# Molybdenum-Catalyzed Conversion of Diols and Biomass-Derived Polyols to Alkenes Using Isopropyl Alcohol as Reductant and Solvent

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S *Supporting Information*

ABSTRACT: Chemical processes capable of reducing the high oxygen content of biomass-derived polyols are in demand in order to produce renewable substitutes for chemicals of fossil origin. Deoxydehydration (DODH) is an attractive reaction that in a single step transforms a vicinal diol into an alkene, but the reaction requires a homogeneous catalyst, a reductant, and a solvent, which are typically expensive, unsustainable, or inefficient. Herein, we present the use of molybdenum(VI)-based compounds, in particular the cheap and commercially available $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, as catalysts for the DODH of vicinal diols in isopropyl alcohol (^iPrOH), which serves as both the solvent and reductant. The reaction proceeds at 240−250 °C in a pressurized autoclave, and the alkene yield from simple aliphatic diols can be as high as 77%. The major byproducts are carbonyl compounds—formed by dehydration of the diol—and the alcohols formed by transfer hydrogenation of the carbonyl compounds; the total yield of reduced species (i.e., alkene and alcohols) can be as high as 92%. The DODH of glycerol yields allyl alcohol, which undergoes subsequent Mo-catalyzed deoxygenation to propylene driven by the oxidation of ^iPrOH; a major byproduct is the homocoupled product 1,5-hexadiene. Further insight in this Mo-catalyzed deoxygenation is gained by an investigation of model compounds: The allylic alcohol 1-hexen-3-ol is deoxygenated to hexene isomers in a yield of 65%, while benzyl alcohol is deoxygenated to toluene in a yield of 93%. The DODH of erythritol yields 39% 2,5-dihydrofuran, while the DODH of the proposed intermediate 1,4-anhydroerythritol yields 75%. The mechanism of the DODH of 1,4-anhydroerythritol was investigated by means of density functional theory (DFT), and the rate-determining step (24.1 kcal/mol) was found to be reduction of a molybdenum(VI) diolate to a molybdenum(IV) diolate.
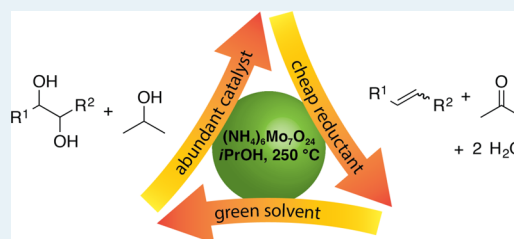
KEYWORDS: *biomass, deoxydehydration, deoxygenation, molybdenum, polyols*

■ INTRODUCTION

The realization of an economy completely independent of fossil reserves requires not only the exploitation of alternative energy sources but also the development of new processes for the production of organic platform chemicals from renewable feedstocks. Apart from transportation fuels, most petroleum is used for the production of polymers (e.g., polyethylene, polypropylene, polyvinyl chloride, and polystyrene),[1] and it is therefore desirable to find cheap, abundant, and preferably nonedible biomass feedstocks that can be converted into plastic precursors. Notwithstanding the promising prospect of novel platform molecules like lactic acid, 5-hydroxymethylfurfural, and levulinic acid,[2] these compounds are typically formed by redox-neutral processing of biomass, and reactions capable of not only dehydrating but also reducing biomass can serve as a supplement that makes a wider range of biomass-derived molecules available. An abundant motif in biomass is the hydroxyl group that is found both in carbohydrates (obtained from cellulose, hemicellulose, and starch) and glycerol (obtained from triglycerides), and an emerging strategy to reduce the oxygen content of such compounds is to deploy the deoxydehydration (DODH) reaction. This reaction transforms a vicinal diol into the corresponding alkene in a single step; the typical DODH

reaction is catalyzed by a rhenium compound and driven by the oxidation of a sacrificial reductant (Scheme 1).[3,4]

Scheme 1. Generalized Rhenium-Catalyzed DODH of a Vicinal Diol into an Alkene Driven by the Oxidation of a Sacrificial Reductant ("red")
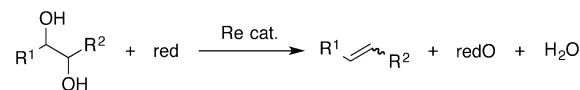
In addition to the transformation of a number of model compounds resembling biomass-derived polyols, the rhenium-catalyzed DODH has been employed in the conversion of the sugar alcohol sorbitol (i.e., reduced glucose) into 1,3,5-hexatriene[5] and—in combination with a subsequent hydrogenation—mucic acid (i.e., oxidized galactose) into adipic acid;[5,6] 1,3,5-hexatriene might become a plastic precursor similar to 1,3-butadiene, while adipic acid is already today used as a nylon precursor. Furthermore, the DODH of glycerol yields allyl

alcohol.[5,7] Despite the fact that a major use of allyl alcohol today is in the production of glycerol, the expected gradually lower price of waste glycerol from the manufacture of biodiesel could make the use of allyl alcohol as a plastic precursor economically viable,[8,9] and it has recently been demonstrated that allyl alcohol can be deoxygenated to propylene[10] and that glycerol can undergo hydrodeoxygenation (HDO, i.e., deoxygenation using hydrogen as reductant) to propylene in aqueous solution at 300 °C.[11] The major advantage of the DODH process over the HDO process is the preservation of functionality: The DODH of a vicinal diol yields an *alkene*, whereas the HDO typically yields an *alkane*. Therefore, the latter process has primarily been proposed for the production of biofuels[12−16] and in the processing of the entire lignocellulosic biomass[17−19] and not only the hydrolyzed carbohydrate fractions.

This—for some purposes excessive—hydrogenation of alkenes to alkanes has also been noted by Abu-Omar and co-workers, who observed that the use of the cheap and clean reductant H_2 in the CH_3ReO_3-catalyzed DODH of vicinal diols in thf at 150 °C yielded a mixture of the corresponding alkenes (always <60%) and alkanes.[20] If hydrogen could drive the Mo-catalyzed DODH, hydrogenation of the alkenes could probably be avoided as molybdenum is expected to be a poorer hydrogenation catalyst than rhenium, and this has indeed been observed in the MoO_3-catalyzed HDO of acetone into propylene at 400 °C.[21]

The implementation of the DODH process on an industrial scale is not only hampered by the use of the remarkably scarce element rhenium—which as a byproduct of molybdenum has an extremely volatile price[22]—but also by the use of reductants and solvents that are neither cheap nor green. The highest alkene yields (almost quantitative) have been obtained using the expensive PPh_3 as a reductant, and although Nicholas and co-workers have obtained high yields using the cheaper alternatives Na_2SO_3[23,24] and elemental carbon, iron, zinc, and manganese,[25] these reductants are only efficient in solvents like benzene or chlorobenzene, which are cheap but neither green nor good at dissolving biomass-derived polyols. The use of the secondary alcohols 3-octanol[26] and 3-pentanol[5,6] as both reductants and solvents is promising, but they are relatively expensive, and the solubility of polyols is still low. Shiramizu and Toste[5] attempted to employ ethanol, 1-propanol, and isopropyl alcohol in the CH_3ReO_3-catalyzed DODH of 1,4-anhydroerythritol, but the diol only underwent conversion in 1-propanol and the yield of 2,5-dihydrofuran was low (28%). The efficiency of a number of vanadium-based catalysts has been surveyed by Chapman and Nicholas;[27] notwithstanding the high yields, the use of PPh_3 as a reductant and benzene or chlorobenzene as solvent limits the large-scale applications of the process. The use of molybdenum-based catalysts—and in particular the cheap and commercially available $(NH_4)_6Mo_7O_{24}·4H_2O$ (AHM)—has also been demonstrated,[28,29] but the only reductant that was able to drive the Mo-catalyzed DODH was the diol itself; that is, half the diol underwent DODH to the corresponding alkene while the other half underwent oxidative deformylation (Scheme 2).[29,30] A cheap diol could have justified sacrificing half of it as reductant—and this strategy has indeed been pursued by Abu-Omar and co-workers[7]—but the oxidative deformylation leads to the formation of aldehydes and inevitably related acetals and polymerization products, which poses a significant problem with respect to product separation and recyclability of the solvent and the catalyst.

Scheme 2. Molybdenum-Catalyzed DODH of a Vicinal Diol into an Alkene Driven by the Oxidative Deformylation of the Diol Itself into Formaldehyde and the Aldehyde with One Less Carbon Atom than the Diol
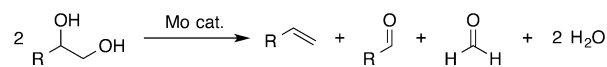
With the objective of conducting the molybdenum-catalyzed DODH of not only diol model compounds but also the biomass-derived polyols glycerol and erythritol under conditions that could realistically be implemented on an industrial scale, we set out to find a green and cheap reductant capable of outcompeting the diol in reducing the catalyst as well as a green and cheap solvent capable of dissolving large amounts of glycerol or other biomass-derived polyols. In the present work, we show that isopropyl alcohol can be used as both a reductant and a solvent in the AHM-catalyzed DODH of vicinal diols at 240−250 °C in a pressurized autoclave (Scheme 3a) and that the allyl alcohol

Scheme 3. Molybdenum-Catalyzed (a) DODH of a Vicinal Diol into an Alkene and (b) Sequential DODH and Deoxygenation of Glycerol to Propylene Driven by Oxidation of ^iPrOH to Acetone
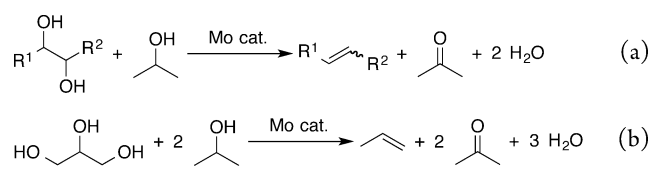
formed in situ by DODH of glycerol undergoes deoxygenation to propylene (Scheme 3b). In the following sections, an investigation of these two reactions—including tests of other reductants, solvents, and molybdenum-based catalysts—will be presented.

■ RESULTS AND DISCUSSION

Test of Hydrogen as Reductant. We had previously observed that AHM catalyzed the DODH of 1,2-tetradecanediol in dodecane according to Scheme 2; using 1 mmol of diol, 5 mol % of AHM (calculated with respect to Mo), and 2 mL of dodecane, the reaction was complete within 1 h at 200 °C.[29] Although none of the tested reductants (PPh_3 and primary, secondary, and benzylic alcohols) were able to outcompete the consumption of the diol itself as the reductant, attempts were made to use H_2.

The viability of using hydrogen as a reductant was initially tested by heating a solution of 1,2-decanediol and AHM in hexane to 247 °C under 22 bar of hydrogen; this reaction is similar to the aforementioned AHM-catalyzed DODH of 1,2-tetradecanediol in dodecane, although the highest attainable temperature in an open system was ∼205 °C. After 12 h, the conversion was complete and 31% of 1-decene (**C=C**) had formed together with 17% of 2-decanone (**C=O**), 2% of 2-decanol (**2°OH**), and 5% of 1-decanol (**1°OH**), that is, a total yield of reduced species (alkene and monohydric alcohols) of 38%, which did not exclude the possibility that the diol itself was oxidized. The reaction was therefore repeated using nitrogen instead of hydrogen, which resulted in the same product distribution (Table 1), thus excluding the possibility that hydrogen was consumed.

Table 1. Comparison of Hydrogen and Nitrogen Gas in the AHM-Catalyzed DODH of 1,2-Decanediol in the Solvents Hexane and ^{i}PrOH[a]

gas	solvent	T_{max} [°C]	yields [%] of			
			C=C	C=O	2°OH	1°OH
H_2	hexane	247	31	17	2	5
N_2	hexane	246	30	19	3	4
H_2	^{i}PrOH	242	49	10	5	15
N_2	^{i}PrOH	242	46	10	6	13

[a]Reaction conditions A were employed (see Experimental Section).

As hexane was never intended to be the solvent for the DODH of biomass-derived polyols, the two experiments were repeated in ^{i}PrOH, which is a cheap and environmentally benign solvent that is miscible with glycerol at room temperature. Isopropyl alcohol was initially favored over the even cheaper monohydric alcohols methanol and ethanol because its potential oxidation product acetone would be easy to detect; that said, we had previously shown that the secondary alcohol 3-octanol could not be oxidized in the molybdenum-catalyzed DODH at 200 °C and that its presence was indeed detrimental to the alkene yield.[29] Regardless of the choice of gas, up to 49% of alkene did, however, form, and the total yield of reduced species was above 65% (Table 1), thus excluding the oxidation of not only hydrogen but also the diol. In confirmation of ^{i}PrOH being the reductant, the presence of acetone in the reaction mixture was observed by NMR spectroscopy. The regeneration of ^{i}PrOH by hydrogenation of acetone can proceed with 99.9% selectivity and 99.9% conversion over a Raney-nickel catalyst in the liquid phase;[31] the process has primarily been implemented where excess acetone has been readily available from another process, which would be the case here.

Molybdenum-catalyzed transfer hydrogenation is rare but not unprecedented: the transfer hydrogenation from ^{i}PrOH to 1-hexene catalyzed by the molybdenum(0) complex Mo-$(N_2)_2$(dpe)$_2$ (dpe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) was investigated by Tominaga and co-workers more than 30 years ago.[32−34] The transfer hydrogenation proceeded through the formation of the hydride complex MoH$_4$(dpe)$_2$, but considering the significantly lower temperatures (only 80 °C) and the fact that the reaction was used for hydrogenation of 1-hexene to hexane, we have no reason to assume that this reaction is related to the DODH reaction by anything else than a common transition metal.

A preliminary optimization of reaction conditions with respect to time, temperature, pressure, and catalyst loading (Table S1) showed that the highest accessible temperature (240−250 °C) was best; higher temperatures were inaccessible due to limited power and the accelerated degradation of PTFE above 230 °C. The pressure had no influence on yields or product distributions, which was expected due to the inert nature of the employed gases. The reaction time was dependent on the catalyst loading, but we settled for 5 mol % of catalyst and a reaction time of 800 min as the standard conditions (referred to as reaction conditions A, see Experimental Section for details).

Solvent Screening. Although only ^{i}PrOH and presumably the diol itself were found to be able to serve as reductants in the AHM-catalyzed DODH of 1,2-decanediol, the viability of hydrogen as a reductant was tested again in a number of other solvents (Table 2). The simple alcohols MeOH, EtOH, and ^{n}PrOH gave poor alkene yields, and the alkene yield in MeOH was even lower than that in nonoxidizable hexane. The alkene

Table 2. Comparison of Solvents in the AHM-Catalyzed DODH of 1,2-Decanediol[a]

solvent	T_{max} [°C]	conv. [%]	yields [%] of			
			C=C	C=O	2°OH	1°OH
MeOH[b]	239	57	17	5	<1	2
EtOH	247	full	37	11	5	10
^{n}PrOH	251	full	36	13	7	11
^{i}PrOH	242	full	49	10	5	15
^{t}BuOH[c]	232	39	~0	~0	~0	~0
3-pentanol	252	full	33	8	5	14
acetone	249	96	11	23	1	~0
hexane	247	full	31	17	2	5
water[d]	241	~0	~0	~0	~0	~0

[a]Reaction conditions A were employed (see Experimental Section) unless otherwise noted; the autoclave was pressurized with hydrogen. [b]Heated for 900 min. [c]Heating stopped after 350 min due to rapidly increasing pressure. [d]The diol was 1,2-hexanediol; heating stopped after 220 min.

yield in 3-pentanol was comparable to that in the primary alcohols, but as 3-pentanol is neither cheap nor miscible with glycerol, it was not investigated further. The tertiary alcohol ^{t}BuOH quickly underwent dehydration to isobutylene (observed and identified by GC-MS). The attempted DODH of 1,2-hexanediol in water showed very little conversion and not even traces of any of the expected products. For comparison, Shiramizu and Toste[5] tested the efficiency of various alcohols for the CH$_3$ReO$_3$-catalyzed DODH of 1,4-anhydroerythritol to 2,5-dihydrofuran and observed that while 1-butanol was a much better reductant than 2-butanol (70% vs 0% yield), 3-pentanol was better than 2-pentanol which in turn was better than 1-pentanol (alkene yields of 91%, 78%, and 51%, respectively).

Catalyst Screening and Characterization. Having established that ^{i}PrOH was the most efficient reductant, other molybdenum-based catalysts were tested (Table 3; additional catalysts are shown in Table S2). Gratifyingly, the cheapest catalyst, AHM, was the most efficient—the only coordination compound with a comparable efficiency was

Table 3. Comparison of Molybdenum-Based Catalysts in the DODH of 1,2-Decanediol in ^{i}PrOH[a]

catalyst	yields [%] of			
	C=C	C=O	2°OH	1°OH
AHM	49	10	5	15
MoO$_2$Me$_2$(bipy)[b]	46	11	3	12
(Bu$_4$N)$_2$Mo$_6$O$_{19}$	42	8	9	23
AHM + Bu$_4$NOH[c]	55	~0	22	3
AHM + AcOH[d]	37	8	3	11
recycled catalyst 1[e]	38	10	4	18
recycled catalyst 2[f]	20	4	2	10

[a]Reaction conditions A were employed (see Experimental Section); additional catalysts are shown in Table S2 in the Supporting Information. Unless otherwise noted, the conversion of the diol was >98%. [b]bipy = 2,2′-bipyridine; 89% conversion. [c]Six milliliters of a 1 M solution of Bu$_4$NOH in MeOH was added. [d]Acetic acid (1.2 equiv with respect to 1,2-decanediol) was added to the reaction mixture; 92% conversion. [e]The black precipitate obtained from the AHM-catalyzed DODH of 1,2-hexanediol; the alkene yield includes 1-decene (24%) and isomers of decene and decane (14%). [f]The black precipitate obtained by heating AHM in ^{i}PrOH in the absence of a diol; 58% conversion.

MoO$_2$(CH$_3$)$_2$(bipy) which, although not very difficult to prepare,[35−37] is much more expensive. Among the tested polyoxomolybdates, the compound (Bu$_4$N)$_2$Mo$_6$O$_{19}$[38] resulted in an alkene yield almost as high as that for AHM (42% vs 49%), a slightly higher yield of reduced species (74% vs 69%), and very little catalyst precipitation at the end of the experiment. The addition of a weak acid, 1.2 equiv of acetic acid (in order to mimic the acidity of sugar acids like mucic acid[6,39]), resulted in a lower yield, but the product distribution was unaffected. The addition of a strong base (15 mol % of Bu$_4$NOH),[40] on the other hand, not only improved the alkene yield but also changed the product distribution; this will be discussed in more detail below. Since strongly acidic conditions ultimately result in the precipitation of MoO$_3$, acids stronger than acetic acid were not added.

Upon completion of an experiment, a black powder could typically be isolated by filtration; in order to characterize it and test its recyclability or regeneration, a large amount was intentionally prepared by conducting a regular DODH of 5 g of 1,2-hexanediol in 100 mL of ^{i}PrOH under hydrogen using 1.23 g of AHM; after 12 h, 1.1 g of black precipitate (elemental analysis: 13.0% C, 2.4% H, 1.8% N, and 55.7% Mo) was isolated. As evidenced by X-ray powder diffraction, the powder was amorphous; its infrared spectrum is shown in Figure S2. Due to mechanical loss during the isolation, it cannot be unequivocally concluded that all of the molybdenum precipitates at the end of the reaction, but at least 90% could be recovered, and it was demonstrated that AHM could be regenerated from the precipitate: Pyrolysis at 500 °C for 5 h resulted in a gray-blue powder (MoO$_{<3}$) that by dissolution in aqueous ammonia followed by slow evaporation of the solvent was converted to AHM (identified by X-ray powder diffraction).

Based on the relatively high carbon content of the powder, it was tentatively assumed to contain a polyoxomolybdate and at least one coordinated diolate ion, although it cannot be excluded that it is a mixture of compounds. The presence of a diolate ion in the formula was supported by the preparation of a similar black precipitate by heating 2.43 g of AHM in 100 mL of ^{i}PrOH to 240−250 °C with no diol present; after 12 h, 1.8 g of black precipitate containing less carbon (elemental analysis: 1.8% C, 1.2% H, 2.8% N, 64.3% Mo) and with a markedly different infrared spectrum (Figure S2) was isolated. The catalytic activities of the two black precipitates were tested; although both were less efficient than AHM, the black powder that had been precipitated in the presence of a diol resulted in a total yield of reduced species of 60%. Notwithstanding the benefits of being able to recycle a pseudoheterogeneous catalyst (AHM is insoluble in ^{i}PrOH at room temperature) without the need for regeneration, the low cost of AHM in combination with its trivial regeneration makes the direct recycling less important, and repeated use of the black precipitate was therefore not attempted.

Side Reactions and Byproducts. In addition to the desired DODH reaction, two molybdenum-catalyzed side reactions took place, namely dehydration of the diol and transfer hydrogenation of the hereby-formed aldehyde and ketone. Thus, the DODH of 1,2-decanediol always resulted in the formation of 2-decanone, 2-decanol, and 1-decanol, which were routinely quantified; although decanal was never observed, the two acetals formed by condensation of decanal and 1,2-decanediol were observed, when the reaction was stopped before completion (see Supporting Information). Although the dehydration of diols was not the desired reaction, the rhenium- and molybdenum-catalyzed dehydration of alcohols to alkenes has been investigated, in particular by Klein Gebbink and co-work-

ers.[4,41−44] The viability of the proposed pathway was confirmed by adding 15 mmol of either 2-decanone or decanal to the AHM-catalyzed DODH of 1,2-hexanediol in ^{i}PrOH under reaction conditions A (see Experimental Section). Fifty-four percent of the ketone remained unconverted, and the yield of 2-decanol was 39%; neither 1-decanol nor 1-decene was observed. The conversion of the aldehyde was complete, but the yield of 1-decanol was only 46%; the remaining products were not immediately identified, but the aldehyde is likely to form acetals or undergo aldol condensation. The product distribution from these experiments is in agreement with the composition of the reaction mixtures in ^{i}PrOH (10% **C═O**, 5% **2°OH**, 15% **1°OH**), where no decanal was ever observed, and the absence of 1-decene in both experiments excludes the possibility that the alkene is formed through a sequential dehydration−reduction−dehydration of the diol.

Three other minor byproducts were 1-isopropoxy-2-decanol (see Supporting Information for characterization; estimated GC yield 5−10%), diisopropyl ether, and propylene; the quantification of propylene will be discussed below.

Reactivity of Various C$_6$ Diols. The characteristic group of the model compound 1,2-decanediol, that is, a vicinal diol with a primary and a secondary OH group, is a common motif in glycerol, sorbitol, and open-chain sugars, but it does not necessarily describe the reactivity of vicinal diols containing two secondary OH groups adequately, and the AHM-catalyzed DODH of 3,4-hexanediol and cis- and trans-1,2-cyclohexanediol in ^{i}PrOH was therefore investigated. These results are summarized in Table 4, whereas the results for the DODH of

Table 4. Comparison of the AHM-Catalyzed DODH of C$_6$ Diols in ^{i}PrOH^a

substrate	yields [%] of			
	C═C	C═O	2°OH	1°OH
1,2-hexanediol	46	9	traces	16
+ 3 mL of MeOH	49	15	3	11
+ 3 mmol of Bu$_4$NOH^b	77	3	5	5
+ 3 mmol of pyridine	42	15	13	15
3,4-hexanediol^c	42^c	17	5	
+ 3 mmol of Bu$_4$NOH^b	69^c	16	3	
cis-1,2-cyclohexanediol	29	traces	42	
+ 3 mmol of Bu$_4$NOH^b	47	traces	45^e	
trans-1,2-cyclohexanediol^d	14	4	24	

^{a}Reaction conditions B were employed (see Experimental Section); more substrates are shown in Table S3 in the Supporting Information. Unless otherwise noted, the conversion of the diol was >98%. ^{b}Three milliliters of 1 M Bu$_4$NOH in MeOH was added. ^{c}Mixture of isomers; calculation of 3-hexene yield was complicated by partial overlap with ^{i}Pr$_2$O on the GC. ^{d}Conversion was incomplete. ^{e}Yield based on GC-MS due to partial overlap with Bu$_3$N on the GC.

diols containing one or two tertiary alcohol groups are compiled in Table S3. The hexene yields from 1,2-hexanediol—which was included to take the effect of the shorter aliphatic chain into account—and from 3,4-hexanediol were similar to the yield of 1-decene from 1,2-decanediol, but the cyclic diols displayed a markedly different reactivity: The cis isomer underwent complete conversion, but only 29% of cyclohexene formed; the major product (42%) was cyclohexanol, while only traces of cyclohexanone were observed, indicating that transfer hydrogenation of cyclohexanone is very efficient. The conversion of the trans isomer was incomplete, and the yields of alkene and alcohol were

14% and 24%, respectively. Different reactivities of the *cis* and *trans* isomers have also been observed for rhenium,[5,7,45] but only the *cis* isomer was investigated for vanadium:[27] It displayed low conversion (25%) and an alkene yield of 15%.

The addition of base was even more beneficial for the C_6 diols than for 1,2-decanediol: The addition of 15 mol % of Bu_4NOH (added as a 1 M solution of Bu_4NOH in MeOH) resulted in yields of hexene from the DODH of 1,2-hexanediol and 3,4-hexanediol of 77% and 69%, respectively, while the combined yield of the reduced species cyclohexene and cyclohexanol from the DODH and from the sequential dehydration and reduction of *cis*-1,2-cyclohexanediol was 92%. Even though the addition of only methanol did result in a slightly higher alkene yield and a different selectivity, the major improvement was a result of the base. The addition of 15 mol % of the six bases NaOH, Na_2CO_3, CH_3COONa, LiOMe, Et_3N, and pyridine was not beneficial: The three sodium salts and the lithium salt resulted in 1-hexene yields of 0%, 7%, 2%, and 6%, respectively, and very low conversions; Et_3N resulted in an alkene yield of 32% and incomplete conversion, and pyridine had only a minor effect. The different behavior of NaOH and Bu_4NOH can probably be ascribed to the insolubility of Na_2MoO_4, which displayed no catalytic activity at all. The same is possibly true for Li_2MoO_4, whereas the lower alkene yield upon the addition of Et_3N might be ascribed to coordination of the amine to the molybdenum center.

Deoxygenation of Allylic Alcohols and Benzyl Alcohol. We had previously[29] observed a Mo-catalyzed reductive homocoupling of benzyl alcohol (BnOH) to bibenzyl, and if this reactivity also applied to allylic alcohols, the main product from the DODH of glycerol might not be allyl alcohol (as would be expected from Scheme 3a) but 1,5-hexadiene, presumably formed by reductive homocoupling of the allyl alcohol formed by DODH of glycerol. The reactivity of BnOH and allylic alcohols was therefore investigated by subjecting them to reaction conditions similar to those of the diols.

First, a mixture of 80 mmol of BnOH and 2.5 mol % of AHM in 100 mL of ^iPrOH was heated to 220 °C for 12 h in a pressurized autoclave, which led to the incomplete conversion to 7% of bibenzyl (yield multiplied by 2 to take the stoichiometry into account) and 60% of toluene; the only oxidation product was acetone, which was observed by NMR. The addition of 7.5 mol % of base (1 M Bu_4NOH in MeOH) and prolongation of the heating time to 18 h resulted in a markedly higher toluene yield (93%) and a lower yield of bibenzyl (4%); using EtOH instead of ^iPrOH and still adding the base gave similar yields and product distribution (88% and 2%, respectively) as well as the oxidation product acetaldehyde, which was observed as its diethyl acetal by GC-MS. For comparison, the reactivities of (*R,R*)-hydrobenzoin and *meso*-hydrobenzoin were tested by heating 10 mmol of one of the isomers and 6 mol % of AHM in 50 mL of ^iPrOH to 220 °C for 1000 min in a pressurized cylinder. For both isomers, the major product was toluene (*R,R* 31%, *meso* 44%; the yield has been divided by 2 to take the stoichiometry into account), but significant amounts of *trans*-stilbene (*R,R* 27%, *meso* 23%) and bibenzyl (*R,R* 16%, *meso* 13%) also formed; no benzyl alcohol was detected. The reactivity of 1-phenyl-1,2-ethanediol was tested by heating 20 mmol of 1-phenyl-1,2-ethanediol and 5 mol % of AHM in 50 mL of ^iPrOH to 250 °C for 1000 min in a pressurized cylinder. The main product was 2-phenylethanol (estimated yield 20−25%), while styrene, ethylbenzene, toluene, 1-phenylethanol, and acetophenone were all present in estimated yields below 6%.

Second, a mixture of 80 mmol of the allylic alcohol 1-hexen-3-ol and 2.5 mol % of AHM in 100 mL of ^iPrOH was heated to 220 °C for 12 h, which led to the formation of ∼9% hexene isomers, ∼9% dodecadiene isomers, and acetone as the oxidation product. In addition to ∼25% unconverted 1-hexen-3-ol, 2-hexen-1-ol had formed (the *cis* and *trans* isomers could not be distinguished by GC-MS), thus indicating that AHM catalyzes the 1,3-trans-position of allylic alcohols; the molybdenum-catalyzed 1,3-transposition of allylic alcohols has previously been investigated,[46−49] and this reaction can explain the formation of isomers of hexene and dodecadiene. In confirmation, the subjection of *trans*-2-hexen-1-ol to the same conditions resulted in a reaction mixture with an almost identical composition. The addition of 7.5 mol % base (1 M Bu_4NOH in MeOH), prolongation of the heating time to 18 h, and increase of the temperature to 250 °C resulted in a significantly higher hexenes yield (65%); the use of EtOH instead of ^iPrOH resulted in a practically identical yield and the formation of acetaldehyde as the oxidation product, while the hexenes yield in MeOH was only 7%.

Third, a mixture of 70 mmol of allyl alcohol, 1.4 mol % of AHM, and 4.2 mol % base (1 M Bu_4NOH in MeOH) in 50 mL of ^iPrOH was heated to 250 °C for 18 h, which led to the formation of 8% 1,5-hexadiene and 22% propylene; the conversion was 86%. In EtOH, the yields were 9% and 28%, respectively, while the conversion was 86%. Although a yield of 28% is not high, the absence of other significant byproducts than 1,5-hexadiene as well as the high yields of deoxygenation products from the allylic alcohol 1-hexen-3-ol are promising for the attainment of a higher yield under conditions optimized for the quantification of gases.

The yield of propylene was determined by allowing the gas from a cylinder that had cooled to room temperature to pass through 250 mL of CH_2Cl_2 containing 1.5 mL of bromine and 1 g of PhBr as a reference; the amount of 1,2-dibromopropane was determined by GC. The quantification of propylene was not only complicated by the fact that propylene is a gas that might escape prior to its bromination—which might not be quantitative—but also by the aforementioned formation of propylene by dehydration of ^iPrOH. To take the dehydration into account, an AHM-catalyzed DODH of 1,2-hexanediol in ^iPrOH using reaction conditions B and adding 15 mol % of Bu_4NOH was conducted, and the amount of propylene formed by dehydration of ^iPrOH was quantified (2.2 mmol from 50 mL of ^iPrOH); this has been subtracted from the amount of propylene formed by the deoxygenation of allyl alcohol in ^iPrOH.

In summary, we find that not only benzyl alcohol but also allylic alcohols undergo two molybdenum-catalyzed reactions, namely a deoxygenation (Scheme 4a) and a reductive homocoupling (Scheme 4b). Formally, both reactions are reductions, and the corresponding oxidation products are acetone, when the solvent/reductant is ^iPrOH, and acetaldehyde diethyl acetal, when the solvent/reductant is EtOH.

Scheme 4. Molybdenum-Catalyzed Transformations of Allyl Alcohol: (a) Deoxygenation to Propylene; (b) Reductive Homocoupling to 1,5-Hexadiene
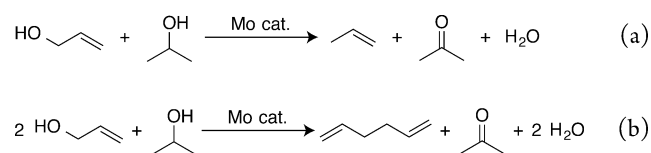
The preparation[50,51] and use[52−55] of 1,5-hexadiene has received some attention, but it is not a commonly employed unsaturated hydrocarbon today; this might, however, change, if the selectivity of the molybdenum-catalyzed deoxygenation can be tuned toward the reductive homocoupling of allyl alcohol instead. The deoxygenation and reductive homocoupling of allylic alcohols are not unprecedented reactions: titanium-mediated[56,57] and lanthanum metal-assisted[58] examples exist, and allyl and benzyl ether have been shown to undergo TiCl₄- or (C₅H₅)TiCl₂-catalyzed hydrogenolysis by LiAlH₄.[59] In addition, propylene—and many other species—form when allyl alcohol reacts with PdCl₄²⁻,[60] and HCo(CN)₅³⁻ catalyzes the deoxygenation of allylic alcohols using hydrogen as the reductant.[61] That said, the molybdenum-catalyzed deoxygenation of allylic alcohols using another alcohol as the reductant has, to the best of our knowledge, not been described before.

DODH of Glycerol and Erythritol. Moving on to a biomass-derived polyol, the AHM-catalyzed DODH of glycerol in *i*PrOH was attempted. The amounts of glycerol available from biomass pale in comparison to carbohydrates and their reduced sugar alcohols, but—in contrast to higher polyols like sorbitol—glycerol is stable under the reaction conditions and therefore serves as a reasonable model compound. In addition, large amounts of waste glycerol are inevitably obtained in the production of biodiesel by trans-esterification of triglycerides, and the conversion of this waste product into the more valuable chemical allyl alcohol could benefit the overall economy of a biorefinery.

When glycerol was subjected to reaction conditions B at 250 °C and adding 15 mol % of base (1 M Bu₄NOH in MeOH), the conversion was complete, and in addition to 4% of allyl alcohol and traces of 1,5-hexadiene, 19% of propylene was quantified as 1,2-dibromopropane as described above. In EtOH, the conversion was still complete, and in addition to traces of allyl alcohol and 1,5-hexadiene, 9% of propylene was quantified. It is worth noting that although *i*PrOH and EtOH gave similar yields for the AHM-catalyzed deoxygenation of allylic alcohols, *i*PrOH was more efficient for the DODH, thus explaining the different yields of propylene from glycerol, which requires a sequential DODH and deoxygenation. As discussed above, a higher yield of propylene might be found under conditions optimized for the quantification of gases.

The DODH of the C₄ sugar alcohol erythritol resulted in the formation of 39% of 2,5-dihydrofuran using reaction conditions B at 250 °C; addition of 15 mol % of base (1 M Bu₄NOH in MeOH) lowered the yield to 27%, which might be explained by a smaller tendency for erythritol to form the proposed intermediate 1,4-anhydroerytrhitol under basic conditions. Isomers of butene were only observed in very small amounts, and no 1,3-butadiene was detected. The DODH of the proposed intermediate 1,4-anhydroerythritol using reaction conditions B yielded 75% of 2,5-dihydrofuran in the absence of base and 74% in the presence.

DFT Calculations. To rationalize the different reactivities of the employed reductants (diol, *i*PrOH, and H₂), a density functional theory (DFT) study of the reduction of molybdenum-(VI) to molybdenum(IV) was performed as an extension to our previously published results on the mechanism on the molybdenum-catalyzed DODH of diols using the diol itself as the reductant.[30] Using the diol itself or *i*PrOH as reductants, the reduction was found to be most favorable when a diolate ion was coordinated to the molybdenum center (i.e., when the diol itself was the reductant, two diolate ions were coordinated to the

molybdenum center). Using H₂ as the reductant, the simultaneous addition of hydrogen to both oxide ligands proved most favorable; a mechanism involving the formation of a molybdenum hydride as intermediate as suggested by Mayer and co-workers[62] was also studied. All investigated structures are compiled in Supporting Information.

As seen in Figure 1, the transition state for the reduction with the diol is lower than the one for *i*PrOH (by 10.4 kcal/mol),
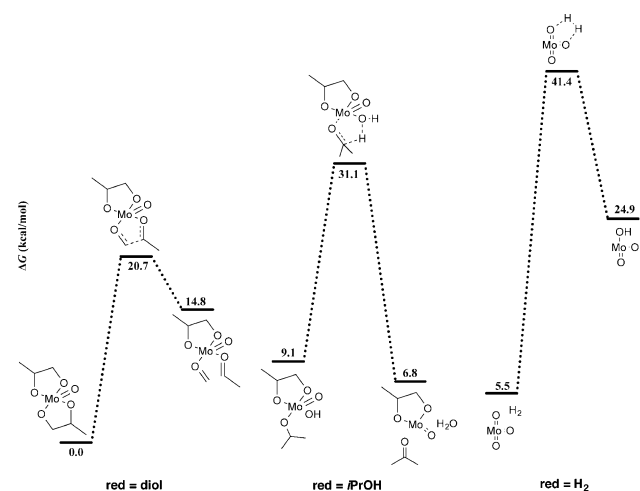

Figure 1. Comparison of the free energies for the reduction of molybdenum(VI) to molybdenum(IV) by 1,2-propanediol, *i*PrOH, and H₂.
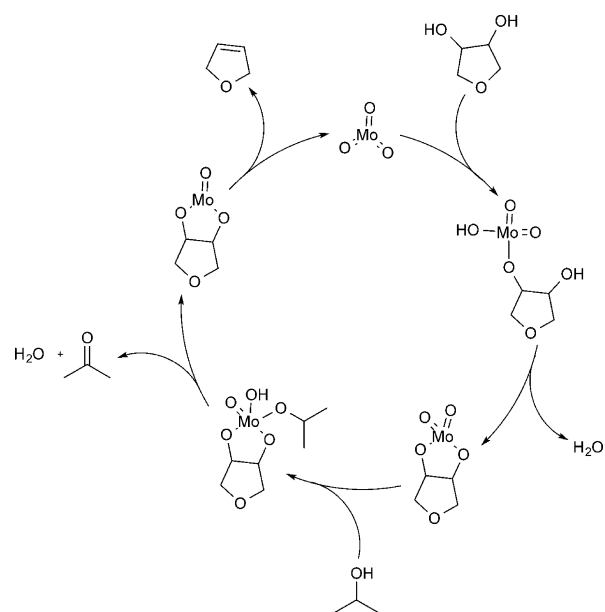
which is in turn lower than the one for H₂ (by 10.3 kcal/mol). These results are in agreement with the observed lack of reduction by hydrogen even at high pressures and also explain the need for higher temperatures when *i*PrOH is oxidized instead of the diol (240−250 °C vs 190−200 °C).

In analogy with a previously published investigation of the CH₃ReO₃-catalyzed DODH of 1,4-anhydroerythritol driven by the oxidation of 3-octanol,[63] we studied the mechanism of the molybdenum-catalyzed DODH of 1,4-anhydroerythritol driven by the oxidation of *i*PrOH. The catalytic cycle is shown in Scheme 5.

The proposed reaction mechanism consists of condensation of MoO₃ with the diol in two steps to form the molybdenum(VI) diolate, followed by coordination and transfer hydrogenation of *i*PrOH and finally alkene extrusion to form 2,5-dihydrofuran and MoO₃. The corresponding free-energy diagram is shown in Figure 2. Formation of the diolate complex from MoO₃ and 1,4-anhydroerythritol via **TS1−2** and **TS3−4** is relatively facile since the diol is already in the right conformation to form the five-membered diolate complex. Coordination of *i*PrOH to the already crowded diolate complex (**TS5−6**) is more demanding with an activation barrier of 7.1 kcal/mol. The step with the highest activation barrier, however, is the oxidation of *i*PrOH (**TS7−8**) with an activation barrier of 24.1 kcal/mol. The last step in the reaction sequence, the extrusion of 2,5-dihydrofuran, has the second-highest activation barrier at 13.8 kcal/mol. An illustration of the transition state for the alkene extrusion (**TS9−10**) is shown in Figure 3, while the transition state for the reduction of *i*PrOH (**TS7−8**) is shown in Figure 4.

The DFT calculations carried out in this work reproduced the marked differences between the three fundamentally different types of reductants, namely the diol, *i*PrOH, and hydrogen. This agreement with experimental data gives promise that further

Scheme 5. Catalytic Cycle for the DODH of 1,4-Anhydroerythritol Driven by Oxidation of ^{i}PrOH

Figure 3. Transition state **TS9−10** for the extrusion of 2,5-dihydrofuran.
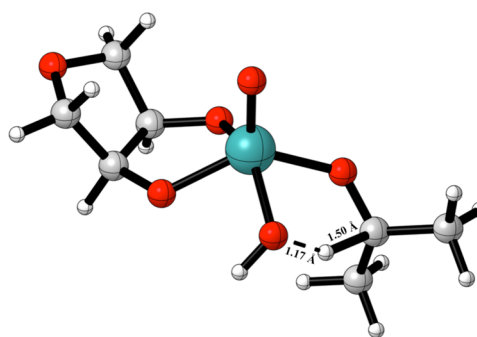
Figure 4. Transition state **TS7−8** for the reduction of ^{i}PrOH.

theoretical studies could aid in the discovery of new and more efficient transition-metal catalyzed DODH processes. Furthermore, the calculated energy profile for the deoxydehydration of erythritol clearly pinpoints the reduction of the metal center prior to extrusion of the alkene as the rate-limiting transition state.

■ CONCLUSIONS

In summary, a cheaper and more sustainable DODH process for the conversion of vicinal diols into the corresponding alkenes has been developed. The process relies on a molybdenum-based
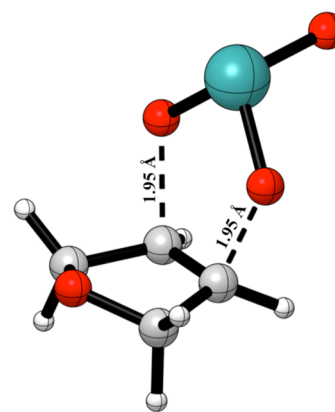
catalyst, in particular the cheap and commercially available $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (AHM), and the use of ^{i}PrOH as both a solvent and reductant: Using 5 mol % of catalyst and heating the reaction mixture to 240−250 °C for 12−18 h, alkene yields can
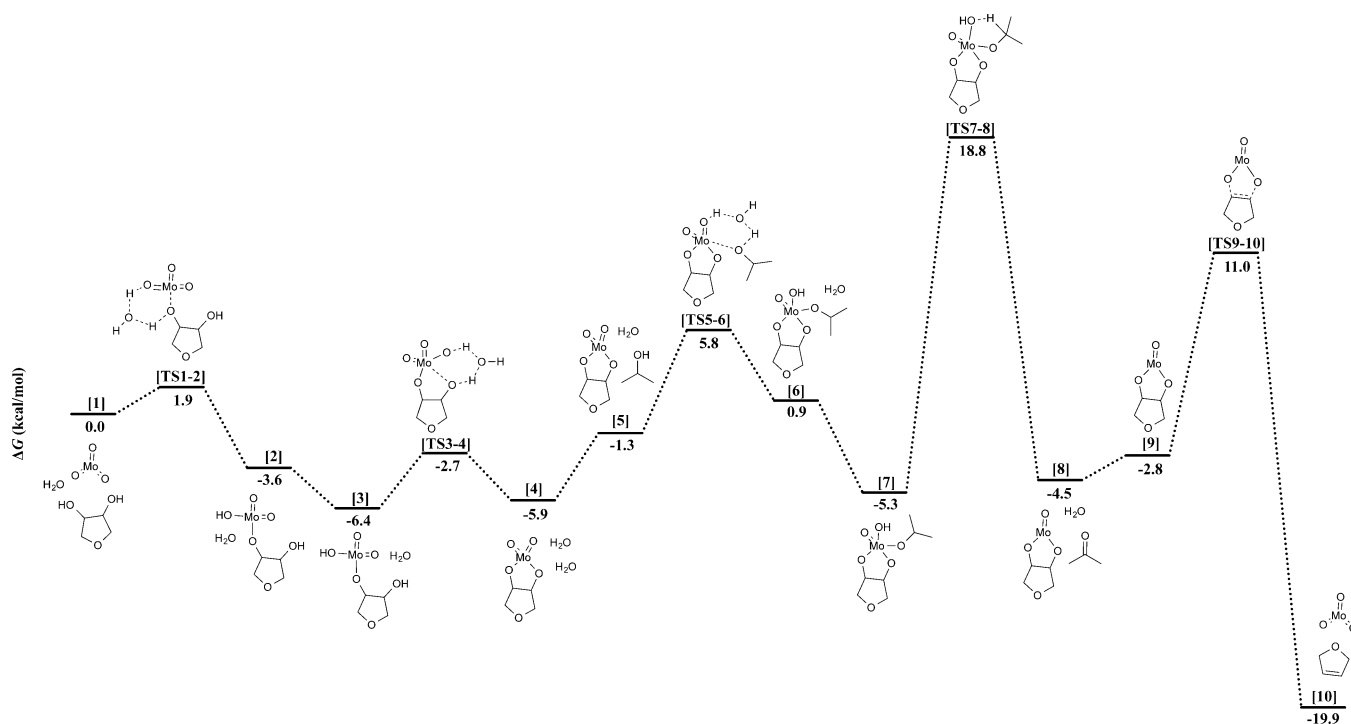

Figure 2. Free-energy diagram for the DODH of 1,4-anhydroerythritol at 298 K.

be as high as 77%, and the combined yield of reduced species can reach 92%. The scope of the reaction has been expanded to glycerol, which undergoes DODH to allyl alcohol followed by deoxygenation to propylene, and to erythritol, which undergoes etherification to 1,4-anhydroerythritol followed by DODH to 2,5-dihydrofuran. The molybdenum-catalyzed deoxygenation of allylic alcohols and benzyl alcohol driven by the oxidation of either ^{i}PrOH or EtOH has been optimized experimentally, and—under basic conditions—the yield can reach 65% for allylic alcohols and 93% for benzyl alcohol.

Neither the cost nor the sustainability of the catalyst, the solvent, and the reductant hamper the implementation of this DODH process on an industrial scale, but the isolation and quantification of propylene from the sequential DODH and deoxygenation of glycerol needs to be vastly optimized to be competitive. In addition, the scope of the reaction needs to be expanded to biomass-derived polyols that are cheaper and more available than erythritol and that lead to products with significantly higher values than propylene and allyl alcohol, for instance, 1,3,5-hexatriene.

EXPERIMENTAL SECTION

Materials. Unless otherwise stated, all materials were purchased from Sigma-Aldrich in ≥98% purity and used as received. The molybdenum-based catalysts $MoO_2Cl_2(dmso)_2$,[64] $MoO_2(CH_3)_2(bipy)$,[37] $MoO_2Cl_2(bipy)$,[36] $MoO_2Br_2(bipy)$,[36] $(Bu_4N)_2Mo_6O_{19}$,[38] and $(NH_4)_6MnMo_9O_{32}·8H_2O$[65] were prepared by literature procedures. The preparation of 3,4-hexanediol is described in the Supporting Information. 2-Ethyl-1,2-butanediol was prepared by a Sharpless dihydroxylation[66] of 2-ethyl-1-butene, which was prepared by the Wittig reaction[67] of 3-pentanone with $Ph_3P=CH_2$; 3-ethyl-3,4-hexanediol was prepared by a Sharpless dihydroxylation[66] of 2-ethyl-3-hexene, which was prepared by the Wittig reaction[67] of 3-pentanone with $Ph_3P=CHCH_2CH_3$.

Reaction Conditions A. Forty millimoles of diol, 2.0 mmol of catalyst (5 mol %, calculated with respect to the amount of molybdenum), 500 mg of hexadecane (internal standard), and 100 mL of solvent were mixed in a 300 mL PTFE cup and placed in a 400 mL Berghof autoclave with a magnetic stir bar (500 r.p.m.) and computer-controlled heating plate. The autoclave was sealed, pressurized with 10−25 bar of H_2 or N_2, and heated to 250 °C for 800 min; the temperature typically stabilized between 240 and 250 °C, while the maximum pressure was 60−90 bar (a typical heating profile is shown in Figure S1). When the system had cooled to room temperature, the pressure was released, and the reaction mixture was filtered to remove a fine, black precipitate and analyzed by GC (for determination of conversion and yields) and GC-MS (for observation and identification of other products).

Reaction Conditions B. The experimental setup was identical to that in reaction conditions A except for the following changes: The reactions were conducted on half scale in a 150 mL Swagelok cylinder, which for 18 h was placed in an aluminum block that had been preheated to 250 °C. Neither the temperature nor the pressure could be monitored in this experimental setup, but on the other hand, it was possible to conduct up to four parallel experiments.

Computational Methods. Visualization and comparison of structures were performed in Maestro version 9.3.515.[68] DFT calculations were performed in Jaguar[69] with the B3LYP functional[70−72] with added D3 corrections.[73] We used the LACVP** basis set, which applies the Hay−Wadt ECP and basis

set for molybdenum, and the 6-31G** basis set for all other atoms.[74] Transition states were found by a quadratic synchronous transit (QST)[75] search. Intermediates were found by minimizing the transition states toward both the expected starting material and the expected final product. All intermediates and transition states were characterized by a full, analytic frequency calculation at 25 °C that resulted in only positive frequencies for intermediates and exactly one imaginary frequency for transition states. Approximate Gibbs free energies in the solution phase (G_{solv}) were obtained by combining the solution phase SCF energies ($E_{SCF,solv}$), which were calculated with the Poisson−Boltzmann solver (PBF)[76,77] using standard parameters for methanol, with the vibrational contribution from the gas phase ($G_{gas} − E_{SCF,gas}$) in line with earlier work ($G_{solv} = E_{solv} + G_{gas} − E_{gas}$).[78] The computational model system was kept neutral to avoid complications when comparing charged and neutral species computationally.[79] We do not rule out the possibility of charged molecular species but rather suggest the neutral complexes treated in this work to be suitable computational models of the actual complexes. The structural figures in the article were created with CYLview[80] using the POV raytracer for rendering.[81] Structural figures in the Supporting Information were made with XYZViewer.[82]

ASSOCIATED CONTENT

Ⓢ Supporting Information

This file is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00427.

> Typical heating profile obtained under reaction conditions A; infrared spectra of precipitated catalyst; optimization of reaction conditions; test of additional molybdenum-based catalysts; details on the formation of acetals and characterization of an ether; reactivity of diols containing tertiary OH groups; structures and energies for all the relevant complexes (PDF)

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Notes
The authors declare no competing financial interest.

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