

A Cp^{tt}-Based Trioxo-Rhenium Catalyst for the Deoxydehydration of Diols and Polyols

Jing Li,^[a] Martin Lutz,^[b] Matthias Otte,^[a, c] and Robertus J. M. Klein Gebbink^{*[a]}

Trioxo-rhenium complexes are well known catalysts for the deoxydehydration (DODH) of vicinal diols (glycols). In this work, we report on the DODH of diols and biomass-derived polyols using Cp^{tt}ReO₃ as a new catalyst (Cp^{tt} = 1,3-di-*tert*-butylcyclopentadienyl). The DODH reaction was optimized using 2 mol% of Cp^{tt}ReO₃ and 3-octanol as both reductant and solvent. The Cp^{tt}ReO₃ catalyst exhibits an excellent activity for biomass-derived polyols. Specifically, glycerol is almost quantitatively

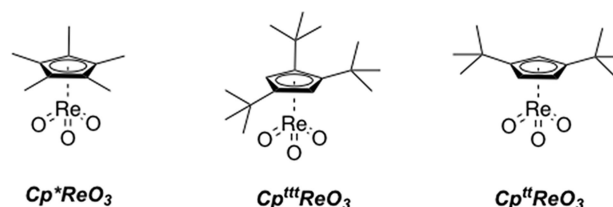
converted to allyl alcohol and mucic acid gives 75% of muconates at 91% conversion. In addition, the loading of Cp^{tt}ReO₃ can be reduced to 0.1 mol% to achieve a turn-over number as high as 900 per Re when using glycerol as substrate. Examination of DODH reaction profiles by NMR spectroscopy indicates that catalysis is related to Cp-ligand release, which raises questions on the nature of the actual catalyst.

Introduction

Due to the anticipated depletion of fossil feedstocks, the search for alternative and renewable chemical feedstocks receives a lot of attention.^[1,2] Biomass is such a potential resource for the sustainable production of commodity chemicals and other chemical building blocks.^[3–5] Biomass-derived feedstocks, such as sugars and polyols, are highly oxygenated, mostly in the form of hydroxyl groups. To make use of these feedstocks, (partial) deoxygenation is required. Deoxydehydration (DODH) reactions,^[6–8] which constitute a combination of deoxygenation^[9,10] and dehydration,^[11] can efficiently convert vicinal diols and polyols into olefins.^[12–14]

Trioxo-rhenium complexes are known as active catalysts for DODH reactions since the first catalytic DODH reaction was described by Cook and Andrews.^[12] In this very early work, a

Cp^{*}ReO₃ complex (Scheme 1, left) was used to catalytically convert polyols into olefins. Later, Gable and co-workers studied



Scheme 1. Cp-base trioxo-rhenium catalysts.

olefin extrusion reactions from Tp^{*}Re(glycolate) complexes (Tp^{*} = hydrido-*tris*-(3,5-dimethylpyrazolyl)borate), and in doing so used the 6e⁻ Tp^{*} ligand as an alternative for the 6e⁻ Cp^{*} ligand.^[15] Recently, we reported on a bulky Cp-based trioxo-rhenium catalyst, Cp^{ttt}ReO₃ (Cp^{ttt} = 1,2,4-tri-*tert*-butylcyclopentadienyl, Scheme 1, middle).^[16] This trioxo-rhenium complex is able to effectively catalyze the DODH of a series of different diols and polyols. The electron-rich Cp^{ttt} ligand of the complex stabilizes the high-valent rhenium center, avoiding over-reduction, and hampers catalyst dimerization leading to decomposition, to result in high TONs. Interestingly, a slight change of the ligand (removing one *tert*-butyl group) resulted in a different DODH reactivity of the trioxo-rhenium complex.^[17] We observed an induction period in the Cp^{ttt}ReO₃-catalyzed DODH of 1,2-octanediol, while there was almost no induction period in the reaction catalyzed by the Cp^{tt}ReO₃ complex (Cp^{tt} = 1,3-di-*tert*-butylcyclopentadienyl, Scheme 1, right). This result encouraged us to further investigate the catalytic properties of the less bulky Cp^{tt}ReO₃ complex. Here, we report on the DODH of diols and biomass-derived polyols using Cp^{tt}ReO₃.

[a] J. Li, Dr. M. Otte, Prof. Dr. R. J. M. Klein Gebbink
Organic Chemistry and Catalysis
Debye Institute for Nanomaterials Science
Utrecht University
Universiteitsweg 99
Utrecht 3584CG (The Netherlands)
E-mail: R.J.M.KleinGebbinck@uu.nl

[b] Dr. M. Lutz
Crystal and Structural Chemistry
Bijvoet Center for Biomolecular Research
Faculty of Science
Utrecht University
Padualaan 8
Utrecht 3584 CH (The Netherlands)

[c] Dr. M. Otte
current address:
Institut für Anorganische Chemie
University of Göttingen
Tammannstraße 4
Göttingen 37077 (Germany)

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Results and Discussion

We started our investigation on the use of $\text{Cp}^{\text{tr}}\text{ReO}_3$ as a catalyst for the DODH of vicinal diols into olefins by using 1,2-octanediol as a substrate (Table 1). Initial reactions were

Table 1. Optimization of reaction conditions and sacrificial reducing agent in the DODH of 1,2-octanediol to 1-octene catalyzed by $\text{Cp}^{\text{tr}}\text{ReO}_3$.^[a]

Entry	Reductant	Conditions	Yield [%]	Conversion [%]
1 ^[b]	PPh_3	135 °C, 15 h, N_2	93	> 99
2 ^[b]	Na_2SO_3	135 °C, 15 h, N_2	N.D.	6
3 ^[b]	C	135 °C, 16 h, N_2	N.D.	40
4 ^[b]	H_2 ^[d]	135 °C, 16 h, N_2	1.2 ^[e]	23
5 ^[c]	3-octanol	135 °C, 15 h, N_2	93	> 99
6 ^[c]	3-octanol	170 °C, 2 h, N_2	81	> 99
7 ^[c]	3-octanol	135 °C, 15 h, air	68	76

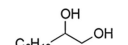

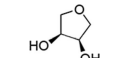

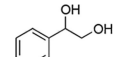

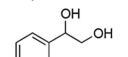

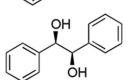

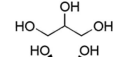

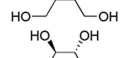

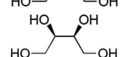

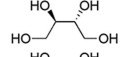

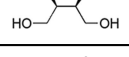

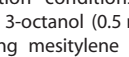

[a] Reaction conditions: 1,2-octanediol (0.5 mmol), $\text{Cp}^{\text{tr}}\text{ReO}_3$ (0.01 mmol, 2 mol%), reductant (0.55 mmol, 1.1 equivalent). [b] PhCl (0.5 mL) was used as solvent, the yield and conversion were determined by gas chromatography using mesitylene (0.5 mmol) as an internal standard. [c] 3-octanol (0.5 mL) was used as both reductant and solvent, the yield and conversion were determined by ^1H NMR using mesitylene (0.5 mmol) as an internal standard. [d] Pressure of H_2 : 40 bar. [e] Yield of n-octane.

performed with 2 mol% $\text{Cp}^{\text{tr}}\text{ReO}_3$ at 135 °C in chlorobenzene and 1.1 equivalent of sacrificial reducing agent under an inert nitrogen atmosphere. The use of triphenylphosphine (PPh_3) as reducing agent gave an excellent yield at full conversion (entry 1), which matched the data reported in our previous study.^[17] Sodium sulfite and active carbon gave a very poor conversion, probably because of their poor solubility in the chlorobenzene reaction medium (entry 2 and 3). The use of molecular hydrogen (40 bar) resulted in only 1.2% n-octane as the over-reduced product at 23% substrate conversion (entry 4).

Secondary alcohols have been reported as both reductants and solvents for Re-catalyzed DODH reactions.^[18] Using 3-octanol as reductant, a 93% yield of 1-octene was achieved when the reaction was carried out at 135 °C for 15 h (entry 5). Increasing the reaction temperature to 170 °C lead to a decreased 1-octene yield at complete conversion (entry 6). Besides, even under aerobic conditions, i.e. carrying the reaction out in air, 68% of 1-octene was formed at 76% conversion using $\text{Cp}^{\text{tr}}\text{ReO}_3$ as catalyst and 3-octanol as reductant (entry 7). In our previous studies on the bulkier $\text{Cp}^{\text{tr}}\text{ReO}_3$ catalyst, we also observed that aerobic reaction conditions would decrease the activity of the catalyst.^[19] Both PPh_3 and 3-octanol gave high yields, considering that the chlorobenzene solvent is neither green nor good at dissolving biomass-derivatives, 3-octanol was chosen as the reducing agent in subsequent DODH reactions with $\text{Cp}^{\text{tr}}\text{ReO}_3$.

Following these optimization studies, the substrate scope using a variety of vicinal diols and biomass-derived polyols was investigated under optimized reaction conditions (Table 2). 1,4-anhydroerythritol gave 83% of 2,5-dihydrofuran (entry 2). The aromatic vicinal diol 1-phenyl-1,2-ethanediol gave 76% yield of styrene at full conversion (entry 3), while (*R,R*)-1,2-diphenyl-1,2-ethanediol selectively gave *trans*-stilbene in 95% yield (entry 5).

Table 2. DODH of vicinal diols and polyols to olefins catalyzed by $\text{Cp}^{\text{tr}}\text{ReO}_3$.^[a]

Entry	Substrate	Product	Yield ^[b] [%]	Conversion [%]
1			93	> 99
2			83	> 99
3			76	> 99
4 ^[c]			90	> 99
5			95	> 99
6			99	> 99
7			69 (74) ^[f]	93
8			71 (84) ^[g]	93
9 ^[d]			87 (94) ^[f]	> 99
10 ^[d]			90 (95) ^[g]	> 99
11 ^[e]			57 (61) ^[f]	87

[a] Reaction conditions: substrates (0.5 mmol), $\text{Cp}^{\text{tr}}\text{ReO}_3$ (0.01 mmol, 2 mol%), 3-octanol (0.5 mL, 0.1 M), N_2 , 135 °C, 15 h. [b] Determined by ^1H NMR using mesitylene (0.5 mmol) as an internal standard. [c] Reaction conditions: substrates (0.5 mmol), $\text{Cp}^{\text{tr}}\text{ReO}_3$ (0.01 mmol, 2 mol%), PPh_3 (0.55 mmol, 1.1 equiv), PhCl (0.5 mL, 0.1 M), N_2 , 135 °C, 15 h. [d] 170 °C, 1.5 h, N_2 . [e] air. [f] Total yield of 1,3-butadiene and 2,5-dihydrofuran. [g] Total yield of 1,3-butadiene and 1,4-anhydrothreitol.

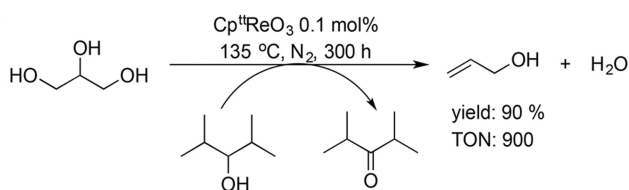
Interestingly, we observed a higher yield (90%) of styrene when PPh_3 was used as reductant (entry 4). The lower yield of styrene could be explained by ketal formation from the diol substrate and 3-octanone (dehydrogenation product of 3-octanol) during the reaction. A 99% styrene yield was realized with the $\text{Cp}^{\text{tr}}\text{ReO}_3$ catalyst when PPh_3 was used as reductant.^[16] Overall though, the conversions and yields that can be achieved in DODH reactions of vicinal diols with the less bulky $\text{Cp}^{\text{tr}}\text{ReO}_3$ catalyst are quite similar to those with the $\text{Cp}^{\text{tr}}\text{ReO}_3$ catalyst.

When $\text{Cp}^{\text{tr}}\text{ReO}_3$ was applied to DODH reactions of biomass-derived polyols it was found to have a much better product selectivity than the previously reported $\text{Cp}^{\text{tr}}\text{ReO}_3$ catalyst. Glycerol is the by-product formed during the transesterification of vegetable oils for the production of biodiesel.^[20,21] Under our optimized reaction conditions, glycerol was almost quantitatively converted to allyl alcohol (entry 6), which is a versatile intermediate for various useful chemicals such as agrochemicals, resins, medicines, perfumes, and so on.^[22] When our previous $\text{Cp}^{\text{tr}}\text{ReO}_3$ was used as catalyst for the deoxydehydration of glycerol, 91% of allyl alcohol was obtained at full conversion.^[16] Erythritol, which can be produced from glucose by fermentation,^[23] was converted to 1,3-butadiene (69%) with 2,5-dihydrofuran (5%) as by-product under optimized reaction conditions (entry 7). Another C_4 sugar alcohol, DL-threitol, gave 71% of 1,3-butadiene with 13% of 1,4-anhydrothreitol as by-

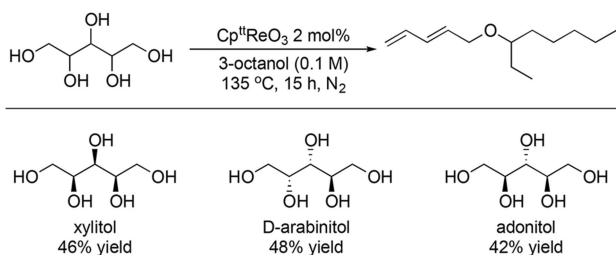
product (entry 8). With these two reactions, 1,3-butadiene, an industrially important building block, can be formed from sustainable starting materials. Interestingly, for these two reactions, increasing the temperature from 135 °C to 170 °C and decreasing the reaction time from 15 h to 1.5 h lead to an increased 1,3-butadiene yield of 87 and 90%, respectively (entry 9 and 10). We also observed that even under aerobic conditions erythritol gave 57% of 1,3-butadiene at 87% conversion with 4% of 2,5-dihydrofuran as by-product (entry 11). For the $\text{Cp}^{\text{tr}}\text{ReO}_3$ -catalyzed DODH of erythritol and DL-threitol, 1,3-butadiene was formed at a lower 67 and 59% yield, respectively, under N_2 at 170 °C.

For the very useful deoxydehydration of glycerol, we planned to investigate this reaction with different $\text{Cp}^{\text{tr}}\text{ReO}_3$ loadings and using different alcohols as sacrificial reductant. Considering there would be a competition between deoxydehydration of glycerol and dehydration of the alcohol, since rhenium complexes can also catalyze the dehydration of secondary alcohols,^[6] we started the investigation with testing different alcohols to find the most suitable reductant (see Supporting information). Finally, 2,4-dimethyl-3-pentanol, which is difficult to be dehydrated, was chosen as the reductant for this experiment. Then different loadings of $\text{Cp}^{\text{tr}}\text{ReO}_3$ were tested and the loading could be lowered to 0.1 mol% (see Supporting information). Using this catalyst loading glycerol could be converted to allyl alcohol at 90% yield with a total turn-over number per Re of 900 (Scheme 2). To our knowledge, this is the highest TON reported for a homogeneous Re-catalyst in the DODH of glycerol.

Encouraged by the results of $\text{Cp}^{\text{tr}}\text{ReO}_3$ -catalyzed DODH reactions of glycerol and C_4 sugar alcohols, we then tested the C_5 sugar alcohols xylitol, D-arabinitol, and adonitol (Scheme 3). Instead of (*E*)-2,4-pentadienol, (*E*)-5-penta-1,3-diene ether was formed in this reaction, as was earlier noted by Toste and coworkers.^[13] Under our reaction conditions, xylitol, D-arabinitol, and adonitol formed the (*E*)-5-penta-1,3-diene ethers at a yield

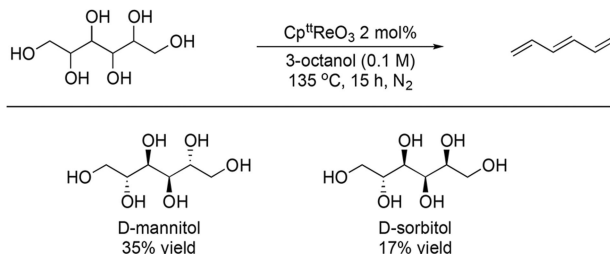


Scheme 2. $\text{Cp}^{\text{tr}}\text{ReO}_3$ -catalyzed DODH of glycerol.



Scheme 3. $\text{Cp}^{\text{tr}}\text{ReO}_3$ -catalyzed DODH of C_5 sugar alcohols.

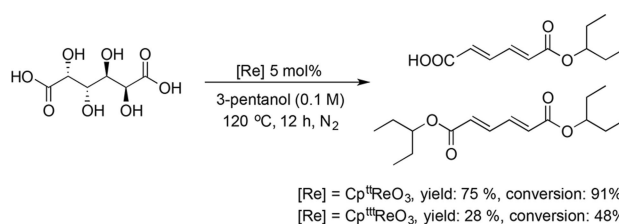
of 46%, 48%, and 42%, respectively. Interestingly, when methyltrioxorhenium (MTO) was used as catalyst for these reactions under more harsh reaction conditions, xylitol gave much more product (61%) than adonitol (33%).^[13] Next to the reactions on C_5 sugar alcohols, we also carried out reactions on two C_6 sugar alcohols (Scheme 4). D-mannitol gave approx.



Scheme 4. $\text{Cp}^{\text{tr}}\text{ReO}_3$ -catalyzed DODH of C_6 sugar alcohols.

35% yield of 1,3,5-hexatriene, while D-sorbitol only gave 17% yield of 1,3,5-hexatriene (see supporting information).

Adipic acid, a building block for the large-volume production of nylon-6,6 polyamide,^[24] is mainly produced from non-renewable petroleum-based cyclohexane. The production procedures include a nitric acid oxidation process, which emits large amounts of nitrous oxides.^[25] An alternative way to produce adipic acid is using sustainable mucic acid to form muconates through DODH chemistry, followed by hydrogenation and hydrolysis.^[26] Accordingly, we have investigated the activity of the $\text{Cp}^{\text{tr}}\text{ReO}_3$ catalyst in the DODH of mucic acid. Under modified reaction conditions, mucic acid gave 75% of isopentylmuconate at 91% conversion after 12 h using 3-pentanol as reducing agent at 120 °C. Under the same reaction conditions, when our previous $\text{Cp}^{\text{tr}}\text{ReO}_3$ catalyst was used as catalyst only 28% of muconates were formed at 48% conversion (Scheme 5), and when MTO was used as catalyst 71% of muconates were formed at 98% conversion.^[26]



Scheme 5. $\text{Cp}^{\text{tr}}\text{ReO}_3$ -catalyzed DODH of mucic acid.

Finally, we have also applied the $\text{Cp}^{\text{tr}}\text{ReO}_3$ catalyst to DODH reactions of a number of sugar compounds. 2-Vinylfuran (2-VF) and furan were formed as the main products, which is in line with the observations of Toste.^[13] Under our optimized reaction conditions, using 3-octanol as the reducing agent at 135 °C for 15 h, 2-vinylfuran was the main product albeit at low yield (Table 3, entries 1–3). An interesting observation was that when using 3-pentanol as reductant and solvent, the reaction mixture

Table 3. DODH of sugars to 2-vinylfuran (2-VF) and furan catalyzed by $\text{Cp}^{\text{II}}\text{ReO}_3$.^[a]

Entry	Sugar	Conditions	Yield ^[b] [%]	Ratio (2-VF :furan)
1	D-glucose	3-octanol, 135 °C, 15 h	8	1.7:1
2	D-galactose	3-octanol, 135 °C, 15 h	22	1.2:1
3	D-mannose	3-octanol, 135 °C, 15 h	21	2.5:1
4	D-glucose	3-pentanol, 135 °C, 15 h	trace	–
5	D-galactose	3-pentanol, 135 °C, 15 h	13	1:1.6
6	D-mannose	3-pentanol, 135 °C, 15 h	26	2.3:1
7	D-glucose	3-pentanol, 155 °C, 12 h	trace	–
8 ^[c]	D-galactose	3-pentanol, 155 °C, 12 h	14	–
9	D-mannose	3-pentanol, 155 °C, 12 h	39	2.3:1

[a] Reaction conditions: sugars (0.5 mmol), $\text{Cp}^{\text{II}}\text{ReO}_3$ (0.01 mmol, 2 mol %), N_2 . [b] Total yield of 2-VF and furan, determined by ^1H NMR using mesitylene (0.5 mmol) as an internal standard. [c] No 2-VF formation.

was more homogenous than when using 3-octanol. 3-pentanol was then chosen as the reductant and solvent for the DODH of sugar compounds. For the three sugars we have tested, D-glucose gave a very poor yield (entry 1, 4, 7), while D-mannose gave the highest yield up to 39% (entry 9). Besides, in terms of product selectivity, the reaction of D-galactose is quite sensitive to the reaction conditions; the ratio of 2-VF and furan products changes when using a different reductant (entry 2, 5, 8). D-galactose selectively forms furan as the only product when 3-pentanol was used as reductant (entry 8). For D-mannose, a different reductant does not have an obvious effect on product selectivity (entry 3, 6, 9), although consistently giving the highest product yields amongst the three sugar substrates.

The above results show that the less bulky $\text{Cp}^{\text{II}}\text{ReO}_3$ complex catalyzes the DODH of both aromatic and aliphatic vicinal diols with high yield and product selectivity. Extending the substrate scope to bio-based polyols, the high yield and product selectivity for this catalyst remains. Specifically, glycerol is almost quantitatively converted to allyl alcohol and mucic acid gives 75% of muconates at 91% conversion. Besides, even for more complicated sugar alcohols and sugars, the DODH reaction can be realized at moderate yields. Based on these data, we compared the $\text{Cp}^{\text{II}}\text{ReO}_3$ catalyst with our previous generation catalyst $\text{Cp}^{\text{III}}\text{ReO}_3$ for which the advantageous performance in DODH catalysis was attributed to its overall steric bulk provide by the Cp^{III} ligand. Both catalysts show a high DODH reactivity and selectivity for general vicinal diols, while in particular for bio-based polyols $\text{Cp}^{\text{II}}\text{ReO}_3$ shows a significantly improved reactivity and product selectivity. This comparison challenges the initial hypothesis that DODH catalysis improves with ligand bulk for $\text{Cp}'\text{ReO}_3$ type catalysts.

In our previous work, we found a difference in the kinetic profile of the DODH reaction of 1,2-octanediol when either $\text{Cp}^{\text{III}}\text{ReO}_3$ or $\text{Cp}^{\text{II}}\text{ReO}_3$ was used as catalyst.^[17] A clear induction period was observed for the $\text{Cp}^{\text{III}}\text{ReO}_3$ -catalyzed DODH reaction, while there was almost no induction period for the $\text{Cp}^{\text{II}}\text{ReO}_3$ -catalyzed reaction. This observation was a further indication that the Cp-ligand structure has an effect on DODH catalysis, not only in terms of activity and selectivity, but also in terms of kinetics and catalyst evolution.

In order to further investigate catalyst evolution under catalytic conditions, the catalytic DODH of 1,2-octanediol by a number of $\text{Cp}'\text{Re}$ complexes was examined using *in situ* NMR experiments. Considering side reactions of secondary alcohols and possible peak overlap, the following reaction conditions were chosen: 1,2-octanediol (0.05 mmol), PPh_3 (0.055 mmol, 1.1 equiv.), mesitylene (0.05 mmol, 1.0 equiv, internal standard), Re-catalyst (10 mol % Re), toluene- D_8 (0.5 mL), 135 °C, N_2 .

In the experiment using $\text{Cp}^{\text{II}}\text{ReO}_3$, peaks in the vinylic and the allylic region, e.g. between 6.30–5.70 and 2.85–2.70 ppm, started to appear from the very start of the experiment (see Supporting Information). These peaks could be assigned to free $\text{Cp}^{\text{II}}\text{H}$ ligand. The observation of free ligand during catalysis was interpreted to originate from ligand dissociation. In a similar manner, ligand dissociation was also observed in the experiment using $\text{Cp}^{\text{III}}\text{ReO}_3$, albeit at a slower rate than for $\text{Cp}^{\text{II}}\text{ReO}_3$. In the former case, 60% of ligand dissociation occurred after 5 min, during which 8% of 1-octene was formed. After 30 min, maximum ligand dissociation (94%) was reached, and the DODH reaction finished after 50 min at 88% 1-octene yield (Figure 1, top). When $\text{Cp}^{\text{III}}\text{ReO}_3$ was used as catalyst, maximum ligand dissociation (27%) was reached at 80 min, and the DODH reaction finished after 150 min at 93% product yield (Figure 1, middle). In this case, NMR signals related to typical $\text{Cp}'\text{Re}$ -based reaction intermediates like $\text{Cp}'\text{Re}$ -glycolates were also observed (see Supporting Information).^[27]

The time course profile of the olefin generation matches our previous results, i.e. there is no clear induction period for the $\text{Cp}^{\text{II}}\text{ReO}_3$ -catalyzed DODH reaction, while there is an obvious induction period for the $\text{Cp}^{\text{III}}\text{ReO}_3$ -catalyzed reaction. In addition, initial olefin product formation is related to the rate of ligand dissociation, while the final amount of product is not related to the extent of overall ligand dissociation.

The observation of ligand dissociation raises questions on the nature of the active species in $\text{Cp}'\text{ReO}_3$ -catalyzed DODH reactions. We have therefore also examined ligand dissociation for some other molecular $\text{Cp}'\text{Re}$ complexes under catalytic conditions using the NMR protocol. The tetranuclear Re-complex $\text{Cp}^{\text{II}}\text{Re}_2\text{O}_3(\text{ReO}_4)_2$, which is formed by stirring $\text{Cp}^{\text{II}}\text{ReO}_3$ in dichloromethane overnight at room temperature, was earlier reported to catalyze the DODH reaction.^[17] Also for this complex, free $\text{Cp}^{\text{II}}\text{H}$ ligand was detected during the reaction. Interestingly, ligand dissociation was even faster than for $\text{Cp}^{\text{II}}\text{ReO}_3$; 88% of ligand dissociation occurred after 10 min and the DODH reaction was finished in about 50 min at 90% product yield and without a significant induction period (Figure 1, bottom). Re(V) -diolate species have been reported as intermediates in DODH reactions from which olefin extrusion takes place to form Re(VII) trioxo species to close the catalytic cycle.^[8] The $\text{Cp}'\text{ReO}(\text{OCH}_2\text{CH}_2\text{O})$ complexes ($\text{Cp}' = \text{Cp}^{\text{II}}, \text{Cp}^{\text{III}}$) were synthesized on the basis of a reported procedure.^[28] Investigation of these glycolate complexes using the same NMR experiment showed that these have similar DODH reaction and ligand dissociation profiles as the corresponding trioxo-Re species (see Supporting information). When $\text{Cp}^{\text{II}}\text{ReO}(\text{OCH}_2\text{CH}_2\text{O})$ was used as catalyst, the signals of $\text{Cp}^{\text{II}}\text{ReO}(\text{OCH}_2\text{CH}_2\text{O})$ disappeared almost at the beginning of the

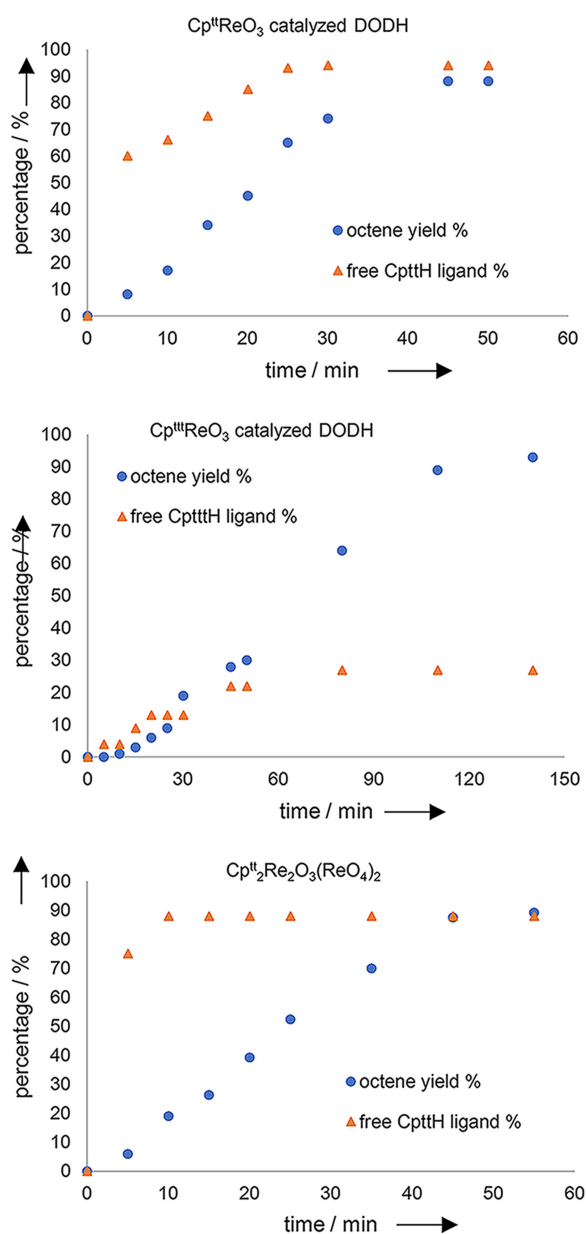


Figure 1. *In situ* NMR experiments of Cp*ReO₃-catalyzed DODH of 1,2-octanediol; monitoring of product yield and free Cp* ligand formation (for details see Supporting Information). Reaction conditions: 1,2-octanediol (0.05 mmol), PPh₃ (0.055 mmol, 1.1 equiv.), mesitylene (0.05 mmol, 1.0 equiv, internal standard), Re-catalyst (10 mol% Re), toluene-D₈ (0.5 mL), 135 °C, N₂.

reaction. When Cp**ReO(OCH₂CH₂O) was used as catalyst, it was slowly converted in around 30 min, and next to olefin product formation concomitant formation of Cp**ReO-octanediolate was also observed.

Since ligand dissociation was observed for all Cp*Re complexes tested above, one could hypothesize that the actual active species in these systems does not contain a Cp* ligand. The same catalytic NMR-experiment was therefore carried out using a perrhenate devoid of a Cp*-ligand as catalyst, i.e. Bu₄NReO₄. In this case, no olefin product formation could be detected at all. For perrhenate-catalyzed DODH of aliphatic diols,^[29–35] either a long reaction time (> 24 h) or a high catalyst

loading (10 mol%) is needed in order to reach full conversion. Besides, even in the case of full conversion of aliphatic diols and polyols, product selectivity was not as high as for Cp*ReO₃ systems. Especially, for the DODH of glycerol, when lutidinium perrhenate was used as catalyst, only moderate amounts (21 %) of allyl alcohol were formed,^[33] while glycerol is almost quantitatively converted to allyl alcohol using Cp*ReO₃. These data strongly indicate that inorganic perrhenate is not the active species in Cp*ReO₃-catalyzed DODH reactions. We also compared our Cp*ReO₃ catalyst with another homogenous trioxo-rhenium catalyst, MTO (MeReO₃).^[13,14] For the DODH of simple diols, both of them show good activity. For more complicated polyol substrates like sugar alcohols and sugars, the two catalysts have a very different product selectivity. This notion indicates that the active species in the case of Cp*ReO₃ and MTO are not the same.

Conclusions

In conclusion, we have shown efficient catalytic DODH reactions of vicinal diols and biomass-derived polyols to olefins using the new Cp*ReO₃ catalyst. Secondary alcohols like 3-octanol and 3-pentanol are the reductant and solvent of choice for these reactions. Under optimized reaction conditions, Cp*ReO₃ not only initiates the catalytic conversion of vicinal diols into olefins at high yields, but also exhibits an excellent activity for biomass-derived polyols. Specifically, when using Cp*ReO₃ as catalyst, glycerol is almost quantitatively converted to allyl alcohol and mucic acid gives 75% of muconates at 91% conversion. Besides, the loading of Cp*ReO₃ can be reduced to 0.1 mol% to achieve a turn-over number as high as 900 per Re in the DODH of glycerol, indicating a rather stable active species. Time course profile experiments have shown ligand dissociation during the reaction with different dissociation rates for different substituted Cp* ligands. In addition, ligand dissociation seems to be related to (initial) catalytic activity. These observations raise questions on the nature of the active species in DODH catalysis, on the role of the Cp* ligand in catalysis, and in a more general sense on the relation between the Cp* ligand structure and the stability of the corresponding Cp*ReO₃ complexes. Comparison with perrhenate salts seems to rule out a simple and purely inorganic active species in DODH catalysis using Cp*ReO₃ complexes. Current investigations in our laboratories focus on further DODH catalyst development and optimization, and on deciphering the role of organometallic, ligand-based species and the nature of active species in DODH catalysis.

Experimental Section

All chemicals including solvents were degassed by either freeze-pump-thaw cycles or degasification under vacuum. Triphenylphosphine was crystallized in ethanol and dried under vacuum. Unless otherwise stated, all other commercial chemicals were used without further purification. NMR spectra were recorded on a Varian VNMRS400 (400 MHz) at 298 K. ESI-MS spectra were recorded using a

Waters LCT Premier XE instrument. GC measurements were performed using a Perkin Elmer Autosystem XL Gas Chromatograph equipped with a Perkin Elmer Elite-17 column (Length: 30 m, I.D.: 0.32 mm, Film thickness: 0.50 μm), and with FID detector. GC method: 40 $^{\circ}\text{C}$, 5 min; 3 $^{\circ}\text{C}/\text{min}$ to 55 $^{\circ}\text{C}$; 20 $^{\circ}\text{C}/\text{min}$ to 250 $^{\circ}\text{C}$; 250 $^{\circ}\text{C}$, 10 min. All olefinic products are known compounds and were calibrated against mesitylene for quantification.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: homogenous catalysts · deoxydehydration · biomass conversion · trioxo-rhenium complexes · ligand design

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