

A Cp-based Molybdenum Catalyst for the Deoxydehydration of Biomass-derived Diols

Jing Li,^[a] Martin Lutz,^[b] and Robertus J. M. Klein Gebbink*^[a]

Dioxo-molybdenum complexes have been reported as catalysts for the deoxydehydration (DODH) of diols and polyols. Here, we report on the DODH of diols using $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ as catalyst ($\text{Cp}^* = 1,2,3,4,5\text{-pentamethylcyclopentadienyl}$). The DODH reaction was optimized using 2 mol% of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$, 1.1 equiv. of PPh_3 as reductant, and anisole as solvent. Aliphatic vicinal diols are converted to the corresponding olefins by $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ in up to 65% yield (representing over 30 turnovers per catalyst) and 91% olefin selectivity, which rivals the performance of other Mo-based DODH catalysts. Remarkably, *cis*-1,2-cyclohexanediol, which is known as quite a challenging substrate for

DODH catalysis, is converted to 30% of 1-cyclohexene under optimized reaction conditions. Overall, the mass balances (up to 79%) and TONs per Mo achievable with $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ are amongst the highest reported for molecular Mo-based DODH catalysts. A number of experiments aimed at providing insight in the reaction mechanism of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ have led to the proposal of a catalytic pathway in which the $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ catalyst reacts with the diol substrate to form a putative nonsymmetric dimeric diolate species, which is reduced in the next step at only one of its Mo-centers before extrusion of the olefin product.

Introduction

Deoxydehydration (DODH), known as a combination of deoxygenation and dehydration, provides an efficient means for removing vicinal hydroxyl groups from diols and polyols to form the corresponding olefins.^[1] DODH reactions allow for high oxygen-content starting materials, such as cellulosic biomass derivatives, to be converted into useful olefins. Next to a number of heterogeneous catalysts, soluble metal complexes based on rhenium,^[1–4] vanadium,^[5–13] and molybdenum,^[14–23] have been reported to catalyze the DODH of diols and polyols. In terms of activity and selectivity, rhenium complexes so far outperform homogeneous catalysts based on vanadium and molybdenum. However, the scarcity and high cost of rhenium asks for the availability of alternative catalysts based on less expensive and more abundant metals, such as Mo and V. It is for this reason that there is a current interest in the develop-

ment of homogeneous catalysts derived from these latter metals for the DODH of (biomass-derived) diols and polyols.

For the homogeneous molybdenum-catalyzed DODH of diols and polyols, a relatively limited number of examples have been reported,^[24] mainly including the use of molybdate salts^[15–17,21] or dioxo-Mo(VI) complexes.^[14,18–20] Ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, AHM), a commercially available molybdate salt, has been reported as a catalyst for the deoxydehydration of diols. The first example was reported by Frirstrup and co-workers in 2014.^[21] Using 0.5 mol% of AHM in a reactive distillation set-up, 16% of 1-hexene was formed as well as 5% of 2-hexanone (dehydration product of 1,2-hexanediol) in neat 1,2-hexanediol, after heating the mixture at 190–220 °C. Under these conditions, 1,2-hexanediol serves as substrate, solvent, as well as sacrificial reductant. Based on a density functional theory (DFT) study, the authors proposed a catalytic cycle that involves the condensation of two diols with a Mo(VI)-trioxo species to form an oxo-Mo(VI) bisdiolate intermediate, subsequent oxidative cleavage of one of the diolate ligands resulting in a reduced oxo-Mo(IV) monodiolate species, formaldehyde and an aldehyde (for example formaldehyde and pentanal through oxidative cleavage of 1,2-hexanediol), followed by a final olefin extrusion step that also forms back the trioxo-Mo(VI) species (Scheme 1, a).^[17] Operating through this proposed mechanism, this catalytic system forms carbonyl compounds either via the oxidative cleavage of a diol or via the dehydration of the diol. These carbonyl compounds can further react with the diol substrate to generate ketals (Scheme 2). For this reason, the olefin product selectivity of the DODH catalyzed by AHM will be substantially lower compared to the Re-catalyzed DODH of diols.

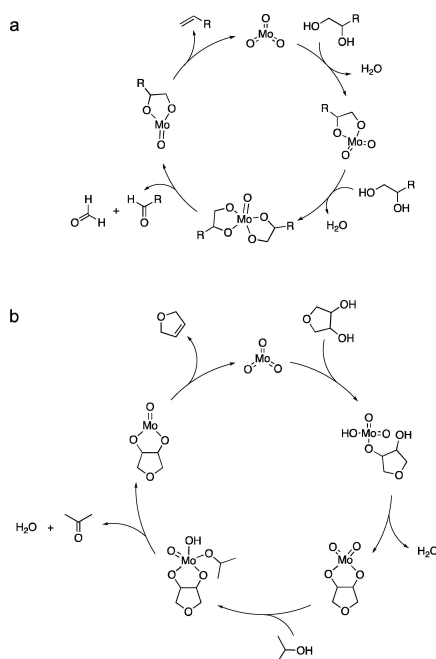
The secondary alcohol isopropanol was then used as the sacrificial reductant in the AHM-catalyzed deoxydehydration reaction.^[16] In this case, the reaction proceeded at 240–250 °C in a pressurized autoclave, and the olefin yield from simple

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

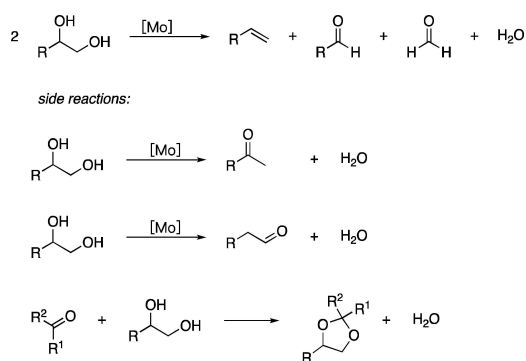
[b] Dr. M. Lutz
Crystal and Structural Chemistry
Bijvoet Centre for Biomolecular Research
Faculty of Science
Utrecht University
Padualaan 8
3584 CH, Utrecht (The Netherlands)

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cctc.202001115>

© 2020 The Authors. Published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.



Scheme 1. Proposed catalytic cycles for AHM-catalysed DODH of diols based on DFT studies: a) using the diol itself as reductant,^[17] b) using iPrOH as reductant.^[16]



Scheme 2. Mo-catalyzed DODH of diols and side reactions observed when using the diol itself as sacrificial reductant.^[15]

aliphatic diols was as high as 77% when NBu_4OH was added to the reaction (46% of 1-hexene was formed from 1,2-hexanediol when no base was applied). The authors claimed that the use of this particular base would not only affect the alkene yield but also change the product distribution. The use of a number of other bases did not lead to an overall improvement in catalysis, which the authors explained as a result of the high solubility of the $(\text{Bu}_4\text{N})_2\text{MoO}_4$ salt, while other molybdate salts are quite insoluble. On the basis of DFT calculations, the reduction step under these conditions was found to be most favorable when both a diolate and an isopropoxide ion are coordinated to the molybdenum center (Scheme 1, b). The computed catalytic cycle consists of the condensation of the diol with MoO_3 in two steps to form the dioxo-Mo(VI) diolate, followed by coordination of the isopropoxide and reduction to form an oxo-Mo(IV)

diolate, water and acetone, and finally olefin extrusion. These calculations furthermore showed that the reduction of the metal center prior to extrusion of the alkene is rate-limiting under these conditions. Not only alcohols were investigated as reductant for AHM-catalyzed DODH, Na_2SO_3 was also applied for this reaction. John and co-workers reported on the Na_2SO_3 -mediated AHM-catalyzed DODH of diols using 5 mol% of AHM as catalyst and 1.5 equiv. of Na_2SO_3 as reductant. This allowed for 23% formation of styrene from 1-phenylethane-1,2-diol.^[21] For all these AHM-catalyzed DODH systems, the TON per “ MoO_2 ” unit was quite low, at maximum less than 5.

Only four examples have been reported of diol DODH catalysed by ligand-supported “ MoO_2 ” complexes. In 2013, a dioxo-Mo(VI) complex bearing an acylpyrazolonate ligand was reported as a DODH catalyst.^[14] This complex is able to form 10% of styrene from 60% conversion of 1-phenylethane-1,2-diol using a catalyst loading of 2 mol% and 1.1 equiv. of PPh_3 as the sacrificial reductant. The reaction can be carried out at a reaction temperature of only 110°C , which is quite low for a Mo-catalyzed DODH reaction. Octahedral dioxo-Mo(VI) complexes derived from (OSSO)-type bis(phenolate) ligands were reported as DODH catalyst precursors by Okuda and co-workers in 2016.^[18] 1,4-Anhydroerythritol was successfully converted into 2,5-dihydrofuran with 49% product yield and 89% substrate conversion using 5 mol% of Mo complex and 3-octanol as reductant within 1 h at 200°C under microwave irradiation. According to the authors, microwave irradiation prevents the use of high reaction temperatures and long reaction times. Last year, $\text{MoO}_2(\text{acac})_2$ catalysed DODH reactions were reported by De Vos *et al.*^[19] It was shown that the addition of the β -diketone 2,2,6,6-tetramethylheptanedione (TMHDH) leads to a strong increase in yield of the desired olefin product. The excess amount of the diketone ligand (4.0 equiv. on the basis of substrate) was claimed to stabilize the Mo complexes and inhibit catalyst decomposition through oligomerization of Mo, which is the proposed decomposition pathway of Mo DODH-catalysts. Very recently, Kilyanek *et al.* reported a dioxo-molybdenum complex supported by a dianionic ONO pincer ligand, which catalyzes the DODH of diols using PPh_3 , Na_2SO_3 , Zn, C, 3-octanol or 2-propanol as reductant.^[20] For these ligand-supported “ MoO_2 ” DODH catalysts similarly low TONs per “ MoO_2 ” were found as for the AHM systems; the highest TON being around 9.

Overall, there has not been a lot of activity in the research field of homogeneous Mo-based DODH-catalysis. Next to the overall number of reported studies, in particular the number of ligands that have been applied in this field is rather limited. From our experience in Re-catalyzed DODH-reactions, substituted cyclopentadienyl (Cp) ligands represent a versatile ligand platform for the development of different trioxo-Re complexes and their application in DODH-catalysis.^[25–27] Previous studies have shown that the catalytic properties of CpReO_3 type complexes in DODH reactions are affected by modifications of the Cp ligand. We were therefore curious to investigate if the corresponding Cp-based Mo-complexes would also show catalytic activity towards the deoxydehydration of diols and polyols.

Results and Discussion

For our studies on Cp-based molybdenum-oxo complexes in DODH catalysis, we have considered the use of a number of different complexes. The dinuclear oxo-bridged complex $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ ^[28] was first reported by Herberhold and Thewalt *et al.* in 1985.^[29] This complex can be synthesized either by direct oxidation of suitable low-valent precursors (typically carbonyl-based precursors), or by hydrolysis of easily accessible high-valent precursors.^[28] This oxophilic complex has earlier been reported as a catalyst for the epoxidation of olefins.^[30,31] The bulkier $[\text{Cp}^t\text{MoO}_2]_2\text{O}$ complex, derived from the 1,3-di-*tert*-butylcyclopentadienyl ligand, was also synthesized according to a literature procedure starting from $\text{Mo}(\text{CO})_6$.^[32,33] The substituted cyclopentadiene preligand Cp^tH was refluxed with $\text{Mo}(\text{CO})_6$ in *p*-xylene overnight under nitrogen to form $[\text{Cp}^t\text{Mo}(\text{CO})_2]_2$, which was oxidized by stirring under air for 3 days to obtain the target dinuclear $[\text{Cp}^t\text{MoO}_2]_2\text{O}$ complex as yellow needle-like crystals. Previous work discussed above has shown that the active site of Mo-based DODH-catalysts is based on the “ MoO_2 ” motif. Accordingly, these bridged Cp-based MoO_2 dimers could be interesting catalyst candidates for DODH reactions.

Besides, considering that the Cp-based trioxo-rhenium catalysts are mononuclear species, the $[\text{Cp}^*\text{MoO}_3]^-$ anion would be a close structural analogue of the CpRe-catalysts. On basis of a literature report, $\text{NBu}_4[\text{Cp}^*\text{MoO}_3]$ was synthesized by slowly adding a NBu_4OH solution into a $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ solution in THF, to form colorless crystals of $\text{NBu}_4[\text{Cp}^*\text{MoO}_3]$ after recrystallization in THF at -30°C .^[34] In this case, it would be interesting to investigate which effect the difference in overall charge of the complex will have on catalytic activity. In addition, no trioxo-molybdenum complexes have so far been investigated for DODH reactions. Alternatively, the Cp-based ligand could be replaced by a different and neutral $6e^-$ spectator ligand, for example Me_3tacn (1,4,7-trimethyl-1,4,7-triazacyclononane). The complex $(\text{Me}_3\text{tacn})\text{MoO}_3$ has been synthesized on the basis of a literature procedure reported by McGowan *et al.* from 2001.^[35]

Accordingly, we started our investigations on Mo-based DODH-catalysis by screening a number of reported Mo-complexes for their activity in the DODH reaction of 1,2-octanediol to form 1-octene, using PPh_3 as the reductant and anisole as solvent. The reaction was performed at 200°C under an N_2 atmosphere for 15 h in a closed pressure tube with a catalyst loading of 4% based on Mo (Table 1). When $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ and $[\text{Cp}^t\text{MoO}_2]_2\text{O}$ were used as catalyst, they gave almost the same 1-octene yield (55%, 51%) at full substrate conversion (entries 1 and 2). For the corresponding mononuclear species, $\text{NBu}_4[\text{Cp}^*\text{MoO}_3]$, the 1-octene yield was 38% at full substrate conversion (entry 3). Yet, changing catalyst to the trioxo-complex $(\text{Me}_3\text{tacn})\text{MoO}_3$ gave a 1-octene yield of only 9% at 38% of substrate conversion (entry 4). This observation suggests that the anionic Cp-ligand is preferred over a neutral $6e^-$ ligand like Me_3tacn in enabling DODH reactivity with Mo. Remarkably, when the commercially available $\text{MoO}_2(\text{acac})_2$ complex was applied under our reaction conditions, the 1-octene yield was 47% with full substrate conversion, which was

Table 1. Mo-catalyzed DODH of 1,2-octanediol with different Mo complexes.^[a]

| Entry | [Mo] | Yield ^[b] [%] | Conversion ^[b] [%] | Alkene selectivity [%] |
|------------------|--|-----------------------------|----------------------------------|---------------------------|
| 1 | $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ | 55 | > 99 | 55 |
| 2 | $[\text{Cp}^t\text{MoO}_2]_2\text{O}$ | 51 | > 99 | 51 |
| 3 | $\text{NBu}_4[\text{Cp}^*\text{MoO}_3]$ | 38 | > 99 | 38 |
| 4 | $(\text{Me}_3\text{tacn})\text{MoO}_3$ | 9 | 38 | 24 |
| 5 | $\text{MoO}_2(\text{acac})_2$ | 47 | > 99 | 47 |
| 6 | $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ | 38 | 87 | 44 |
| 7 ^[c] | $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ | 38 | > 99 | 38 |
| 8 ^[d] | $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ | 38 | > 99 | 38 |

[a] Reaction conditions: 1,2-octanediol (0.5 mmol), PPh_3 (0.55 mmol, 1.1 equiv.), Mo complex (4 mol% on the basis of Mo), anisole (5 mL), 200°C (temperature of oil bath), 15 h, N_2 , closed pressure tube. Reported values are the average of three independent runs. [b] Determined by gas chromatography using mesitylene (0.5 mmol) as an internal standard. [c] 6 mol% of NBu_4OH was added as a 1 M solution of NBu_4OH in methanol. [d] Under aerobic conditions.

also quite acceptable (entry 5). The commercially available AHM was also tested here and 38% of 1-octene had formed from 87% of 1,2-octanediol conversion (entry 6).

Among the molybdenum complexes we have tested, $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ gave the highest olefin yield as well as alkene product selectivity, but still not as high as in some rhenium-catalyzed DODH reactions. Since the use of NBu_4OH was reported to significantly improve the olefin yield for AHM-catalyzed DODH,^[16] we examined the effect of this additive. Yet, the use of NBu_4OH did not increase the olefin yield when $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ was used as catalyst (entry 7). The olefin yield and substrate conversion in this case were the same as when using $\text{NBu}_4[\text{Cp}^*\text{MoO}_3]$ as the catalyst (entry 3). This result is in line with the visual changes while setting up the reaction: the reaction mixture changed color from bright yellow to colorless when adding NBu_4OH , which indicates the *in situ* formation of $\text{NBu}_4[\text{Cp}^*\text{MoO}_3]$. Furthermore, 38% of 1-octene was formed when $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ was used as catalyst under aerobic condition (entry 8). This finding is suggestive of the formation of trioxo-molybdenum species under aerobic conditions. Last but not the least, 30% conversion of 1,2-octanediol was observed in the absence of any catalyst under the reaction conditions, albeit without olefin formation. This result indicates that thermal substrate degradation can take place to a substantial extent during the reaction. So far, we have not been able to track down which organic products form during this thermal reaction.

In conclusion, from all the Mo catalysts we have tested here, $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ gave the highest 1-octene yield as well as alkene product selectivity. Accordingly, $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ was used in further optimization studies. Its higher reactivity compared to that of the mononuclear trioxo complex $\text{NBu}_4[\text{Cp}^*\text{MoO}_3]$ could suggest that it operates via a dinuclear mechanism, instead of breaking up in monomeric entities during catalysis (*vide infra*). If so, the reactivity of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ is significantly higher than that of $\text{MoO}_2(\text{acac})_2$ per catalytic entity. The low to moderate alkene product selectivity indicates that side reactions take place when using $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ as catalyst. Except 1-octene, 2,4-

dihexyl-1,3-dioxolane and 2-heptyl-4-hexyl-1,3-dioxolane were detected by GC and GC-MS (*vide infra*). These two products indicate the formation of 1-heptanal (oxidative C–C bond cleavage product of 1,2-octanediol) and 1-octanal (dehydration product of 1,2-octanediol). Accordingly, the side reactions for AHM-catalyzed DODH reaction described by Frstrup^[15] also take place for the [Cp*MoO₂]₂O catalyst. In addition, triphenylphosphine oxide (OPPh₃) was also detected by GC and GC-MS, which indicates that PPh₃ can also act as reductant for this catalyst. Accordingly, both PPh₃ and 1,2-octanediol may act as the reductant in the deoxydehydration of 1,2-octanediol by [Cp*MoO₂]₂O.

Continuing, different solvents were investigated in the DODH reaction of 1,2-octanediol with [Cp*MoO₂]₂O as catalyst (Table 2). Under neat conditions, 26% of 1-octene formed at 35% substrate conversion and an alkene product selectivity of 74% (entry 1). When substituted benzenes were used as the solvent, the 1-octene yield varied from 36% to 65% (entries 2–10), while very high substrate conversions of >90% could be reached for several solvents. The highest 1-octene yield (65%, representing over 30 turnovers per catalyst) was obtained by using *m*-dichlorobenzene as the solvent (entry 4), while the highest alkene selectivity (91%) was achieved by using 1,2,4-trichlorobenzene as solvent (entry 7). In the latter solvent, a somewhat lower substrate conversion of 44% was found after a reaction time of 15 h. In order to reach higher substrate conversion in this solvent, the reaction time was prolonged to 30 h, which gave an overall conversion of 59% and a 1-octene yield of 52%, leading to a slightly decreased alkene product selectivity of 88% (entry 12). This result indicates that catalyst

decomposition is likely to occur during prolonged reaction times. When either anisole or mesitylene were used as the reaction solvent, full substrate conversion resulted in 55% and 52% 1-octene yield, respectively (entries 9 and 10).

Although the halogenated benzene solvents *m*-dichlorobenzene and 1,2,4-trichlorobenzene gave the highest alkene yield and the highest alkene selectivity, respectively, these solvents were disregarded in our further catalytic studies because of the implications of their high halogen-content on practical applications. Alternatively, the Innovative Medicines Initiative (IMI)-Chem21, a public–private partnership of pharmaceutical companies, universities and small-to-medium enterprises supporting research into sustainable pharmaceuticals manufacturing (<http://www.chem21.eu/>), has listed anisole as a recommended solvent on the basis of safety (S), occupational health (H), environment (E), quality (risk of impurities in the drug substance), industrial constraints (e.g. boiling point, freezing temperature, density, recyclability), and cost.^[36,37] Accordingly, we set out to evaluate anisole as the solvent of choice for further catalyst optimization.

As mentioned above, both PPh₃ and 1,2-octanediol can act as sacrificial reductant in the DODH reaction catalyzed by [Cp*MoO₂]₂O. In order to enhance the formation of 1-octene, both the dehydration of 1,2-octanediol and the oxidative cleavage of 1,2-octanediol should be limited. The use of a more competitive reductant will then benefit alkene formation. Different reducing agents were tested for the DODH-reaction of 1,2-octanediol with [Cp*MoO₂]₂O as the catalyst (Table 3). Interestingly, when the more reducing PⁿBu₃ was used as reductant, a lower 1-octene yield (39%) was obtained compared to the use of PPh₃ (entries 1 and 2). The less reducing triethylphosphite gave a low 9% yield, albeit at full substrate conversion (entry 3). The use of indoline, Na₂SO₃, 3-octanol, or zinc powder as reductant gave 1-octene yields in the range of 20–32%. Without an additional reductant, *i.e.* only using the diol itself as reductant, 18% of 1-octene was formed (entry 8). Considering that the maximum yield of 1-octene is 50% in this case, the alkene product selectivity was 36%. On the basis of these findings, PPh₃ was selected as the reductant for further studies.

Table 2. [Cp*MoO₂]₂O-catalyzed DODH of 1,2-octanediol in different solvents.^[a]

| Entry | Solvent | Yield ^[b] [%] | Conversion ^[c] [%] | Selectivity ^[e] [%] | b.p. ^[f] [°C] |
|-------------------|---------------------------|--------------------------|-------------------------------|--------------------------------|--------------------------|
| 1 | – | 26 | 35 | 74 | – |
| 2 | PhCl | 37 | 94 | 39 | 132 |
| 3 | toluene | 36 | 95 | 38 | 111 |
| 4 | <i>m</i> -dichlorobenzene | 65 | 92 | 70 | 172–173 |
| 5 | <i>o</i> -dichlorobenzene | 46 | 70 | 66 | 178–180 |
| 6 | <i>p</i> -xylene | 36 | 97 | 40 | 138 |
| 7 | trichlorobenzene | 40 | 44 | 91 | 214 |
| 8 | ^t BuPh | 39 | 82 | 48 | 169 |
| 9 | anisole | 55 | >99 | 55 | 154 |
| 10 ^[d] | mesitylene | 52 | >99 | 52 | 163–166 |
| 11 | sulfolane | 5 | 28 | 18 | 285 |
| 12 ^[g] | trichlorobenzene | 52 | 59 | 88 | 214 |

[a] Reaction conditions: 1,2-octanediol (0.5 mmol), PPh₃ (0.55 mmol, 1.1 equiv.), [Cp*MoO₂]₂O (0.01 mmol, 2 mol%), solvent (5 mL), 200 °C (temperature of oil bath), 15 h, N₂, closed pressure tube. Reported values are the average of three independent runs. [b] Yield of 1-octene, determined by gas chromatography using mesitylene (0.5 mmol) as an internal standard. [c] Determined by gas chromatography using mesitylene (0.5 mmol) as an internal standard. [d] Determined by ¹H NMR using dibromomethane (0.5 mmol) as an internal standard. [e] Alkene product selectivity. [f] All solvents were purchased from Sigma-Aldrich, boiling points are reported on the basis of corresponding Safety Data Sheet. [g] Reaction time: 30 h.

Table 3. [Cp*MoO₂]₂O-catalyzed DODH of 1,2-octanediol with different reductants.^[a]

| Entry | Reductants | Yield ^[b] [%] | Conversion ^[b] [%] | Alkene selectivity [%] |
|------------------|---------------------------------|--------------------------|-------------------------------|------------------------|
| 1 | PPh ₃ | 55 | >99 | 55 |
| 2 | P ⁿ Bu ₃ | 39 | >99 | 39 |
| 3 | P(OEt) ₃ | 9 | >99 | 9 |
| 4 | indoline | 26 | 77 | 34 |
| 5 | Na ₂ SO ₃ | 24 | 98 | 24 |
| 6 | 3-octanol | 20 | 76 | 26 |
| 7 | Zn | 32 | 94 | 34 |
| 8 ^[c] | 1,2-octanediol | 18 | >99 | 36 |

[a] Reaction conditions: 1,2-octanediol (0.5 mmol), reductant (0.55 mmol, 1.1 equiv.), [Cp*MoO₂]₂O (0.01 mmol, 2 mol%), anisole (5 mL), 200 °C (temperature of oil bath), 15 h, N₂, closed pressure tube. Reported values are the average of three independent runs. [b] Determined by gas chromatography using mesitylene (0.5 mmol) as an internal standard. [c] 3-Octanol (5 mL) was used as solvent instead of anisole.

For most of the above reactions, very high substrate conversions were observed, indicating that other products than 1-octene dominate for most reducing agents. As described in the introduction, this phenomenon is not only observed for our Cp-based molybdenum system. Without excess amount of ligand or additives, low to moderate alkene product selectivities are typically obtained for Mo-catalysts. The use of excesses of organic ligands has been found to affect the alkene product selectivity. In case of the $\text{MoO}_2(\text{acac})_2$ -catalyzed DODH of 1,2-hexanediol, the yield of 1-hexene dramatically increased when 40 equiv. of TMHDH (on the basis of $\text{MoO}_2(\text{acac})_2$) were added. The alkene product selectivity was 93% and the TON per Mo was 9.^[19] By tuning the ligand on molybdenum increased alkene product selectivities can also be obtained. The alkene product selectivity is 70% with (OSSO)-type bis-phenolate ligands in the DODH of 1,4-anhydroerythritol, and 60% with a dianionic ONO pincer-type ligand in the DODH of 1,2-octanediol. The TON per Mo in these cases is 11 and 6, respectively.^[18,20] In our case, the application of the Cp* ligand also gives a quite good alkene product selectivity (55%) and TON per catalyst (27; *i.e.* 14 per Mo).

Given the fact that full substrate conversions were observed in many of the reactions described in Tables 1–3, the high reaction temperature that was employed could be the reason for the lower alkene product selectivities. Accordingly, different reaction temperatures were investigated (Table 4). No conversion was obtained at temperatures below 170 °C. When the reaction was performed at 170 °C, only 9% of 1-octene was formed while the substrate conversion was also 9%, which means that the alkene product selectivity was 100% albeit at a TON per Mo of only 2. When the reaction temperature was increased to 185 °C, the 1-octene yield increased from 9% to 13%, while the 1,2-octanediol conversion increased from 9% to 36%, so the alkene product selectivity dropped dramatically from 100% to 36%. When the reaction temperature was further raised to 190 °C, the 1-octene yield was 24%, the 1,2-octanediol conversion was 62%, and the alkene product selectivity of 39% was very close to the one at 185 °C. At an elevated reaction temperature of 225 °C, the same 1-octene yield was achieved compared to the reaction carried out at 200 °C. All the reactions described here were performed in a closed pressure tube and the temperatures are based on the temperature of the oil bath,

Table 4. $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ -catalyzed DODH of 1,2-octanediol at different temperature.^[a]

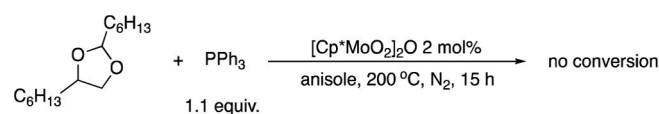
| Entry | Temperature [°C] | Yield ^[b] [%] | Conversion ^[b] [%] | Alkene selectivity [%] |
|-------|------------------|--------------------------|-------------------------------|------------------------|
| 1 | 170 | 9 | 9 | 100 |
| 2 | 185 | 13 | 36 | 36 |
| 3 | 190 | 24 | 62 | 39 |
| 4 | 200 | 55 | >99 | 55 |
| 5 | 225 | 55 | >99 | 55 |

[a] Reaction conditions: 1,2-octanediol (0.5 mmol), PPh_3 (0.55 mmol, 1.1 equiv.), $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ (0.01 mmol, 2 mol%), anisole (5 mL), 15 h, N_2 , in closed pressure tube. Reported values are the average of three independent runs. [b] Determined by gas chromatography using mesitylene (0.5 mmol) as an internal standard.

which means neither the actual temperature nor the pressure in the reaction tube could be monitored in this experimental setup. Table 4 clearly shows that an oil bath temperature of 200 °C is most optimal under the current reaction conditions. Comparing entry 4 and entry 5, olefin formation more than doubled by a 10 °C change in temperature. Moreover, the alkene product selectivity increased when the temperature was increased from 190 to 200 °C. An explanation for the latter observation could be that ketal formation during the reaction is reversible and that ketal formation is less favored at higher temperatures. Accordingly, a control experiment was done by using the ketal as substrate, but no ketal conversion was observed (Scheme 3), likely due to the lack of water in this control experiment. Water is required in the diol-ketal equilibrium to form the diol from the ketal.




As mentioned before, poor to moderate alkene product selectivities are generally obtained for Mo-catalyzed DODH reactions. For these reactions, it is believed that reduction of Mo *via* oxo-abstraction and *via* deformylation are competitive,^[20,23] which could explain why the alkene product selectivity is not very high. Also, it is known from literature that dehydration of the diol takes place in Mo-catalyzed DODH reactions as a side-reaction, forming ketone and aldehyde byproducts.^[15,16] Furthermore, ketals can be formed as by-products in reactions where carbonyl compounds are formed (Scheme 3). For our $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ -catalyzed DODH reactions, ketals were indeed detected by a combined GC and GC-MS analysis (Table 5), which is in line with findings by the Frstrup group.^[15] Two different ketals actually formed during these reaction: one derived from 1,2-octanediol and heptanal (the oxidative cleavage product of 1,2-octanediol) and one derived from 1,2-octanediol and octanal (the dehydration product of 1,2-octanediol).

In order to increase the alkene product selectivity, or to avoid the formation of by-products, several bases were tested by Frstrup and co-workers. The use of NBu_4OH did significantly increase the yield of olefin as well as change the distribution of products for the AHM catalyst.^[16] We did also use NBu_4OH as an additive for our reaction system, but did not notice an increase in the olefin yield (Table 2, entry 7). However, the use of NBu_4OH seems to change the distribution of product and by-products (Table 5, entry 3). Most importantly, less formation of 1-octene was noticed after applying this base (from 55% to 38%). In addition, there are some differences in the product distribution between directly using $\text{NBu}_4[\text{Cp}^*\text{MoO}_3]$ as catalyst and forming $\text{NBu}_4[\text{Cp}^*\text{MoO}_3]$ *in situ*, *i.e.* by applying a slight excess amount of base (compare Table 5, entries 2 and 3). It seems that less diol dehydration occurs, leading to a different ketal distribution; 1-octene formation is the same though in



Scheme 3. Use of 2,4-dihexyl-1,3-dioxolane as a DODH substrate to form 1-octene.

Table 5. Product profile in the DODH of 1,2-octanediol using different Mo catalysts.^[a]

| Entry | [Mo] |  |  |  | Conversion [%] | Mass balance [%] |
|------------------|---|---|---|--|----------------|------------------|
| 1 | [Cp*MoO ₂] ₂ O | 55 | 6 | 6 | > 99 | 79 |
| 2 | NBu ₄ [Cp*MoO ₃] | 38 | 7 | 8 | > 99 | 68 |
| 3 ^[b] | [Cp*MoO ₂] ₂ O | 38 | 11 | 4 | > 99 | 68 |

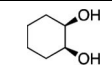
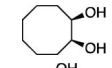
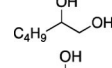
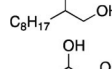
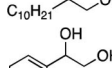
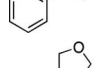
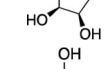
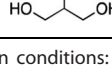
[a] Reaction conditions: 1,2-octanediol (0.5 mmol), PPh₃ (0.55 mmol, 1.1 equiv.), [Mo] (4 mol % on basis of Mo atom), anisole (5 mL), 200 °C, 15 h, N₂, closed pressure tube. Reported values are the average of three independent runs. Products were determined by gas chromatography using mesitylene (0.5 mmol) as an internal standard. [b] 6 mol % of NBu₄OH was added as a 1 M solution of NBu₄OH in methanol. [c]. mass balance = ((yield_(1-octene) + 2*yield_(2,4-dihexyl-1,3-dioxolane) + 2*yield_(2-heptyl-4-hexyl-1,3-dioxolane))/conversion)*100%.

these cases. Based on the ratio of different ketals formed, we are not able to distinct the operation of a dinuclear catalyst from that of a mononuclear catalyst, even though a significantly higher amount of olefin is formed when starting from a dinuclear catalyst.

The quantification of ketal by-products provides a clearer view of the overall mass balance of these reactions. Although far from being perfect, a mass balance close to 80 % was found for the [Cp*MoO₂]₂O catalyst. Since we observed 30 % of 'thermal' 1,2-octanediol conversion, *i.e.* in the absence of catalyst, the observed mass balances are quite acceptable. Last but not least, 2-octanone, *i.e.* the dehydration product of 1,2-octanediol, was difficult to detect because of peak overlap with solvent in the GC spectra. On the basis of Fristrup's work, an approximately equal amount of 2-decanone (detected as 2-decanone and 2-decanol) and decanal (detected as 1-decanol) was obtained.^[16] This result suggests that not only octanal but also 2-octanone will form from 1,2-octanediol while using a Mo-based catalyst.

Next, the substrate scope of the [Cp*MoO₂]₂O catalyst was investigated by applying different diols to the optimized reaction conditions. Both linear and cyclic aliphatic diols were tested (Table 6). In the case of linear diols, when 1,2-hexanediol was used as substrate, the 1-hexene yield was only 22 % (entry 3). Considering 1-hexene is quite a volatile chemical, we assume that the actual yield of 1-hexene could be higher. Other aliphatic diols with longer carbon chain lengths, such as 1,2-decanediol and 1,2-dodecanediol, were therefore tested (entry 4 and 5). The yield of 1-decene and 1-dodecene in these cases is very close to the olefin yield obtained from 1,2-octanediol under the same reaction conditions (55 %). When *cis*-1,2-cyclohexanediol and *cis*-1,2-cyclooctanediol were used as substrate, the corresponding olefin yield was 36 % and 30 %, respectively. Remarkably, for the Cp^{†††}ReO₃-catalyzed DODH of *cis*-1,2-cyclohexanediol, only 10 % of 1-cyclohexene is formed.^[25] In case of using 1,4-anhydroerythritol as substrate, only 5 % of 2,5-dihydrofuran was formed, mainly because of the poor solubility of 1,4-anhydroerythritol in anisole. In short, the [Cp*MoO₂]₂O catalyst system can be applied to the deoxydehydration of linear and cyclic aliphatic diols to form the corresponding olefins with moderate yields. Attempts to extend the substrate scope to aromatic diols lead to 47 % of styrene formation when starting from 1-phenyl-1,2-ethanediol, but in case of (1*R*,2*R*)-1,2-diphenylethane-1,2-diol and (1*R*,2*S*)-1,2-di-

Table 6. [Cp*MoO₂]₂O-catalyzed DODH of diols using PPh₃ as reductant.^[a]

| Entry | Substrate | Yield _{alkene} ^[b] [%] | Conversion ^[b] [%] | Alkene selectivity [%] |
|-------|--|--|-------------------------------|------------------------|
| 1 |  | 36 | 93 | 39 |
| 2 |  | 30 | > 99 | 30 |
| 3 |  | 22 | > 99 | 22 |
| 4 |  | 56 | > 99 | 56 |
| 5 |  | 51 | > 99 | 51 |
| 6 |  | 47 | > 99 | 47 |
| 7 |  | 5 | – | – |
| 8 |  | – | – | – |

[a] Reaction conditions: diol (0.5 mmol), PPh₃ (0.55 mmol, 1.1 equiv.), [Cp*MoO₂]₂O (0.01 mmol, 2 mol %), anisole (5 mL), 15 h, N₂, closed pressure tube. Data in this table is based on a single catalytic run. [b] Determined by gas chromatography using mesitylene (0.5 mmol) as an internal standard.

phenylethane-1,2-diol as substrate, only benzaldehyde was formed as a detectable product. This observation indicates that Mo-catalyzed cleavage of aromatic diols apparently outperforms DODH pathways.^[38,23]

Additionally, biomass-derived glycerol was investigated under the optimized reaction conditions (entry 8). No allyl alcohol was detected, likely due to the poor solubility of glycerol in anisole. No glycerol was dissolved in anisole during the reaction while [Cp*MoO₂]₂O did completely dissolve, resulting in a biphasic mixture during the reaction. Normally, a color changing from bright yellow to yellow-orange and ending with light brown was observed for [Cp*MoO₂]₂O-catalyzed DODH reactions. But in case of the reaction with glycerol, the anisole phase containing the catalyst maintained a bright yellow color, which indicated that no catalysis took place in this case. Neat conditions were also applied to this reaction, *i.e.* glycerol was explored as solvent, substrate, and reductant. [Cp*MoO₂]₂O did dissolve in glycerol at higher temperatures, but because of the reflux of glycerol in the top part of the

reaction tube, a black residue was obtained in the bottom of the reaction tube without formation of allyl alcohol.

The above study shows that the $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ complex can be used as a catalyst for the DODH of aliphatic diols using PPh_3 as reductant. In previous work of our group on related Re-based DODH catalysts, dissociation of the Cp-ligand was observed when using CpReO_3 type complexes as catalyst,^[27] in addition to an induction period in the case of using $\text{Cp}^{\text{III}}\text{ReO}_3$ and Cp^*ReO_3 as catalyst.^[26] Accordingly, we were wondering if ligand dissociation accompanied by an induction period would also be observed when using $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ as catalyst. A time course profile experiment was carried out by using 1,2-octanediol as the substrate, 5 mol% of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ as catalyst, 1.1 equiv. of PPh_3 as reductant, and deuterated toluene as the solvent in a J-Young NMR tube under N_2 atmosphere at 200°C . Progression of the reaction over time was monitored by ^1H NMR. In time intervals of 10 to 20 minutes, the reaction mixture was taken out of the heating bath and cooled to room temperature to record an ^1H NMR spectrum, after which the mixture was re-heated to allow the reaction to progress further. As shown in Figure 1, the reaction showed a zeroth-order rate profile without an induction period. After 10 min, 2% of 1-octene was detected, while after 260 min 44% of 1-octene had formed. Because of the way the reaction was carried out, the final 1-octene yield was not as high as reported in Table 1. No free ligand was detected by ^1H NMR in this time course experiment. On the other hand, free ligand was detected by GC-MS analysis at the end of the experiment. These observations suggest that the Cp^* ligand does not dissociate in the course of the DODH reaction, but does dissociate during the GC-measurement.

For our $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ catalyst system both mononuclear as well as dinuclear catalytic pathways can be considered. A mononuclear pathway similar to the one put forward for the $\text{Cp}^*\text{ReO}_3/\text{PPh}_3$ system would involve the formation of either the $[\text{Cp}^*\text{MoO}_2]^+$ cation or the $[\text{Cp}^*\text{MoO}_3]^-$ anion as the active species. These species could form simultaneously upon cleavage of the Mo–O–Mo linkage in $[\text{Cp}^*\text{MoO}_2]_2\text{O}$. Either active species would then engage in a sequence of diol condensation and Mo=O reduction (in either order), followed by olefin extrusion. However, when the mononuclear complex $\text{NBu}_4[\text{Cp}^*\text{MoO}_3]$ (as well as the related neutral complex $(\text{Me}_3\text{tacn})\text{MoO}_3$) were explored as catalyst for the DODH of 1,2-octanediol, a lower 1-

octene yield was obtained (Table 1, entry 3 and 4), compared to the ones using dinuclear complexes as catalyst (Table 1, entry 1 and 2). In addition, O-atom abstraction from the $[\text{Cp}^*\text{MoO}_2]^+$ cation is expected to be energetically rather unfavorable, which rules out this mononuclear dioxo cation as the active species. These considerations suggest that the catalytic cycle going through a mononuclear pathway is not favorable for the $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ catalyst system.

Dinuclear catalytic pathways for $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ could either start by an initial reduction step or an initial diol condensation step. In view of the mechanism put forward for the related $\text{Cp}^*\text{ReO}_3/\text{PPh}_3$ catalyst system, in which reduction precedes diol condensation, we considered pathways in which the $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ catalyst is initially reduced to the symmetric $\text{Mo}^{\text{V}}\text{Mo}^{\text{V}}$ dimer $[\text{Cp}^*\text{MoO}_2]_2$ (Scheme 4). In pathway A, $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ is reduced to form $[\text{Cp}^*\text{MoO}_2]_2$, which will then condense with the diol to form $[\text{Cp}^*\text{Mo}(\text{diolate})](\mu\text{-O})[\text{Cp}^*\text{MoO}_2]$, followed by extrusion of the olefin product to regenerate $[\text{Cp}^*\text{MoO}_2]_2\text{O}$. In this case, half of the $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ complex is 'untouched' during catalysis. In pathway B, $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ is reduced in two steps to initially form $[\text{Cp}^*\text{MoO}_2]_2$ and subsequently $[\text{Cp}^*\text{Mo}(\mu\text{-O})_3]$. This kind of " $\text{Mo}_2(\mu\text{-O})_3$ " moiety commonly exists in molybdates.^[39] The doubly reduced $[\text{Cp}^*\text{Mo}(\mu\text{-O})_3]$ will then condense with the diol to form an unsymmetrical $[\text{Cp}^*\text{Mo}(\text{diolate})](\mu\text{-O})[\text{Cp}^*\text{MoO}]$ complex, followed by olefin product extrusion to reform $[\text{Cp}^*\text{MoO}_2]_2$. Within this binuclear reaction manifold, the singly reduced $[\text{Cp}^*\text{MoO}_2]_2$ complex connects pathways A and B. Pathway A proceeds through a $\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}} \leftrightarrow \text{Mo}^{\text{V}}\text{Mo}^{\text{V}}$ redox cycle including the non-symmetric mixed-valent $\text{Mo}^{\text{VI}}\text{Mo}^{\text{IV}}$ species $[\text{Cp}^*\text{Mo}(\text{diolate})](\mu\text{-O})[\text{Cp}^*\text{MoO}_2]$, while pathway B proceeds through a $\text{Mo}^{\text{V}}\text{Mo}^{\text{V}} \leftrightarrow \text{Mo}^{\text{IV}}\text{Mo}^{\text{IV}}$ redox cycle without the involvement of a mixed-valence intermediate. Likewise, for pathway A the starting complex $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ can be considered as the actual catalyst, while in pathway B it would be a pre-catalyst. The absence of an induction period in the time course study may not support pathway B from this point of view. Since the dinuclear Mo^{V} complex $[\text{Cp}^*\text{MoO}_2]_2$ is pivotal in both mechanisms, our attention focused on addressing the possible role of $[\text{Cp}^*\text{MoO}_2]_2$ in DODH catalysis.

First, we considered the formation of $[\text{Cp}^*\text{MoO}_2]_2$ through the reduction of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$. Upon treatment of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$

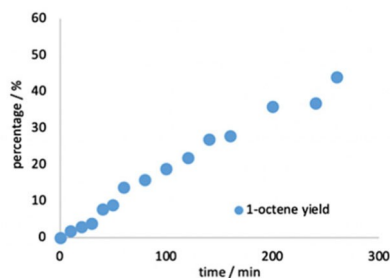
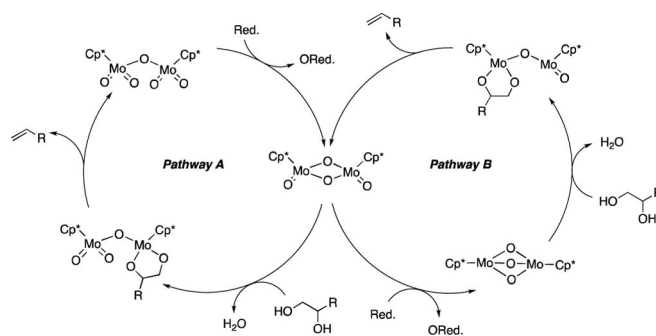


Figure 1. Time profile of the $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ catalyzed DODH of 1,2-octanediol.



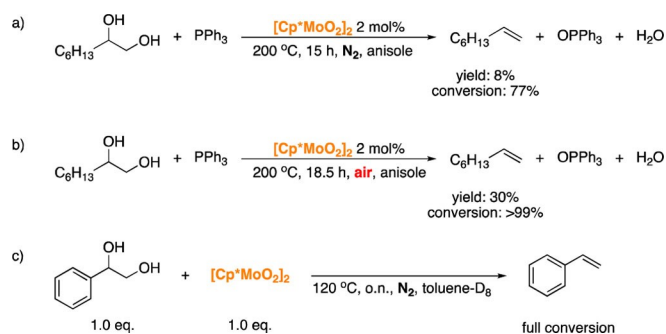
Scheme 4. Proposed dinuclear pathways A and B for DODH-catalysis by $[\text{Cp}^*\text{MoO}_2]_2\text{O}$.

with PPh_3 (the reductant used in DODH catalysis), the progression of the reaction was very slow at 120°C ; only 27% PPh_3 conversion occurred after 2 h, with the color changing from bright yellow to brown. Remarkably, the reduction of Cp^*ReO_3 by PPh_3 happens instantly at room temperature. Treatment of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ with 2.0 equiv. of the stronger reductant $\text{P}(\text{tBu})_3$ in toluene- D_8 at 80°C under N_2 overnight gave a brown solution, and 55% of $\text{P}(\text{tBu})_3$ was consumed based on ^{31}P NMR. Monitoring the reaction by means of ^1H NMR showed the appearance of new signals at 1.83 ppm and 1.79 ppm. A red-orange crystal separated from the mixture and a solution of the crystal showed a signal at 1.79 ppm in ^1H NMR. The identity of the red-orange crystal could be traced back to $[\text{Cp}^*\text{MoO}_2]_2$ after comparison with data from the literature.^[40] These experiments lend credit to the formation of $[\text{Cp}^*\text{MoO}_2]_2$ as the reduction product of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ under DODH conditions. In addition, these experiments clearly show that unlike in the case of Cp^*ReO_3 catalyzed DODH reactions, reduction of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ does not take place readily. These observations are in line with the work of Frstrup, which showed that the reduction of $\text{Mo}=\text{O}$ is the rate limiting step in catalytic DODH reactions using AHM as catalyst and isopropanol as reductant.^[16]

For the reduction of $\text{Mo}=\text{O}$ units, a vicinal diol can also be used as the reductant according to literature reports.^[15,17] When heating a 1:2 ratio of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ and 1,2-octanediol at 120°C , ^1H NMR analysis showed the appearance of signals at 1.83 ppm and 1.79 ppm, again indicating the formation of $[\text{Cp}^*\text{MoO}_2]_2$. In addition, no indication for the formation of 1-octene was obtained for this reaction. In a similar reaction, equimolar amounts of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ and 1-phenyl-1,2-ethanediol were reacted in toluene- D_8 . By increasing the temperature from room temperature to 100°C , new signals were detected by ^1H NMR. After keeping the mixture at 100°C overnight, 6% of styrene had formed, while no acetophenone or aldehydes were detected and a significant amount of 1-phenyl-1,2-ethanediol was still present.

These reduction experiments, combined with our results for the reductant screening (Table 3, entry 1 and entry 8), as well as the formation of ketals in our system, indicate that phosphines as well as diols can be used as reductant for catalytic DODH reactions using $[\text{Cp}^*\text{MoO}_2]_2\text{O}$. In addition, the experiments confirm the formation of $[\text{Cp}^*\text{MoO}_2]_2$ as a reduction product from $[\text{Cp}^*\text{MoO}_2]_2\text{O}$.

Next, our experiments focused on the reactivity of $[\text{Cp}^*\text{MoO}_2]_2$. If $[\text{Cp}^*\text{MoO}_2]_2$ is indeed the reduced product of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ involved in the proposed catalytic cycle, it should be active in DODH catalysis. Therefore, we investigated $[\text{Cp}^*\text{MoO}_2]_2$ as catalyst for the deoxydehydration of 1,2-octanediol under standard reaction conditions. Analysis of this reaction indicated that only 8% of 1-octene had formed at 77% substrate conversion (Scheme 5a). Since it is known that $[\text{Cp}^*\text{MoO}_2]_2$ is oxidized to $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ under aerobic conditions,^[28] we performed the same reaction under aerobic conditions (Scheme 5b). In this case, 30% of 1-octene formed at full substrate conversion, indicating that $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ formed *in situ* under these aerobic conditions is responsible for

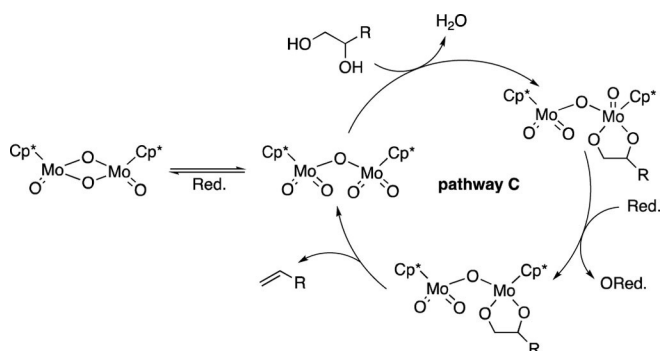


Scheme 5. Experiments probing the role of $[\text{Cp}^*\text{MoO}_2]_2$ in DODH catalysis: a) use of $[\text{Cp}^*\text{MoO}_2]_2$ as catalyst under inert conditions; b) use of $[\text{Cp}^*\text{MoO}_2]_2$ as catalyst under aerobic conditions; c) stoichiometric reaction of 1-phenyl-1,2-ethanediol and $[\text{Cp}^*\text{MoO}_2]_2$ under inert conditions.

catalysis. These experiments cast doubts on the overall involvement of $[\text{Cp}^*\text{MoO}_2]_2$ as an intermediate in DODH catalysis by $[\text{Cp}^*\text{MoO}_2]_2\text{O}$, and, furthermore, seem to rule out pathway B, since in that case $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ would act as a pre-catalyst and catalytic turn-over could be achieved through $[\text{Cp}^*\text{MoO}_2]_2$ without $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ being involved at all.

In a next, stoichiometric experiment $[\text{Cp}^*\text{MoO}_2]_2$ was reacted with 1 equiv. of the more reactive diol substrate 1-phenyl-1,2-ethanediol at 120°C to result in full conversion of 1-phenyl-1,2-ethanediol, as well as formation of styrene (Scheme 5c). No aldehydes were detected in this reaction. The outcome of this stoichiometric reaction indicates that $[\text{Cp}^*\text{MoO}_2]_2$ is able to engage in a condensation reaction with a diol substrate and in a subsequent olefin extrusion step to form an olefin at a relatively low temperature. Yet, catalytic turnover starting from $[\text{Cp}^*\text{MoO}_2]_2$ seems very limited (vide supra), possibly through the formation of oxidized species other than $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ that do not allow for the regeneration of $[\text{Cp}^*\text{MoO}_2]_2$ upon reduction. These considerations also seem to rule out pathway A.

Overall, our data do not provide strong evidence for either a mononuclear catalytic mechanism for DODH reactions with $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ or for the dinuclear pathways A and B. The next mechanism to consider would be a dinuclear mechanism in which diol condensation precedes $\text{Mo}=\text{O}$ reduction. In experiments to show the formation of $[\text{Cp}^*\text{MoO}_2]_2$ upon reduction of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ with an excess of diol, additional Mo-based species were observed by NMR analysis (vide supra). Although not conclusive, we tentatively assign these species as diolates of either $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ or $[\text{Cp}^*\text{MoO}_2]_2$. On the basis of this tentative assignment, we propose the putative mechanism C shown in Scheme 6 for DODH reactions catalyzed by $[\text{Cp}^*\text{MoO}_2]_2\text{O}$. In this mechanism, $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ is either reduced to $[\text{Cp}^*\text{MoO}_2]_2$ or reacts with a diol to form a nonsymmetric diolate. As shown in our mechanistic studies, $[\text{Cp}^*\text{MoO}_2]_2$ cannot be considered as a kinetically competent species involved in catalysis. Instead, catalysis in pathway C evolves through the reduction of the nonsymmetric diolate formed from $[\text{Cp}^*\text{MoO}_2]_2\text{O}$, followed by olefin extrusion to yield the react product and form back $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ to close the cycle.



Scheme 6. Proposed catalytic pathway C for $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ -catalyzed DODH reactions involving $[\text{Cp}^*\text{MoO}_2]_2$ is an off-cycle species. Red. = PPh_3 or diol. ORed. = OPPh_3 or carbonyl compounds.

Accordingly, we propose that $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ is the actual DODH catalyst and that it operates via a formal $\text{Mo}^{\text{VI}}\text{Mo}^{\text{IV}} \leftrightarrow \text{Mo}^{\text{VI}}\text{Mo}^{\text{IV}}$ redox cycle. Pathway C seems to agree with our observation that catalysis proceeds without an induction period. Further mechanistic studies will have to shed further light on the viability of pathway C, e.g. with respect to the identity of the diolate intermediate, the number of diols that can condense to $[\text{Cp}^*\text{MoO}_2]_2\text{O}$, and the energy profile of the individual reaction steps and the overall catalytic reaction. Efforts to this extent are ongoing in our labs.

Conclusion

Exploratory studies have shown that the dinuclear complex $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ is able to catalyze the DODH of diols using PPh_3 as reductant and anisole as solvent. The reaction requires a high reaction temperature (200°C) to reach high substrate conversion. Under these optimized reaction conditions, the $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ catalyst can be applied to the DODH of aliphatic vicinal diols to form the corresponding olefins with moderate yields up to 55% yield. Product yields and selectivities have also always been an issue in Mo-catalyzed DODH reaction, with the exception of using excess amounts of ligands or additives. Also for our current catalyst system, the dehydration of diol substrate and its oxidative cleavage seem to be part of the overall reactions that take place. Yet, the $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ catalyst rivals other Mo-based catalysts in its DODH performance, with mass balances (up to 79%) and TONs per Mo (up to 27) amongst the highest reported for molecular Mo-based DODH catalysts. Interestingly, the rather challenging substrate *cis*-1,2-cyclohexanediol can be converted to 30% 1-cyclohexene by $[\text{Cp}^*\text{MoO}_2]_2\text{O}$, thereby outperforming the typical $\text{Cp}^{\text{III}}\text{ReO}_3$ -catalyzed DODH reaction.

Mechanistic studies have detected $[\text{Cp}^*\text{MoO}_2]_2$ as one of the reduction products arising from $[\text{Cp}^*\text{MoO}_2]_2\text{O}$. While, $[\text{Cp}^*\text{MoO}_2]_2$ is able to engage in a condensation reaction with a diol substrate and a subsequent olefin extrusion step to form an olefin, the catalytic activity of $[\text{Cp}^*\text{MoO}_2]_2$ is much lower than that of $[\text{Cp}^*\text{MoO}_2]_2\text{O}$. Along with the observation of zero-

order reaction kinetics and the formation of other reaction species when treating $[\text{Cp}^*\text{MoO}_2]_2\text{O}$ with diols, we have proposed an reaction pathway in which $[\text{Cp}^*\text{MoO}_2]_2$ is an off-cycle species and where catalysis proceeds via initial diol condensation to $[\text{Cp}^*\text{MoO}_2]_2\text{O}$. Further studies aim at identifying the diolate intermediate and at shedding further light on the DODH reaction mechanism, to ultimately aid further catalyst development.

Experimental Section

All chemicals including solvents were degassed by either freeze-pump-thaw cycles or degasification under vacuum. Triphenylphosphine was crystallized from ethanol and dried under vacuum. $[\text{Cp}^*\text{MoO}_2]_2\text{O}$,^[32,33] $(\text{tacn})\text{MoO}_3$,^[35] and $\text{NBu}_4[\text{Cp}^*\text{MoO}_3]$ ^[34] was prepared according to a known literature procedure. Unless otherwise stated, all other commercial chemicals were used without further purification. NMR spectra were recorded on a Varian V NMR5400 (400 MHz) instrument at 298 K. ESI-MS spectra were recorded using a Waters LCT Premier XE instrument. GC measurements were performed using a Perkin Elmer Clarus 500 Gas Chromatograph equipped with a Perkin Elmer Elite-5 column (Length: 30 m, I.D.: 0.32 mm, Film thickness: 0.25 μm , 5% phenyl-95% methylpolysiloxane), and with FID detector. GC method: 40°C , 5 min; $3^\circ\text{C}/\text{min}$ to 55°C ; $20^\circ\text{C}/\text{min}$ to 250°C ; 250°C , 10 min; $20^\circ\text{C}/\text{min}$ to 300°C ; 300°C , 5 min. All olefinic products are known compounds and were calibrated against mesitylene for quantification. CCDC 1991496 contain the supplementary crystallographic data for $[\text{Cp}^*\text{MoO}_2]_2\text{O}$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

JL acknowledges financial support through the Chinese Scholarship Council and Utrecht University. The X-ray diffractometer has been financed by the Netherlands Organization for Scientific Research (NWO).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: deoxydehydration · homogeneous catalysis · molybdenum complexes · biomass conversion

- [1] S. Raju, M.-E. Moret, R. J. M. Klein Gebbink, *ACS Catal.* **2015**, *5*, 281–300.
- [2] J. R. Dethlefsen, P. Fristrup, *ChemSusChem* **2015**, *8*, 767–775.
- [3] K. A. Denike, S. M. Kilyanek, *R. Soc. Open Sci.* **2019**, *6*, 1–16.
- [4] L. J. Donnelly, S. P. Thomas, J. B. Love, *Chem. Asian J.* **2019**, *14*, 3782–3790.
- [5] S. C. C. van de Lubbe, C. Fonseca Guerra, *Chem. Eur. J.* **2017**, *23*, 10249–10253.
- [6] E. Steffensmeier, K. M. Nicholas, *Chem. Commun.* **2018**, *54*, 790–793.
- [7] G. Chapman, K. M. Nicholas, *Chem. Commun.* **2013**, *49*, 8199–8201.
- [8] T. V. Gopaladasu, K. M. Nicholas, *ACS Catal.* **2016**, *6*, 1901–1904.
- [9] Y. Y. Jiang, J. L. Jiang, Y. Fu, *Organometallics* **2016**, *35*, 3388–3396.
- [10] A. Galindo, *Inorg. Chem.* **2016**, *55*, 2284–2289.

- [11] L. C. De Vicente Poutás, M. Castiñeira Reis, R. Sanz, C. Sliva López, O. Nieto Faza, *Inorg. Chem.* **2016**, *55*, 11372–11382.
- [12] A. R. Petersen, L. B. Nielsen, J. R. Dethlefsen, P. Fristrup, *ChemCatChem* **2018**, *10*, 769–778.
- [13] K. M. Kwok, C. K. S. Choong, D. S. W. Ong, J. C. Q. Ng, C. G. Gwie, L. Chen, A. Borgna, *ChemCatChem* **2017**, *9*, 2443–2447.
- [14] L. Hills, R. Moyano, F. Montilla, A. Pastor, A. Galindo, E. Álvarez, F. Marchetti, C. Pettinari, *Eur. J. Inorg. Chem.* **2013**, *19*, 3352–3361.
- [15] J. R. Dethlefsen, D. Lupp, B.-C. Oh, P. Fristrup, *ChemSusChem* **2014**, *7*, 425–428.
- [16] J. R. Dethlefsen, D. Lupp, A. Teshome, L. B. Nielsen, P. Fristrup, *ACS Catal.* **2015**, *5*, 3638–3647.
- [17] D. Lupp, N. J. Christensen, J. R. Dethlefsen, P. Fristrup, *Chem. Eur. J.* **2015**, *21*, 3435–3442.
- [18] K. Beckerle, A. Sauer, T. P. Spaniol, J. Okuda, *Polyhedron* **2016**, *116*, 105–110.
- [19] M. Stalpaert, D. De Vos, *ACS Sustainable Chem. Eng.* **2018**, *6*, 12197–12204.
- [20] R. Tran, S. M. Kilyanek, *Dalton Trans.* **2019**, *48*, 16304–16311.
- [21] C. A. Navarro, A. John, *Inorg. Chem. Commun.* **2019**, *99*, 145–148.
- [22] S. C. A. Sousa, A. C. Fernandes, *Coord. Chem. Rev.*, **2015**, *284*, 67–92.
- [23] N. García, R. Rubio-Presa, P. García-García, M. A. Fernández-Rodríguez, M. R. Pedrosa, F. J. Arnáiz, R. Sanz, *Green Chem.* **2016**, *18*, 2335–2340.
- [24] A. R. Petersen, P. Fristrup, *Chem. Eur. J.* **2017**, *23*, 10235–10243.
- [25] S. Raju, J. T. B. H. Jastrzebski, M. Lutz, R. J. M. Klein Gebbink, *ChemSusChem* **2013**, *6*, 1673–1680.
- [26] S. Raju, C. A. M. R. Van Slagmaat, J. Li, M. Lutz, J. T. B. H. Jastrzebski, M.-E. Moret, R. J. M. Klein Gebbink, *Organometallics* **2016**, *35*, 2178–2187.
- [27] J. Li, M. Lutz, M. Otte, R. J. M. Klein Gebbink, *ChemCatChem* **2018**, *10*, 4755–4760.
- [28] R. Poli, *Coord. Chem. Rev.* **2008**, *252*, 1592–1612.
- [29] M. Herberhold, W. Kremnitz, A. Razavi, H. Schöllhorn, U. Thewalt, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 601–611.
- [30] P. Sözen-aktas, E. Manoury, F. Demirhan, R. Poli, *Eur. J. Inorg. Chem.* **2013**, *15*, 2728–2735.
- [31] C. Bhaumik, E. Manoury, J. Daran, P. Sözen-aktas, F. Demirhan, R. Poli, *J. Organomet. Chem.* **2014**, *760*, 115–123.
- [32] M. Scheer, K. Schuster, K. Schenzel, E. Herrmann, *Z. Anorg. Allg. Chem.* **1991**, *600*, 109–119.
- [33] K. Umakoshi, K. Isobe, *J. Organomet. Chem.* **1990**, *395*, 47–53.
- [34] J. Sundermeyer, U. Radius, C. Burschka, *Chem. Ber.* **1992**, *125*, 2379–2384.
- [35] P. C. McGowan, T. J. Podesta, M. Thornton-Pett, *Inorg. Chem.* **2001**, *40*, 1445–1453.
- [36] T. Welton, *R. Soc. Publ.* **2015**, *471*, 1–26.
- [37] D. Prat, J. Hayler, A. Wells, *Green Chem.* **2014**, *16*, 4546–4551.
- [38] A. M. Khenkin, R. Neumann, *Adv. Synth. Catal.* **2002**, *344*, 1017–1021.
- [39] S. T. Pritam, S. Harbans, M. Parveen, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1536–1538.
- [40] H. Arzoumanian, A. Baldy, M. Pierrot, J.-F. Petignani, *J. Organomet. Chem.* **1985**, *294*, 327–331.

Manuscript received: July 7, 2020

Revised manuscript received: September 16, 2020

Accepted manuscript online: September 22, 2020

Version of record online: November 4, 2020