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Influence of the pendant arm in deoxydehydration catalyzed by dioxomolybdenum complexes supported by amine bisphenolate ligands†

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Dioxomolybdenum complexes supported by aminebisphenolate ligands were evaluated for their potential in catalyzing the deoxydehydration (DODH) reaction to establish structure−activity relationships. The nature of the pendant arm in these aminebisphenolate ligands was found to be crucial in determining reactivity in the deoxydehydration of styrene glycol (1-phenyl-1,2-ethanediol) to styrene. Pendant arms bearing strongly coordinating N-based groups such as pyridyl or amino substituents were found to hinder activity while those bearing non-coordinating pendant arms (benzyl) or even weakly coordinating groups (an ether) resulted in up to 6 fold enhancement in catalytic activity. A dioxomolybdenum complex featuring an aminemonophenolate ligand derived from the aminebisphenolate skeleton also resulted in similar yield enhancements. Although aromatic solvents were found to be ideal for performing these catalytic reactions, polar solvents such as N,N-dimethylformamide (DMF) and N,N′-dimethylpropyleneurea (DMPU) were also suitable. The catalyst was found to maintain its structural integrity under the optimized conditions and could be recycled for a second catalytic run without loss of activity. With the activated substrate meso-hydrobenzoin, trans-stilbene was obtained in a 56% yield at 220 °C along with benzaldehyde (71%) suggesting that the diol is a competing reductant under these conditions.
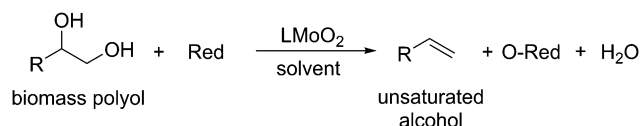
Introduction

Deoxygenation of biomass is gaining momentum as a process to produce, and complement bulk chemicals currently manufactured by petrochemical industries.[1] The highly oxygenated nature of biomass has proven to be an obstacle when attempting to reduce these molecules into platform chemicals. This challenge in reduction reactions has prompted chemists to develop new methods in the removal of oxygen from biomass.[2] In this respect, the deoxydehydration (DODH) reaction has proven to be a favorable reaction for the production of olefins from vicinal diols, a functionality abundantly present in lignocellulosic biomass (Scheme 1).[3] The reaction typically employs high oxidation state oxometal complexes as catalysts and a reducing agent in an aromatic or alcoholic solvent.[4]

The most effective catalysts reported thus far for the deoxydehydration reaction are rhenium-based that have achieved

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Scheme 1   Deoxydehydration of vicinal diol to an olefin.

alkene yields well over 90%.[5] Cook and Andrews documented early findings of the deoxydehydration reaction with the use of Cp*ReO₃ for the conversion of styrene glycol to styrene (Fig. 1(a)).[6] Other research groups have studied heterogeneous rhenium catalysts that are often coupled with precious metals to act as promoters.[7] Alternatively, researchers have turned to vanadium and molybdenum as an economically viable option for catalysts.[8] However, these readily available catalysts were found to have relatively low DODH activity when compared to rhenium-based catalysts. In order to increase reactivity, complexes where the metal is supported by different ancillary ligands have been evaluated.[8] The choice of reductant has been demonstrated to be crucial in achieving effective catalysis using molybdenum complexes.[9]

In the initial phases of using molybdenum complexes for DODH catalysis, most reactions involved molybdate salts, though, further research has been conducted on molybdenum complexes
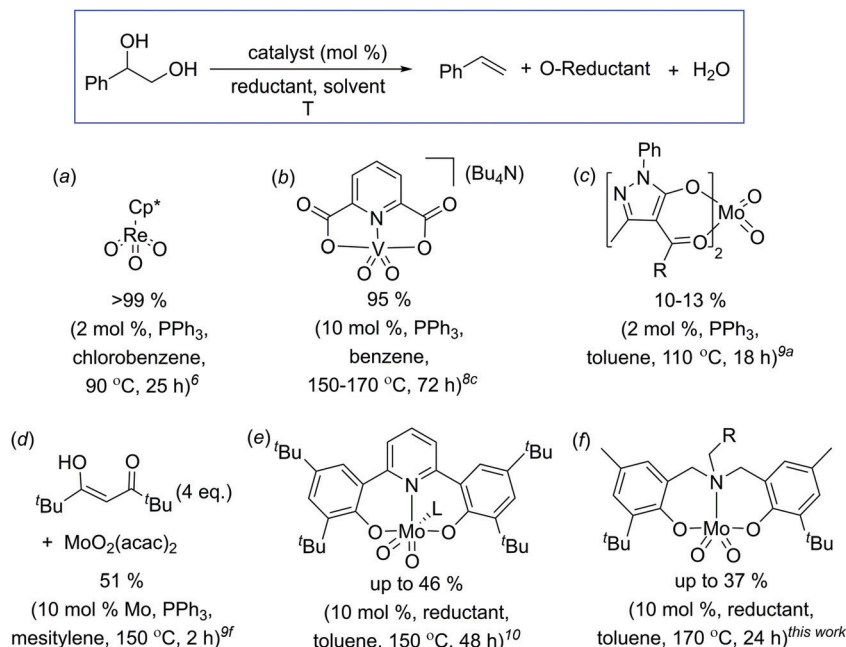
Fig. 1 DODH of styrene glycol catalyzed by selected metal complexes.

which feature supporting ligands.[9] Molybdenum complexes evaluated thus far for DODH reactivity are based on a wide range of ancillary ligands. Acylpyrazolonate ligand based molybdenum complexes were the first to be tested for their reactivity in DODH reactions by Hills and coworkers in 2013 (Fig. 1(c)).[9a] These complexes were found to be moderately effective in reducing 1-phenylethane-1,2-diol to styrene (10–13%) and cyclooctane-1,2-diol to cyclooctene (55%) using a 2 mol% loading of the catalyst at 110 °C over 18 h. The higher yield obtained with an aliphatic diol (1,2-octanediol) compared to the activated diol (1-phenylethane-1,2-diol) is notable. The Okuda group used bis(phenolate)molybdenum complexes as catalysts for the DODH of anhydroerythritol at 200 °C employing 3-octanol as solvent and reductant.[9d] The olefin product (2,5-dihydrofuran) was obtained in a 57% yield with conventional heating while a 49% yield was obtained under microwave irradiation using their best catalyst. In 2018, De Vos and Stalpaert investigated the stabilizing effects of bulky β-diketone ligands (Fig. 1(d) and Table S1, ESI†), and demonstrated that the bulky β-diketone 2,2,6,6-tetramethylheptane-3,5-dione (4 equiv.) gave a significant increase in alkene yield (up to 93%) with several different substrates (at 170–200 °C) using 10 mol% of MoO$_2$(acac)$_2$.[9f] The addition of the bulky ligand was demonstrated to inhibit catalyst oligomerization under the reaction conditions, which was proposed to prevent catalyst precipitation and hence increase catalytic activity. More recently, Kilyanek and Tran demonstrated the reactivity of a five-coordinate dioxomolybdenum complex and its OPPh$_3$ adduct (six-coordinate) in the DODH reaction (Fig. 1(e) and Table S1, ESI†).[10] The five-coordinate complex (up to 46% alkene yield) was found to be marginally inferior to its OPPh$_3$ adduct (up to 62% alkene yield) for several substrates using various reductants in temperature range from 150–190 °C.

Our research group is interested in developing catalytic processes based on molybdenum catalysts for converting vicinal diols to olefins. We recently reported on deoxydehydration of glycols using catalytic amounts of ammonium heptamolybdate (AHM) in the presence of Na$_2$SO$_3$ as a benign reductant.[11] Our interest in evaluating the role of ancillary ligands in supporting dioxomolybdenum centers in facilitating the deoxydehydration reaction, prompted us to explore the use of amine bisphenolate ligands. These ligands have been used extensively in stabilizing metal centers from across the periodic table for various catalytic applications.[12] We were particularly attracted by the modular synthesis of this class of ligands which allows incorporating subtle changes to sterics and electronics as well as the nature of the pendant arm. All of these features can be favorably tuned to study the effect of the ligand backbone on catalytic activity, and thus develop structure–activity relationships (SAR). Similar SARs have been previously reported in olefin polymerization studies catalyzed using complexes stabilized by amine bisphenolate ligands. Based on these studies, the presence of a pendant arm featuring an amine donor in the ligands was suggested to yield thermally stable and reactive complexes.[13] Other studies have demonstrated a correlation between the M–X (where X is the donor atom in the pendant arm) bond length in such complexes and olefin polymerization activity.[14] Dioxomolybdenum complexes based on aminebisphenol ligands have previously found utility in various applications including olefin epoxidation, and oxo-transfer catalysis.[15]

In this study, we have evaluated the catalytic promise of dioxomolybdenum complexes supported by amine bisphenolate (N$_x$O$_y$; x = 1 or 2; y = 2 or 3) ligands in effecting the DODH reaction (Fig. 1(f)). Catalytic reactions were conducted using styrene glycol as a model substrate at 170 °C for 24 hours.

Catalytic activity was evaluated as a function of ligand features to establish structure–activity relationships. Based on these studies, the nature of the pendant arm was found to be critical in determining catalytic potential of these complexes and yield enhancements up to 6 times were observed.

Results and discussion

At the outset we synthesized a dioxomolybdenum complex **1b**, based on an aminebisphenolate ligand **1a** featuring a pyridyl pendant arm (Scheme 2). The molybdenum complex was synthesized in a low yield (26%) by the reaction of the ligand with $MoO_2(acac)_2$ in THF at 50 °C, and was characterized by ^1H & $^{13}C\{^1H\}$ NMR, IR spectroscopy and elemental analysis.

Complex **1b** was then evaluated for its catalytic potential in the deoxydehydration of 1-phenyl-1,2-ethanediol (styrene diol/ glycol) using PPh_3 as a reductant in toluene as a solvent at 170 °C; only a 5% yield of styrene was detected under these conditions (Fig. 2). Styrene yield was quantified by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. Since a low styrene yield was obtained with catalyst **1b** we became curious about the feature in the amine bisphenolate ligand which was responsible for impeding catalytic activity. We sought to understand this undesirable effect of the ligand on catalysis by making systematic changes to the ligand backbone and evaluating the resulting molybdenum complexes in the above deoxydehydration reaction.

To uncover the ligand feature which is responsible for the low catalytic activity of complex **1b**, we began by modifying the pendant arm (Scheme 2). We hypothesized that the strength of interaction between the pendant arm and the molybdenum center could potentially influence catalytic activity. A strongly coordinating pendant arm could resist dissociation from the molybdenum center resulting in reduced catalytic activity while a hemilabile pendant arm would create a free coordination-site around the metal when required during the catalytic cycle. When complex **2b** featuring a dialkylamino substituent (NMe_2) was evaluated in the deoxydehydration of styrene diol, a 9%

yield of styrene was obtained (Fig. 2). This modest increase in styrene yield with **2b** suggested that the pyridyl pendant arm in complex **1b** was perhaps impeding its catalytic activity. This is presumably due to the stronger binding ability of the rigid pyridine N to the molybdenum center compared to the amino N in complex **2b**. Alternatively, the hemilabile nature of the pendant arm in **2b** could result from the sterically hindered nature of the tertiary amine donor in the dialkylamino pendant group. To further explore the potential of hemilabile pendant arms in facilitating the deoxydehydration reaction, we synthesized complex **3b** featuring an ether group in the pendant arm. The O donor in the pendant arm should be an even more weakly coordinating group given the higher electronegativity (lower basicity) of O compared to N. Quite significantly, this resulted in a styrene yield of 31% (Fig. 2) under the reaction conditions which is significantly higher compared to the yield (5%) observed with catalyst **1b**. Expanding on this result, when complex **4b** featuring a non-coordinating benzyl arm was used in the deoxydehydration reaction, gratifyingly, styrene was also obtained in 34% yield (Fig. 2). This result further confirms the importance of the coordinating nature of the pendant arm in controlling catalytic activity.

To understand the importance of the phenol arms in amine bisphenolate ligands in controlling the catalytic potential of these molybdenum complexes, we synthesized an amine monophenol ligand (**5a**) through a reductive amination reaction (Scheme 2). The corresponding dioxomolybdenum complex **5b** was obtained as a μ-oxo dimer under the reaction conditions.[16] When the catalysis reaction was performed using 5 mol% **5b** (10 mol% Mo since it is a dimeric complex), styrene was produced in 32% yield suggesting that removal of a phenol arm has the same effect as the transition from a strongly coordinating to a hemilabile or weakly coordinating pendant arm (Fig. 2). It must be noted that the dinuclear nature of the complex **5b** could result in a change in mechanism of the catalytic reaction as compared to the mononuclear complexes **1b–4b**. When the catalyst loading of **5b** was increased to 15 mol%, the reaction resulted in a modest increase of styrene yield to 48%.

The detection of resonances characteristic of the catalyst (**4b**) in ^1H NMR spectra of reactions at the end a catalytic run,
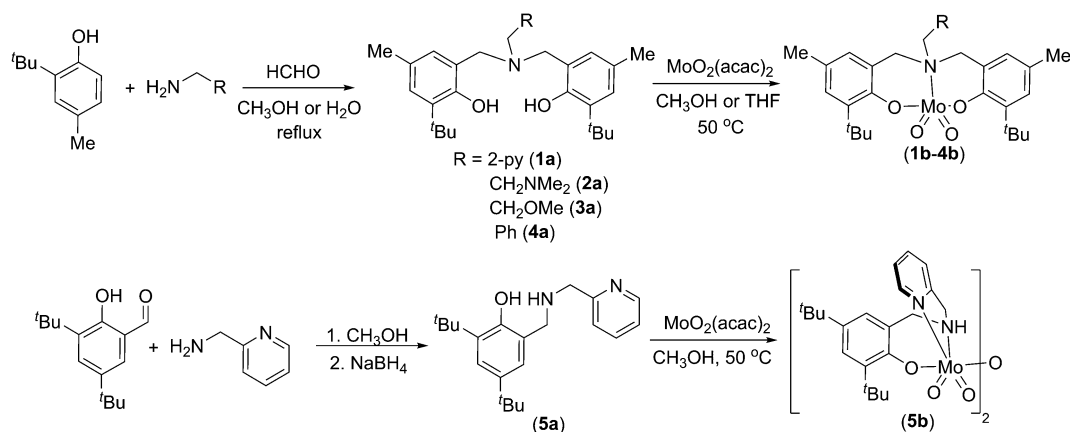
Scheme 2 Synthesis of ligands and molybdenum complexes used in this study.
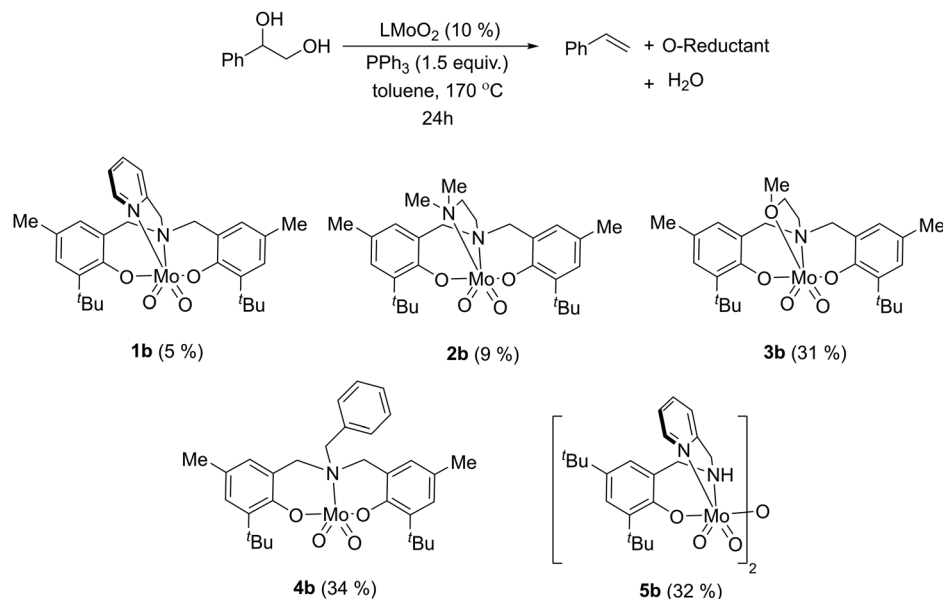
Fig. 2 Molybdenum catalysts supported over amine bisphenolate ligands used in this study.

prompted us to test the reuse of the catalyst. Hence, a second equivalent of the substrate was added to the reaction flask after the first 24 hour period (37% yield of styrene from first run) and the catalytic reaction allowed to run for an additional 16–24 hours. The catalyst in solution was found to be active, and an additional 44% of styrene was formed during the second run. Attempts to further reuse the catalyst were unsuccessful. This loss of activity after the second run could presumably be indicative of the gradual formation of catalytically inactive (heterogeneous) molybdenum species during the catalysis.

The choice of solvent is crucial to realizing the full potential of DODH reaction in converting biobased vicinal diols to corresponding alkenes. Previous studies using rhenium catalysts used alcohols as solvent and sacrificial reductant for effecting conversion of sugar alcohols.[17] A screen was performed to identify solvent compatibility for DODH catalyzed by complex **4b** (Table 1). Aromatic solvents including mesitylene, xylene, chlorobenzene, and toluene were found to be equally effective (30–34%) in promoting catalysis at 170 °C. A catalytic reaction carried out in dry toluene as solvent where reagents were loaded into the reactor inside a glovebox did not offer any improvement, and produced styrene in 33% yield (Table 1, entry 3). Although polar solvents such as DMF and DMPU furnished styrene in comparatively lower yields (~20%), these results are worth noting as further developments in this direction may be imperative to realize the full substrate scope of sugar-based polyols in the DODH reaction. No reaction was observed when H_2O was used as solvent. Although alcohols have been used as a sacrificial reductant and solvent in a variety of prior studies, a low yield of 5% styrene was obtained when 3-octanol was employed under our conditions. Although higher temperatures (200 °C) have been typically employed in molybdenum catalyzed reactions involving alcohol reductants,[9d,g] we did not explore such conditions using 3-octanol. The yield of benzaldehyde formed under the reaction conditions

Table 1 Solvent screen for DODH of styrene glycol using **4b**[a]

| Entry | Solvent | Yield (%) | |
		C=C[b]	C=O[e]
1.	Mesitylene	31	5
2.	Xylene	30	4
3.	Toluene	34 (33)[c]	1
4.	DMF	18	nd
5.	DMPU	22	13
6.	H_2O	0	0
7.[d]	3-Octanol	5	1
8.	Chlorobenzene	33	5

[a] Reaction conditions: styrene glycol (0.5 mmol), PPh$_3$ (0.75 mmol) and **4b** (10 mol%) were combined in the solvent (ca. 2.5 mL) and heated at 170 °C for 16–24 hours. DMF = N,N-dimethylformamide, DMPU = N,N'-dimethylpropyleneurea. [b] Yield of styrene was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c] Dry toluene was used as solvent, and reagents added inside a glovebox. [d] Using 3-octanol as solvent and sacrificial reductant; no PPh$_3$ added. [e] Yield of benzaldehyde.

(Table 1; C=O) for these solvents was in the range of 1–13%; the highest yield was obtained in DMPU, with styrene and benzaldehyde obtained in a 2:1 ratio. The benzaldehyde side-product is obtained by oxidative cleavage of styrene glycol and is indicative of the diol acting as a reductant under our catalytic conditions.[9b,10]

In efforts to improve the catalytic efficiency of **4b**, we explored the effect of temperature and catalyst loading on the DODH of styrene glycol. No significant enhancements in styrene yield were noted in reactions performed at a higher temperature (~190–200 °C) or at a higher catalyst loading (20% at 170 °C). As noted earlier, a marginal improvement in styrene yield (48%) was observed when a higher catalyst loading (15 mol%) of **5b** was used. However, styrene was formed in 36% yield even when the catalysis was performed at 150 °C (Table 2, entry 1). We also explored the possibility of generating the active catalyst *in situ* under the catalytic conditions from the molybdenum precursor

Table 2 Reductant and substrate scope for DODH using **4b**[a]

Entry	Substrate	Reductant	Yield (%)	
			C=C[b]	C=O[c]
1.	Styrene glycol	PPh$_3$	34 (36)[d]	1
2.		3-Octanol	5	2
3.		Na$_2$SO$_3$	37	18
4.		Carbon	31	10
5.		Zn granules	31	12
6.	1,2-Decanediol	PPh$_3$	5	
7.	1,2-Cyclohexanediol	PPh$_3$	3	
8.	Diethyl tartrate	PPh$_3$	18	
9.	(R,R)-(+)-Hydrobenzoin	PPh$_3$	42 (5)[e]	68
10.[f]	meso-Hydrobenzoin	PPh$_3$	56 (4)[e]	71

[a] Reaction conditions: styrene glycol (0.5 mmol), reductant (0.75 mmol) and **4b** (10 mol%) were combined in toluene (ca. 2.5 mL) and heated at 170 °C in an oil bath for 16–24 hours. [b] Yield of styrene was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c] Yield of benzaldehyde. [d] Reaction carried out at 150 °C. [e] The major product is trans-stilbene; yield of cis-stilbene in parentheses. [f] Reaction carried out at 220 °C in a heating block.

MoO$_2$(acac)$_2$ and stoichiometric equivalents of the ligand. Thus, a catalytic reaction carried out using 10 mol% MoO$_2$(acac)$_2$ and 10 mol% of ligand **4a** produced styrene in 30% yield. A higher loading of the ligand (20 mol%) did not offer any improvements under the standard reaction conditions.

Practical limitations to large-scale use of PPh$_3$ as a reducing agent in DODH reactions prompted us to evaluate alternate reductants (Table 2, entries 1–5). Although a variety of reductant classes support rhenium catalyzed DODH reactions,[18] alcohols represent the most explored category of reductants in molybdenum catalyzed reactions apart from PPh$_3$.[9b,c,d] However, most reported studies based on alcohols as reducing agents in DODH reactions catalyzed by molybdenum catalyzed reactions were performed at temperatures around or above 200 °C. Only a low yield of styrene (5%) was detected when 3-octanol was used the reductant under our standard conditions at 170 °C. The inorganic reductant Na$_2$SO$_3$ (37%) as well as elemental reductants C and Zn (31% each) produced styrene in yields at par with PPh$_3$. The relatively inexpensive nature of these reductants as well as the nature of their oxidized byproducts offer advantages from an environmental as well as process standpoint compared to PPh$_3$. The inorganic reductants (Na$_2$SO$_3$, C and Zn) resulted in the formation of higher amounts of benzaldehyde (10–18%) compared to PPh$_3$ (1%).

A brief survey of the substrate scope using dioxomolybdenum catalyst **4b** was also undertaken (Table 2, entries 6–10). The catalyst was found to be ineffective for aliphatic diols such as 1,2-decanediol and 1,2-cyclohexanediol producing the corresponding olefins in low yields (<10%) (Table 2, entries 6 & 7). With the bio-derived substrate diethyltartarate, the corresponding olefin product diethyl fumarate was obtained in 18% yield. Starting from highly activated diol (R,R)-(+)-hydrobenzoin, trans-stilbene was obtained in a 42% yield along with cis-stilbene (5%) at a high diol conversion of 81%. Benzaldehyde, the product resulting from oxidative cleavage of the diol substrate, was also produced in a 68% yield along with the olefin products. This observation is again supportive of the possibility of competitive

reduction from the diol substrate under our catalytic conditions. When meso-hydrobenzoin was used as the substrate at an elevated temperature (220 °C), trans-stilbene was produced in a high yield of 56% along with 71% of benzaldehyde (95% conversion). Although inefficient at converting aliphatic diols, the yields of styrene and stilbene obtained with catalyst **4b** are comparable to other reported molybdenum complexes (Table S1, ESI†).[9a,f,10] Studies based on vanadium complexes exhibit relatively higher catalytic activities for the conversion of styrene glycol.[8c,d] In contrast, rhenium based catalytic systems developed so far display much higher conversions and yields under relatively milder reaction conditions. Generally, quantitative diol conversion as well as high alkene yields (>90%) have been achieved starting from both styrene glycol and hydrobenzoin substrates using various Re catalysts.[5a,18f,19]

Conclusion

To summarize, we have explored the potential of dioxomolybdenum complexes supported over aminebisphenolate ligands in catalyzing the deoxydehydration reaction. A series of aminebisphenol ligands were evaluated, and the coordinating ability of the pendant arm was found to be central in determining catalytic potential with weakly-coordinating or non-coordinating arms exhibiting the highest catalytic activity. The removal of one of the phenol arms also resulted in a similar yield enhancement. The solution of catalyst **4b** featuring a non-coordinating benzyl pendant arm could be recycled for a second catalytic run without loss of activity. Aromatic solvents were found to facilitate the deoxydehydration reaction and inorganic reductants were found to be as effective as PPh$_3$. The detection of benzaldehyde in our catalytic reactions is supportive of a competing reduction by the diol substrate through an oxidative cleavage pathway. Although the catalyst **4b** was ineffective at catalyzing DODH of aliphatic diols, higher yields were obtained with activated substrates such as (R,R)-(+)-hydrobenzoin and meso-hydrobenzoin especially at elevated temperatures. Mechanistic investigations are currently underway in our laboratory to understand these ligand effects.

Experimental section

General procedures

All air and water sensitive manipulations were carried out under a nitrogen atmosphere by using standard Schlenk line techniques or using an MBraun Labstar pro glovebox. All ^{1}H, ^{13}C{^{1}H} and ^{31}P NMR spectra were collected on a Varian 400-MR spectrometer. Chemical shifts (δ) for ^{1}H NMR spectra were referenced to the residual protons on deuterated chloroform (7.26 ppm) and ^{13}C{^{1}H} NMR spectra were referenced to the residual chloroform (77.1 ppm). Infra-red spectra were recorded on a Thermo Scientific NICOLET iS10 Spectrophotometer equipped with a SMART iTR. Gas Chromatography-Mass Spectrometric (GC-MS) analysis was performed on an Agilent 6850 series GC system connected to an Agilent 5973N Mass Selective Detector equipped with a HP-5MS column (30 m × 0.25 mm × 0.25 µm). Elemental analysis

was performed at Robertson Microlit Laboratories (New Jersey, USA). Precursors for ligand and complex synthesis were used as received. $CDCl_3$ was used as received from Sigma. Solvents (methanol, toluene, and hexanes) were purchased from Fisher Scientific and used as received. All starting materials were procured from commercial sources and used without further purification. The ligands (**1a–5a**) and complex **5b** used in this study were synthesized by modifications of literature protocols.[16,20]

Synthesis of dioxomolybdenum complexes

Synthesis of 1b. To an oven dried round bottom flask was added ligand **1a** (0.1 g, 0.217 mmol) and $MoO_2(acac)_2$ (0.071 g, 0.217 mmol) in THF (*ca.* 6 mL). The round bottom flask was stirred in an inert nitrogen atmosphere for 26 hours and gravity filtered to produce an orange precipitate (0.032 g, 26%). ^1H NMR ($CDCl_3$, 400 MHz, 28 °C) δ 9.16 (d, 1H, $^3J_{HH}$ = 8 Hz), 7.55(t, 1H, $^3J_{HH}$ = 8), 7.16 (t, 1H, $^3J_{HH}$ = 8 Hz), 6.89 (s, 2H), 6.80 (d, 1H, $^3J_{HH}$ = 8 Hz), 6.75 (s, 2H), 4.96 (d, 2H, $^2J_{HH}$ = 16 Hz), 3.95 (s, 2H), 3.68 (d, 2H, $^2J_{HH}$ = 12 Hz), 2.21 (s, 6H), 1.25 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 26 °C, 100 MHz) δ 159.3, 155.2, 151.5, 139.3, 138.4, 128.7, 127.7, 127.6, 122.7, 122.1, 121. 1, 63.5, 58.9, 34.6, 29.8, 20.8. Selected IR (cm^{-1}) 922, 898. Anal. calcd for $C_{30}H_{38}N_2O_4Mo$: C, 61.43%; H, 6.53%; N, 4.78%. Found: C, 61.03%; H, 6.52%; N, 4.66%.

Synthesis of 2b. To a round bottom flask was added ligand **2a** (0.257 g, 0.6 mmol) and methanol (*ca.* 2.5 mL). The resulting mixture was heated to 50 °C before addition of $MoO_2(acac)_2$ (0.197 g, 0.6 mmol) and then maintained at 50 °C for 2 hours. The mixture was then gravity filtered and methanol washed to yield bright yellow precipitate (0.330 g, 97%). ^1H NMR ($CDCl_3$, 400 MHz, 28 °C) δ 7.05 (s, 2H), 6.79 (s, 2H), 4.08 (d, 2H, $^2J_{HH}$ = 12 Hz), 3.92 (d, 2H, $^2J_{HH}$ = 12 Hz) 2.90 (s, 6H), 2.87–2.80 (m, 4H), 2.26 (s, 6H), 1.42 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 26 °C, 100 MHz) δ 161.3, 136.8, 129.3, 127.3, 127.2, 123.3, 60.9, 56.6, 53.5, 50.5, 34.7, 30.3, 30.2, 20.8. Selected IR (cm^{-1}) 914, 877. Anal. calcd for $C_{28}H_{42}N_2O_4Mo$: C, 59.35%; H, 7.47%; N, 4.94%. Found: C, 59.50%; H, 7.36%; N, 4.93%.

Synthesis of 3b. To a round bottom flask, ligand **3a** (1.00 g, 2.34 mmol) and methanol (*ca.* ~10 mL) were added together and refluxed for about 3 hours. $MoO_2(acac)_2$ (0.762 g, 2.34 mmol) was then added to the reaction mixture and the solution turned from clear to yellow upon this addition. A yellow precipitate is collected through gravity filtration and washed with cold methanol (1.10 g, 86% yield). ^1H NMR ($CDCl_3$, 28 °C, 400 MHz) δ 7.10 (s, 2H), 6.78 (s, 2H), 4.68 (d, 2H, $^2J_{HH}$ = 16 Hz), 3.78 (s, 3H), 3.68 (d, 2H, $^2J_{HH}$ = 14 Hz), 3.30 (t, 2H, $^3J_{HH}$ = 8 Hz), 2.84 (t, 2H, $^3J_{HH}$ = 8 Hz), 2.28 (s, 6H), 1.42 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 26 °C, 100 MHz) δ 158.0, 138.3, 129.2, 128.0, 127.5, 122.4, 69.4, 63.6, 63.1, 52.7, 34.8, 29.9, 20.9. Selected IR (cm^{-1}) 929, 909. Anal. calcd for $C_{27}H_{39}NO_5Mo$: C, 58.58%; H, 7.10%; N, 2.53%. Found: C, 58.42%; H, 7.02%; N, 2.51%.

Synthesis of 4b. To a round bottom flask, ligand **4a** (3.88 g, 8.45 mmol) and methanol (*ca.* 10 mL) were added together and refluxed for about 3 hours. $MoO_2(acac)_2$ (2.30 g, 7.02 mmol) was then added to the reaction mixture and the solution turned from clear to orange upon this addition. An orange precipitate is collected through gravity filtered and washed with cold methanol (2.96 g, 72% yield). ^1H NMR (DMSO-d_6, 28 °C, 400 MHz) δ 7.35–7.33 (m, 3H), 7.02 (m, 4H), 6.73 (s, 2H), 4.05 (d, 2H, $^2J_{HH}$ = 12 Hz), 3.96 (s, 3H), 3.23 (d, 2H, $^2J_{HH}$ = 12 Hz), 2.25 (s, 6H), 1.38 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 26 °C, 100 MHz) δ 152.3, 137.6, 136.8, 129.6, 129.1, 129.0, 128.0, 128.0, 127.5, 122.1, 58.5, 56.6, 34.7, 29.6, 20.8. Selected IR (cm^{-1}) 928, 908. Anal. calcd for $C_{31}H_{19}NO_4Mo$: C, 63.58%; H, 6.71%; N, 2.39%. Found: C, 63.64%; H, 6.57%; N, 2.39%.

Synthesis of 5b. To a round bottom flask was added $MoO_2(acac)_2$ (0.492 g, 1.50 mmol) and ligand (**5a**) (0.491 g, 1.50 mmol) in methanol (*ca.* 5 mL). The reaction was maintained at 50 °C for 2 hours during which a bright orange crystalline solid formed. The precipitate was then gravity filtered and washed with methanol to obtain the product as an orange solid (0.365 g, 26%). ^1H NMR ($CDCl_3$, 400 MHz, 28 °C) δ, 8.69 (d, 1H, $^3J_{HH}$ = 4 Hz), 7.48 (t, 1H, $^3J_{HH}$ = 8 Hz), 6.99 (t, 1H, $^3J_{HH}$ = 8 Hz), 6.94 (s, 1H), 6.90 (d, 1H, $^3J_{HH}$ = 8 Hz), 6.83 (s, 1H), 5.47 (m, 1H), 5.18–5.12 (m, 1H), 4.72 (d, 1H, $^2J_{HH}$ = 12 Hz), 3.91 (d, 2H, $^2J_{HH}$ = 16 Hz), 3.82 (d, 1H, $^2J_{HH}$ = 12 Hz) 1.22 (s, 9H), 1.17 (s, 9H).

Representative procedure for deoxydehydration reactions

A pressure tube reactor was charged with diol (0.500 mmol), reductant (0.750 mmol), molybdenum complex (0.050 mmol) and 2.5 mL of solvent. The reactor tube was sealed and the reaction mixture was stirred at 170 °C for 24 hours. The reactions were cooled to room temperature before adding the internal standard for analysis. 1,3,5-Trimethoxybenzene (0.010 g, 0.059 mmol) was added after the 24 hours in heat as an internal standard. An aliquot of the sample of the reaction mixture was analyzed by ^1H NMR in $CDCl_3$. The integration of peaks corresponding to the internal standard to diol and alkene product was used to determine yield of alkene product and carbonyl compound.

Conflicts of interest

The authors declare no conflicts of interest.

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