldehyde or ketone) except the corresponding oxidized $[(Py)_nRe(VII)O_3]^+$ (**5A**) species. From this observation, diol condensation−dehydration to Re(V)-diolate followed by olefin extrusion may result in Re(VII)

species **5A**. Further reduction of **5A** by the elemental reductant can form back the original Re(V)dioxo complex **5**. Nonetheless, further reduction of **5** to Re(III) species can not be ruled out with the current data in hand.

3.3. Supported Oxo-Rhenium-Catalyzed DODH. Catalyst separation and reuse after the reaction is very often an issue in homogeneous catalysis. One way to make a homogeneous catalytic process more economical, less toxic, and environmentally more benign is the use of a supported version. The applicability of this approach to high-valent oxo-rhenium compounds has been demonstrated by Arterburn and co-workers. They covalently linked catecholato oxo-rhenium compounds to polystyrene to produce a supported Re(VII) oxo catalyst (5 mol % loading) that provides high olefin yields from deoxygenation of a variety of alkyl and aryl substituted epoxides by using PPh_3 as the reductant.[89] The recovered catalyst was reused repeatedly, and the catalytic performance remained the same. This shows the viability for easy catalyst separation from products and the reuse of the rhenium catalysts.

Nicholas et al. have recently reported a DODH system based on a carbon-supported perrhenate catalyst (ReO_x−C) in combination with H_2 (7−14 bar) at 150−175 °C in benzene.[90] The catalyst (3−4 mass% Re) was prepared by the equilibrium adsorption of perrhenate onto activated carbon by using aqueous ammonium perrhenate. 1,2-tetradecanediol is converted to 1-tetradecene (57%), 2-tetradecanone (13%), and a mixture of cyclic ethers and acetals by this system (10%; Scheme 37). Hot filtration of the reaction mixture after the reaction shows a moderate perrhenate leaching into the solution. The conversion of diethyl tartrate to diethyl fumarate (>95% in 2 days at 150 °C) was monitored by means of in situ IR spectroscopy. An induction period of 2 h was observed when the catalyst was prereduced for only 10 min, whereas the induction period was shorter when the catalyst was reduced for a longer time and a clean correlation curve is obtained for diethyl tartrate conversion and diethyl fumarate formation. When diisopropyl carbinol, benzyl alcohol or tetrahydronaphalene are applied as the reductant for 1,2-tetradecanediol conversion, 40−52% 1-tetradecene is obtained in 3−7 days.

3.4. DODH Catalyzed by Other Transition Metals. Although most efforts in the field have been focused on rhenium (USD 3197/kg) catalysts, the development of scalable DODH technology for biomass conversion would benefit from using less costly metals such as molybdenum (USD 22/kg) or vanadium (USD 409/kg).[91] Recent results in this area are discussed here in comparison with state-of-the-art rhenium catalysts. The initial investigations on molybdenum and vanadium indicate in general a lower reactivity and the requirement of more vigorous reaction conditions compared to rhenium-based catalysts for DODH reactions. Pettinari et al.

Scheme 37. Carbon-Supported Perrhenate-Catalyzed DODH of 1,2-Tetradecanediol to 1-Tetradecene at 150 °C in Benzene
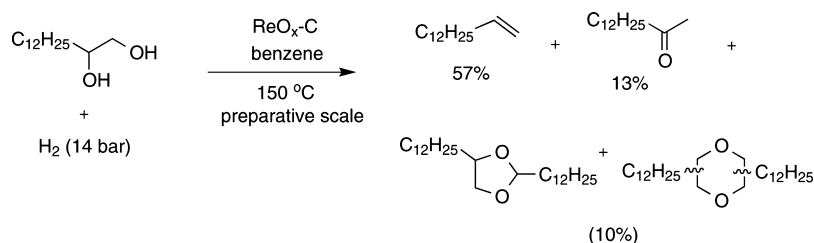
recently were the first to report the use of molybdenum oxo compounds for DODH, albeit with rather low selectivity.[92] Acylpyrazolone Mo(VI)oxo complexes of the type $Mo(Q^R)_2O_2$ (where HQ^R = 3-methyl-1-phenyl-4-alkylcarbonyl-5-pyrazolone: R = cyclohexyl (Q^{Cy}) or hexyl (Q^{He})) give low yields of styrene (10−13%) at 60−90% conversion of 1-phenyl-1,2-ethanediol at 110 °C in toluene with PPh_3 as reductant. Under the same conditions, the complete conversion of *cis*-cyclo-octanediol results in 55% cyclooctene yield with the Mo-$(Q^{Cy})_2O_2$ catalyst. The cause of the poor mass balance was not known at this stage of investigation. In a later study, Fristrup et al. showed that different molybdenum catalysts ($Mo(CO)_6$, $Mo(CO)_4(bipy)$, $MoO_2Cl_2(bipy)$, $MoO_2Br_2(bipy)$, $MoO_2(CH_3)_2(bipy)$, $(NH_4)_6Mo_7O_{24}$, Na_2MoO_4, and $H_3PMo_{12}O_{40}$) can be used to convert 1,2-tetradecanediol to 1-tetradecene with 5 mol % catalyst loading at 190−200 °C, giving up to 37−43% alkene products at complete conversion.[93] They observed the products of an oxidative deformylation reaction in which breaking of a C−O bond occurred to form aldehydes out of diols with subsequent possible dioxolane formation (Scheme 38).[93] Coupled to DODH, this process

Scheme 38. Comparison of Oxidized Side Products for Re and Mo in the Disproportionation of Glycerol
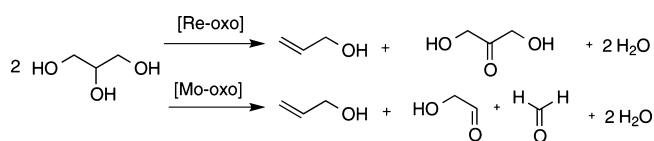
constitutes a new type of disproportionation (associated with a maximum theoretical yield of 50%) distinct from those typically observed for Re catalysts (Scheme 19). Under neat reaction conditions, the formed aldehydes react with 1,2-diols to form acetals, resulting in a low conversion. In an attempt to inhibit this presumably acid-catalyzed side reaction, NaOH (3 mol %) was added to the reaction mixture, but this proved detrimental to the overall olefin yield. In contrast, improved yields were obtained by using 1,5-pentanediol as solvent, in which 1,2-hexanediol and glycerol afford 1-hexene (45%) and allyl alcohol (40%), respectively. Control reactions for the deoxygenation of epoxides resulted in very poor alkene yield (<5%), indicating that the epoxide is not an intermediate in the DODH reaction.

Oxo-vanadium catalysts were also reported for DODH of diols to olefins. Among a series of tested $LVO_{2,3}$ catalysts, $[(n\text{-}butyl)_4N][(pyridine\text{-}2,6\text{-}dicarboxylate)VO_2]$ (10 mol %) is able to give olefins in high yields (85−97%), either with Na_2SO_3 or PPh_3 as the reductant in 2−3 days.[94] Reactions carried out in nonpolar solvents (PhCl, PhH) at 170 °C with PPh_3 (1.5 equiv) were found to be optimal for converting vicinal aromatic diols (1-phenyl-1,2-ethanediol: 95%) and aliphatic diols (1,2-octanediol: 87%; 1,2-hexanediol, diethyl fumarate or pinacol: 85%; *cis*-cyclohexanediol: 15%). The reaction mechanism was thought to involve vanadium(III)diolate intermediate via either V^{III} or V^V anionic species.[95] The oxo catalysts of vanadium (10 mol %, 170 °C) and molybdenum (5 mol %, 200 °C) require high temperature and large amount of catalyst loading with limited diol substrates scope resulting in moderate to good yields to olefins. Further studies on vanadium and molybdenum as affordable catalysts for the valorization of biomass derived polyols are warranted. In particular, mechanistic studies would be valuable for the rational development of new catalysts that

could compete with the highly studied rhenium-based DODH systems.

4. CONCLUSION

One of the main challenges in biomass conversion is the selective deoxygenation of sugars and sugar-derived alcohols to form olefins. Among a number of different viable catalytic transformations, rhenium-mediated deoxygenations in the form of deoxygenation, dehydration, and deoxydehydration reactions have received special attention. Although details on rhenium-mediated deoxygenation reactions of epoxides and pyridine *N*-oxides have been known for quite some time, catalytic dehydrations and DODH reactions of alcohols and polyols to form olefins and polyenes are reported more recently. These recent studies have shown that various diol and polyol substrates can often be converted in high yields and with good selectivity to the corresponding olefins, without these olefins being further converted through, for example, oligo- or polymerization reactions. The number of different Re-based catalysts that are currently used for these reactions is limited to MTO, perrhenate salts, and a selected number of organometallic Re complexes. MTO has received the most attention in the field by far, and using this established catalyst may be of interest for practical applications. Yet, because MTO is the only stable alkyl-ReO_3 compound, further optimization and fine-tuning of its performance will most likely involve chemical technological aspects. From this point of view, the development of new organometallic (homogeneous) and inorganic (heterogeneous) DODH catalysts based on rhenium seems a worthwhile effort.

Another important aspect for further development is the use of reducing agents in DODH chemistry. Although a number of different reducing agents, including the bioalcohols that are converted into olefins themselves, have been explored with quite some success, there is certainly room for improvement. For the practical implementation of any DODH reaction, the cost of the reducing agent (or of its recycling) will contribute significantly to the overall process cost. In this respect, hydrogen gas may at first sight be of interest. The initial studies presented here also show some downsides to its use as a reducing agent in DODH reactions. Not only may its use result in overreduction of the target olefins down to alkanes, overall reaction selectivities are not *per se* optimal when using H_2. The use of H_2 in a relay setup may therefore be of interest. As pointed out by Nicholas et al., one could envision the recovery of oxidized reducing agents, such as benzyl alcohol or secondary alcohols, by means of a coupled reduction with H_2 or another cheap terminal reductant.

Some studies have explicitly been devoted to unraveling the mechanism of catalytic DODH reactions. These have, among others, shown that the reduction of the Re catalyst may follow different mechanisms depending on the reducing agent that is employed in the reaction, which in turn may result in different deactivating pathways. Another important insight that came out of these studies is the dual role of water and of alcohol reagents in the mechanism. Water, being a product of the reaction, in many cases reacts with the (pre)catalyst to actually activate it instead of passivating it. Alcohols may serve a similar role and much still seems to be unclear about the reactivity pattern of the various condensation products arising from the reaction of both water as well as alcohols and the various Re-based reaction intermediates. Accumulation of water in the reaction mixture may also hamper the overall reaction progression, lead to

deactivation of catalysts, and so forth. The efficient removal of water might very well be an intricate part of reaction scale-up, where the chemical technology aspect may again be of importance.

Nevertheless, the development of rhenium-based catalysts for biomass transformations is still in its infancy, which leaves a lot of room for improvement. The overall high energy barrier for the simple rhenium oxides (i.e., perrhenates, MTO) under different catalytic conditions reveals the requirement for the development of new catalyst candidates. Providing further understanding of the mechanisms by which DODH reactions can be catalyzed by means of proper kinetic models and theoretical studies will certainly aid in this endeavor.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: r.j.m.kleingebbink@uu.nl.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411−2502.

(2) Werpy, T.; Petersen, G.; Aden, A.; Bozell, J.; Holladay, J.; White, J.; Manheim, A.; Eliot, D.; Lasure, L.; Jones, S.; *Top Value Added Chemicals from Biomass. Volume 1—Results of Screening for Potential Candidates from Sugars and Synthesis Gas.* U. S. Department of Energy report. Pacific Northwest National Laboratory/U.S. Department of Energy: Oak Ridge, TN, 2004.

(3) Zakzeski, J.; Bruijnincx, P. C. A.; Jongerius, A. L.; Weckhuysen, B. M. *Chem. Rev.* **2010**, *110*, 3552−3559.

(4) Arceo, E.; Marsden, P.; Bergman, R. G.; Ellman, J. A. *Chem. Commun.* **2009**, 3357−3359.

(5) Herrmann, J. M.; König, B. *Eur. J. Org. Chem.* **2013**, 7017−7027.

(6) Sousa, S. C. A.; Fernandes, A. C. *Coord. Chem. Rev.* **2015**, *284*, 67−92.

(7) Buntara, T.; Noel, S.; Phua, P. H.; Melián-Cabrera, I.; de Vries, J. G.; Heeres, H. J. *Top. Catal.* **2012**, *55*, 612−619.

(8) ten Dam, J.; Hanefeld, U. *ChemSusChem* **2011**, *4*, 1017−1034.

(9) Martin, A.; Armbruster, U.; Gandarias, I.; Arias, P. L. *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 9−27.

(10) Huang, Y. B.; Yang, Z.; Chen, M. Y.; Dai, J. J.; Guo, Q. X.; Fu, Y. *ChemSusChem* **2013**, *8*, 1348−1351.

(11) Maetani, S.; Fukuyama, T.; Suzuki, N.; Ishihara, D.; Ryu, I. *Chem. Commun.* **2012**, *19*, 2552−2554.

(12) Hansen, C. A.; Frost, D. A. *J. Am. Chem. Soc.* **2002**, *124*, 5926−5927.

(13) Gosselink, R. W.; Stellwagen, D. R.; Bitter, J. H. *Angew. Chem., Int. Ed.* **2013**, *52*, 5089−5092.

(14) Mitsudome, T.; Noujima, A.; Mikami, Y.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5545−5548.

(15) Adduci, L. L.; McLaughlin, M. P.; Bender, T. A.; Becker, J. J.; Gagné, M. R. *Angew. Chem., Int. Ed.* **2014**, *53*, 1646−1649.

(16) McLaughlin, M. P.; Adduci, L. L.; Becker, J. J.; Gagné, M. R. *J. Am. Chem. Soc.* **2013**, *135*, 1225−1227.

(17) Sutton, A. D.; Waldie, F. D.; Wu, R.; Schlaf, M.; Silks, L. A., 3rd; Gordon, J. C. *Nat. Chem.* **2013**, *5*, 428−432.

(18) Schlaf, M.; Ghosh, P.; Fagan, P. J.; Hauptman, E.; Bullock, R. M. *Adv. Synth. Catal.* **2009**, *351*, 789−800.

(19) Nonconventional acronyms used: DODH − deoxydehydration; OAT − Oxygen atom transfer; MTO − Methyltrioxorhenium; poly-MTO − polymeric methyltrioxorhenium; MDO − Methyldioxorhenium; MODH − Methyloxodihydroxyrhenium; Cp − Cyclopentadienyl; Cp* − 1,2,3,4,5-pentamethylcyclopentadienyl; Cpᵗᵗᵗ − 1,2,4-tris(*tert*-butyl)cyclopentadienyl; Tp − tris(pyrazolyl)borate; Tp* − tris(3,5-dimethylpyrazolyl)borate.

(20) Metzger, J. O. *ChemCatChem* **2013**, *5*, 680−682.

(21) Dutta, S. *ChemSusChem* **2012**, *5*, 2125−2127.

(22) During the preparation of this manuscript, a book chapter appeared on the topic of deoxydehydration of polyols: Boucher-Jacobs, C.; Nicholas, K. M. *Top. Curr. Chem.* **2014**, *353*, 163−184.

(23) Romão, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197−3246.

(24) Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169−180.

(25) Espenson, J. H.; Abu-Omar, M. M. *Advances in Chemistry*; American Chemical Society: Washington, DC, 1997; *253*, Chapter 7, 99−134.

(26) Abu-Omar, M. M.; Appelman, E. H.; Espenson, J. H. *Inorg. Chem.* **1996**, *35*, 7751−7757.

(27) Espenson, J. H. *Adv. Inorg. Chem.* **2003**, *54*, 157−202.

(28) Gable, K. P. *Adv. Organomet. Chem.* **1997**, *41*, 127−161.

(29) Espenson, J. H. *Chem. Commun.* **1999**, 479−488.

(30) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1996**, *61*, 324−328.

(31) Wang, Y.; Espenson, J. H. *Org. Lett.* **2000**, *2*, 3525−3526.

(32) Wang, Y.; Espenson, J. H. *Inorg. Chem.* **2002**, *41*, 2266−2274.

(33) Espenson, J. H. *Coord. Chem. Rev.* **2005**, *249*, 329−341.

(34) Abu-Omar, M. M. *Chem. Commun.* **2003**, *17*, 2102−2111.

(35) McPherson, L. D.; Drees, M.; Khan, S. I.; Strassner, T.; Abu-Omar, M. M. *Inorg. Chem.* **2004**, *43*, 4036−4050.

(36) Jiang, Y.; Blacque, O.; Fox, T.; Frech, C. M.; Berke, H. *Chem.—Eur. J.* **2009**, *15*, 2121−2128.

(37) Lilly, C. P.; Boyle, P. D.; Ison, E. A. *Dalton Trans.* **2011**, *40*, 11815−11821.

(38) Yamamoto, T.; Toganoh, M.; Furuta, H. *Dalton Trans.* **2012**, *41*, 9154−9157.

(39) Espenson, J. H.; Yiu, D. T. Y. *Inorg. Chem.* **2000**, *39*, 4113−4118.

(40) Sousa, S. C. A.; Fernandes, A. C. *Tetrahedron Lett.* **2011**, *52*, 6960−6962.

(41) Gable, K. P.; Juliette, J. J. J.; Gartman, M. A. *Organometallics* **1995**, *14*, 3138−3140.

(42) Gable, K. P.; Zhuravlev, F. A.; Yokochi, A. F. T. *Chem. Commun.* **1998**, 799−800.

(43) Gable, K. P.; Brown, E. C. *Organometallics* **2000**, *19*, 944−946.

(44) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry Part A: Structure and Mechanism*, 5th ed.; Springer: New York, 2007.

(45) Moser, W. R.; Thompson, R. W.; Chiang, C.; Tong, H. *Catal. Today.* **1989**, *117*, 19−32.

(46) Korstanje, T. J.; Jastrzebski, J. T. B. H.; Klein Gebbink, R. J. M. *ChemSusChem* **2010**, *3*, 695−697.

(47) Korstanje, T. J.; Jastrzebski, J. T. B. H.; Klein Gebbink, R. J. M. *Chem.—Eur. J.* **2013**, *19*, 13224−13234.

(48) Korstanje, T. J.; de Waard, E. F.; Jastrzebski, J. T. B. H.; Klein Gebbink, R. J. M. *ACS Catal.* **2012**, *2*, 2173−2181.

(49) Edreva-Kardjieva, R. M.; Andreev, A. A. *J. Catal.* **1986**, *97*, 321−329.

(50) Mol, J. C. *Catal. Today* **1999**, *51*, 289−299.

(51) She, X.; Kwak, J. H.; Sun, J.; Hu, J.; Hu, M. Y.; Wang, C.; Peden, C. H. F.; Wang, Y. *ACS Catal.* **2012**, *2*, 1020−1026.

(52) Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Della Pina, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 4434−4440.

(53) Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165−1182.

(54) Herrmann, W. A.; Serrano, R.; Küsthardt, U.; Guggolz, E.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1985**, *287*, 329−344.

(55) Herrmann, W. A. *J. Organomet. Chem.* **1986**, *300*, 111−137.

(56) Herrmann, W. A.; Okuda, J. *J. Mol. Catal.* **1987**, *41*, 109−122.

(57) Gable, K. P. *Organometallics* **1994**, *13*, 2486−2488.

(58) Cook, G. K.; Andrews, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 9448−9449.

(59) Gable, K. P.; Ross, B. *ACS Symp. Ser.* **2006**, *921*, 143−155.

(60) Raju, S.; Jastrzebski, J. T. B. H.; Lutz, M.; Klein Gebbink, R. J. M. *ChemSusChem* **2013**, *6*, 1673−1680.

(61) Shimogawa, R.; Takao, T.; Suzuki, H. *Organometallics* **2014**, *33*, 289−301.

(62) Yanagi, T.; Suzuki, H.; Oishi, M. *Chem. Lett.* **2013**, *42*, 1403−1405.

(63) Shiramizu, M.; Toste, F. D. *Angew. Chem., Int. Ed.* **2012**, *51*, 8082−8086.

(64) Bergman, R. G.; Cundari, T. R.; Gillespie, A. M.; Gunnoe, T. B.; Harman, W. D.; Klinckman, T. R.; Temple, M. D.; White, D. P. *Organometallics* **2003**, *22*, 2331−2337.

(65) Gable, K. P.; Juliette, J. J. J. *J. Am. Chem. Soc.* **1995**, *117*, 955−962.

(66) Gable, K. P.; Phan, T. N. *J. Am. Chem. Soc.* **1994**, *116*, 833−839.

(67) Gable, K. P.; AbuBaker, A.; Zientara, K.; Wainwright, A. M. *Organometallics* **1999**, *18*, 173−179.

(68) Qu, S.; Dang, Y.; Wen, M.; Wang, Z. X. *Chem.—Eur. J.* **2013**, *19*, 3827−3832.

(69) Shiramizu, M.; Toste, F. D. *Angew. Chem., Int. Ed.* **2013**, *52*, 12905−12909.

(70) Ziegler, J. E.; Zdilla, M. J.; Evans, A. J.; Abu-Omar, M. M. *Inorg. Chem.* **2009**, *48*, 9998−10000.

(71) Bi, S.; Wang, J.; Liu, L.; Li, P.; Lin, Z. *Organometallics* **2012**, *31*, 6139−6147.

(72) Vkuturi, S.; Chapman, G.; Ahmad, I.; Nicholas, K. M. *Inorg. Chem.* **2010**, *49*, 4744−4746.

(73) Ahmad, I.; Chapman, G.; Nicholas, K. M. *Organometallics* **2011**, *30*, 2810−2818.

(74) Herrmann, W. A.; Ladwig, M.; Kiprof, P.; Riede, J. *J. Organomet. Chem.* **1989**, *371*, C13−C17.

(75) Herrmann, W. A.; Kühn, F. F.; Romão, C. C.; Hoa, T. H.; Wang, M.; Fischer, R. W.; Kiprof, P.; Scherer, W. *Chem. Ber.* **1993**, *126*, 45−50.

(76) Liu, P.; Nicholas, K. M. *Organometallics* **2013**, *32*, 1821−1831.

(77) Arceo, E.; Ellman, J. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2010**, *132*, 11408−11409.

(78) Canale, V.; Tonucci, L.; Bressan, M.; d'Alessandro, N. *Catal. Sci. Technol.* **2014**, *4*, 3697−3704.

(79) Bell, V. L. *J. Polym. Sci., Part A: Gen. Pap.* **1964**, *2*, 5291−5303.

(80) Yi, J.; Liu, S.; Abu-Omar, M. M. *ChemSusChem* **2012**, *5*, 1401−1404.

(81) Jacob, J.; Espenson, J. H.; Jensen, J. H.; Gordon, M. S. *Organometallics* **1998**, *17*, 1835−1840.

(82) Wang, G.; Jimtaisong, A.; Luck, R. L. *Organometallics* **2004**, *23*, 4522−4525.

(83) Morrill, C.; Grubbs, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 2842−2843.

(84) Morrill, C.; Beutner, G. L.; Grubbs, R. H. *J. Org. Chem.* **2006**, *71*, 7813−7825.

(85) Herrmann, A. T.; Saito, T.; Stivala, C. E.; Tom, J.; Zakarian, A. *J. Am. Chem. Soc.* **2010**, *132*, 5962−5963.

(86) Li, X.; Wu, D.; Lu, T.; Yi, G.; Su, H.; Zhang, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 4200−4204.

(87) Liu, S.; Senocak, A.; Smeltz, J. L.; Yang, L.; Wegenhart, B.; Yi, J.; Kenttämaa, H. I.; Ison, E. A.; Abu-Omar, M. M. *Organometallics* **2013**, *32*, 3210−3219.

(88) McClain, J. M.; Nicholas, K. M. *ACS Catal.* **2014**, *4*, 2109−2112.

(89) Arterburn, J. B.; Liu, M.; Perry, M. C. *Helv. Chim. Acta* **2002**, *85*, 3225−3236.

(90) Denning, A. L.; Dang, H.; Liu, Z.; Nicholas, K. M.; Jentoft, F. C. *ChemCatChem* **2013**, *5*, 3567−3570.

(91) Average elemental price data collected from http://www.metalprices.com (accessed Nov 11, 2014); Re (Sep 1 − Oct 1, 2013); Mo (Nov 7 − Nov 10, 2014); V in China domestic market (Sep 27 − Oct 11, 2013).

(92) Hills, L.; Moyano, R.; Montilla, F.; Pastor, A.; Galindo, A.; Álvarez, E.; Marchetti, F.; Pettinari, C. *Eur. J. Inorg. Chem.* **2013**, 3352−3361.

(93) Dethlefsen, J. R.; Lupp, D.; Oh, B.; Fristrup, P. *ChemSusChem* **2014**, *7*, 425−428.

(94) Chapman, G., Jr.; Nicholas, K. M. *Chem. Commun.* **2013**, *49*, 8199−8201.

(95) Hanson, S. K.; Baker, R. T.; Gordon, J. C.; Scott, B. L.; Sutton, A. D.; Thorn, D. L. *J. Am. Chem. Soc.* **2009**, *131*, 428−429.

(96) Boucher-Jacobs, C.; Nicholas, K. M. *ChemSusChem* **2013**, *6*, 597−599.

(97) Davis, J.; Srivastava, R. S. *Tetrahedron Lett.* **2014**, *55*, 4178−4180.