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

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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\textsuperscript{\text{tt}}ReO\textsubscript{3} as a new catalyst (Cp\textsuperscript{\text{tt}} = 1,3-di-tert-butylcyclopentadienyl). The DODH reaction was optimized using 2 mol% of Cp\textsuperscript{\text{tt}}ReO\textsubscript{3} and 3-octanol as both reductant and solvent. The Cp\textsuperscript{\text{tt}}ReO\textsubscript{3} catalyst exhibits an excellent activity for biomass-derived polyols. Specifically, glycerol is almost quantitatively converted to allyl alcohol and mucic acid giving 75% of muconates at 91% conversion. In addition, the loading of Cp\textsuperscript{\text{tt}}ReO\textsubscript{3} 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.[3-14] 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 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.[2] In this very early work, a Cp\textsuperscript{\text{tt}}ReO\textsubscript{3} complex (Scheme 1, left) was used to catalytically convert polyols into olefins. Later, Gable and co-workers studied olefin extrusion reactions from Tp\textsuperscript{\text{tt}}Re(glycolate) complexes (Tp\textsuperscript{\text{tt}} = hydrido-tris-(3,5-dimethylpyrazolyl)borate), and in doing so used the 6e\textsuperscript{-} Tp\textsuperscript{\text{tt}} ligand as an alternative for the 6e\textsuperscript{-} Cp\textsuperscript{\text{tt}} ligand.[15] Recently, we reported on a bulky Cp\textsuperscript{\text{tt}} based trioxo-rhenium catalyst, Cp\textsuperscript{\text{tt}}ReO\textsubscript{3} (Cp\textsuperscript{\text{tt}} = 1,2,4-tri-tert-butylcycloocta- dienyl, 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\textsuperscript{\text{tt}} 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\textsuperscript{\text{tt}}ReO\textsubscript{3}-catalyzed DODH of 1,2-octanediol, while there was almost no induction period in the reaction catalyzed by the Cp\textsuperscript{\text{tt}}ReO\textsubscript{3} complex (Cp\textsuperscript{\text{tt}} = 1,3-di-tert-butylcyclooctadienyl, Scheme 1, right). This result encouraged us to further investigate the catalytic properties of the less bulky Cp\textsuperscript{\text{tt}}ReO\textsubscript{3} complex. Here, we report on the DODH of diols and biomass-derived polyols using Cp\textsuperscript{\text{tt}}ReO\textsubscript{3}.

Results and Discussion

We started our investigation on the use of Cp\textsuperscript{\text{tt}}ReO\textsubscript{3} as a catalyst for the DODH of vicinal diols into olefins using 1,2-octanediol as a substrate (Table 1). Initial reactions were performed with 2 mol% Cp\textsuperscript{\text{tt}}ReO\textsubscript{3} at 135 °C in chlorobenzene and 1.1 equivalent of sacrificial reducing agent under an inert nitrogen atmosphere. The use of triphenylphosphine (PPh\textsubscript{3}) as a

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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 Cp^ttReO_3 as catalyst and 3-octanol as reductant (entry 7). In our previous studies on the bulkier Cp^ttReO_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 Cp^ttReO_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). 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 Cp^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 Cp^ReO_3 catalyst are quite similar to those with the Cp^ttReO_3 catalyst.

When Cp^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 Cp^ttReO_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 Cp^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,[21] was converted to 1,3-butanediol (69%) with 2,5-dihydrofuran (5%) as by-product under optimized reaction conditions (entry 7). Another C_6 sugar alcohol, DL-threitol, gave 71% of 1,3-butanediol with 13% of 1,4-anhydrothreitol as by-product (entry 8). With these two reactions, 1,3-butanediol, 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-butanediol yield of 87 and 90%, respectively (entry 9 and 10). We also observed that even under aerobic conditions erythritol gave 57% of 1,3-butanediol at 87% conversion with 4% of 2,5-dihydrofuran as by-product (en-
try 11). For the Cp"ReO₃-catalyzed DODH of erythritol and D-threitol, 1,3-butadiene was formed at a lower 67 and 59 % yield, respectively, under N₂ at 170 °C.

For the very useful deoxydehydration of glycerol, we planned to investigate this reaction with different Cp"ReO₃ 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 alcohol,³¹ 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 Cp"ReO₃ 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.

Encouraged by the results of Cp"ReO₃-catalyzed DODH reactions of glycerol and C₂ sugar alcohols, we then tested the C₅ 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 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 under modified reaction conditions, when our previous Cp"ReO₃ catalyst was uses as reductant and solvent for the DODH of glycerol.

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.²³ An alternative way to produce adipic acid is using sustainable muconic acid to form muconates through DODH chemistry, followed by hydrogenation and hydrolysis.²⁶ Accordingly, we have investigated the activity of the Cp"ReO₃ catalyst in the DODH of muconic acid. Under modified reaction conditions, muconic 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 Cp"ReO₃ 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
were chosen: 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. [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.

Table 3. DODH of sugars to 2-vinylfuran (2-VF) and furan catalyzed by CptttReO₃.[a]

| Entry | Sugar   | Conditions | Yield[b] [%] | Ratio (2-VF : furan) |
|-------|---------|------------|--------------|----------------------|
| 1     | D-glucose | 3-pentanol, 135 °C, 15 h | 8 | 1.7 : 1 |
| 2     | D-galactose | 3-pentanol, 135 °C, 15 h | 22 | 2 : 1 |
| 3     | D-mannose  | 3-pentanol, 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, 135 °C, 12 h | trace | – |
| 8     | 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), CptttReO₃ (0.01 mmol, 2 mol %), N₂. [b] No 2-VF formation.

In the experiment using CptttReO₃, peaks in the vinylic and allylic region, e.g. between 6.30 – 6.70 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 CptttH 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 CptttReO₃, albeit at a slower rate than for CptttReO₃. 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 CptttReO₃ 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 CpRe-based reaction intermediates like CpRe-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 CpOReO3-catalyzed DODH reaction, while there is an obvious induction period for the CpOReO3-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 CpOReO3-catalyzed DODH reactions. We have therefore also examined ligand dissociation for some other molecular CpRe complexes under catalytic conditions using the NMR protocol. The tetranuclear Re complex CpOReO3(OCH2CH2O), which is formed by stirring CpOReO3 in dichloromethane overnight at room temperature, was earlier reported to catalyze the DODH reaction.17 Also for this complex, free CpH ligand was detected during the reaction. Interestingly, ligand dissociation was even faster than for CpOReO3 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(VI)-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.28 The CpOReO3(OCH2CH2O) complexes (Cp′ = Cp, Cp′′) 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 CpOReO3(OCH2CH2O) was used as catalyst, the signals of CpOReO3(OCH2CH2O) disappeared almost at the beginning of the reaction. When CpOReO3(OCH2CH2O) was used as catalyst, it was slowly converted in around 30 min, and next to olefin product formation concomitant formation of CpOReO3-octanediol was also observed.

Since ligand dissociation was observed for all CpRe 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 perrenenate devoid of a Cp′-ligand as catalyst, i.e. Bu3NReO4. In this case, no olefin product formation could be detected at all. For perrenenate-catalyzed DODH of aliphatic diols,22-24 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 CpOReO3 systems. Especially, for the DODH of glycerol, whenlutidinium perrenenate was used as catalyst, only moderate amounts (21%) of allyl alcohol were formed,23 while glycerol is almost quantitatively converted to allyl alcohol using CpOReO3. These data strongly indicate that inorganic perrenenate is not the active species in CpOReO3-catalyzed DODH reactions. We also compared our CpOReO3 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 CpOReO3 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 CpOReO3 catalyst. Secondary alcohols like 3-octanol and 3-pentanol are the reductant and solvent of choice for these reactions. Under optimized reaction conditions, CpOReO3 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 CpOReO3 as catalyst, glycerol is almost quantitatively converted to allyl alcohol and mucic acid gives 75% of muconates at 91% conversion. Besides, the loading of CpOReO3 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 CpOReO3 complexes. Comparison with perrenenate salts seems to rule out a simple and purely inorganic active species in DODH catalysis using CpOReO3 complexes. Current investigations in our laboratories focus on further DODH catalyst development and optimization, and on deciphering the role of organo-metallic, 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 VNMRS500 (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°C, 5 min; 3°C/min to 55°C; 20°C/min to 250°C; 250°C, 10 min. All olefinic products are known compounds and were calibrated against mestilen for quantification.
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Conflict of Interest

The authors declare no conflict of interest.

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