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Deoxydehydration of polyols catalyzed by a molybdenum dioxo-complex supported by a dianionic ONO pincer ligand†

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Deoxydehydration (DODH) is the net reduction of diols and polyols to alkenes or dienes and water. Molybdenum *cis*-dioxo bis-phenolate ONO complexes were synthesized and have been shown to be active for DODH. Catalysts were screened for activity at 150–190 °C, and appreciable yields of up to 59% were obtained. PPh_3, Na_2SO_3, Zn, C, 3-octanol and 2-propanol were screened as reductants. Additionally, the reactivities of a variety of diols were screened. With (R,R)-(+)-hydrobenzoin as substrate, DODH occurs *via* a mechanism where reduction of the Mo catalyst is a result of diol oxidation to form two equivalents of aldehyde. These reactions result in complete conversion and near quantitative yields of trans-stilbene and benzaldehyde.

Introduction

Biomass deoxygenation and up-conversion have gained popularity as methods to produce commodity chemicals currently produced by the petrochemical industry.[1] Deoxydehydration (DODH) is a promising route for converting biomass-derived diols and polyols into alkenes and dienes. The reaction converts vicinal diols into alkenes, typically using high oxidation state metal-oxo complexes as catalysts and PPh_3 or secondary alcohols as reductants.[2]

DODH was first reported by Cook and Andrews.[3] Cp*ReO$_3$ was used as a precatalyst to convert 1-phenyl-1,2-ethanediol to styrene with PPh_3 as an oxo-acceptor and reductant. Toste and coworkers have demonstrated that $MeReO_3$ is an excellent catalyst using secondary alcohols as reductants.[4] Other studies in the literature have shown that a wide variety of reductants can be used.[5–11] Mechanistic studies of $MeReO_3$ by Abu-Omar and co-workers show that a reduced dioxo species is the active form of the catalyst.[6] Recently, a handful of molybdenum complexes have been shown to be active for DODH at high temperatures and pressures.[12–14] Chart 1 summarizes the molybdenum based DODH catalysts reported in the literature. The most notable example is ammonium heptamolybdate (($NH_4)_6Mo_7O_{24} \cdot 4H_2O$, AHM), which was reported by Fristrup to

be an active catalyst while using secondary alcohols as the sacrificial reductant. However, the reported alkene yields were modest (∼10–50%) and required relatively harsh conditions (200–250 °C and >60 bar for 13 h). Alkene yields could be elev-
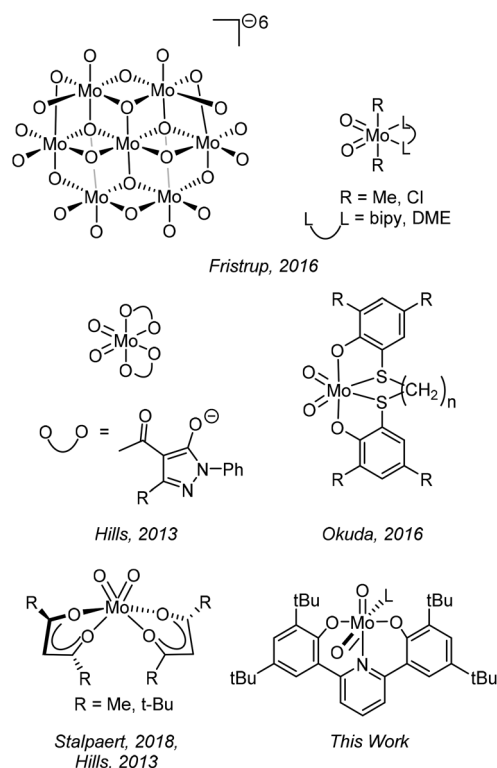

Chart 1 Molybdenum-based DODH catalysts.

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ated to as high 77% at similar temperatures and pressures in the presence of 1.5 mol of base per mol of catalyst. Alkene yields in the presence of base varied between 55% (1,2-decanediol) and 77% (1,2-hexanediol) depending on the length of the alkyl chain of the aliphatic substrate. Clearly, there is a need for further improvement of the yields of Mo-based DODH reactions. Additionally, further catalyst design may result in systems capable of performing DODH under mild reaction conditions. Notably, recent work has shown that manipulating the ligand environment substantially improves the yields of Mo-catalyzed DODH beyond the simple salts reported in the literature.[15,16]

Mo systems are of particular interest because of the earth abundance and relatively low cost of Mo when compared to Re. Additionally, there are several synthetically convenient and commercially available Mo starting materials that can be used to easily install a variety of ligand environments.

To date, the ligand environments of *cis*-dioxo-Mo based DODH catalysts have been six coordinate systems. To our knowledge, this report is the first example of a five coordinate/coordinatively unsaturated *cis*-dioxo-Mo system that performs DODH. Additionally, this is the only DODH system that can lose a labile ligand to form a five coordinate Mo(VI) dioxo species.

There exists a plethora of six coordinate *cis*-dioxo-Mo(VI) complexes in the literature. The primary interest in *cis*-dioxo-Mo(VI) systems has been as models for oxo-transferase enzyme active sites.[17–19] A handful of five coordinate systems are known.[20–25] Berg and Holm reported the first example of a five coordinate *cis*-dioxo.[20] Recently, Stylianou and co-workers have studied the aqueous coordination chemistry of *N,N*-di-substituted-bis(hydroxylamido)-1,3,5-triazine ligands affording a five coordinate species.[26] Additionally, five coordinate *cis*-dioxo units were observed by Osborn and co-workers as an isolated base-free, dimeric structure, where the sixth coordination site of each octahedral Mo is occupied by a bridging O of an adjacent Mo=O bond.[27]

Coordinatively saturated systems have dominated the literature. Acylpyrazolonate-based systems are the first examples of a Mo-catalyzed DODH reaction in the literature.[28] Other early examples of Mo-based DODH catalysts employed tetra-dentate ligands that have sigma donors with reasonable amounts of pi donation. Hills and coworkers found conversions of 60–99% with yields between 10–55% of alkene.[28] This work was followed by OSSO type ligands studied by Okuda and co-workers, finding that phenolate-based systems are competent DODH catalysts.[29] These early systems were found to have conversions as high as 81% and alkene yields of 57%. In addition to screening a number of simple molybdate salts, Fristrup and co-workers examined common six coordinate *cis*-dioxo-Mo compounds including the synthetically convenient [Mo(bipy)O$_2$X$_2$] (X = Cl, Br, Me). In agreement with the results of the simple molybdate salts, these *cis*-dioxo-compounds were found to be competent DODH systems. These common six coordinate systems afforded complete conversion with alkene yields between 10 and 45%. A common feature in the literature
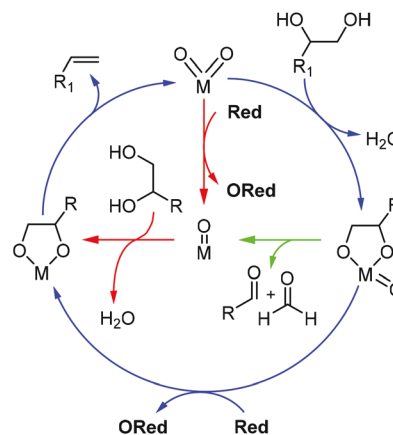
Scheme 1 Competing DODH mechanisms.

of Mo-catalyzed DODH is the use of high temperature and pressure during reactions. One downside to these reaction conditions is that identification of the active species can be quite challenging since numerous Mo species can be formed at elevated temperatures.

There are several possible mechanisms for DODH. The proposed catalytic cycle for DODH involves three steps: (1) reduction of the metal-oxo or metal-oxo abstraction, (2) condensation of a metal-oxo with a vicinal diol to form a metal-diolate and water, and (3) olefin extrusion of the alkene product regenerating a metal-dioxo species. The mechanism of DODH likely varies with reductant and catalyst; for example, metal-oxo reduction and metal-diolate formation could happen in any order. Additionally, reduction of the metal could occur by deformylation of a metal-diolate species.[12] Scheme 1 summarizes the possible mechanisms of DODH.

DFT studies in the literature to date have assumed that the active catalytic species for DODH is a simple MoO$_3$ fragment or a MoO$_2$(diolate)$_2$ type fragment.[13,30] These studies have demonstrated that, consistent with DODH catalyzed by other metals, alkene extrusion is the rate determining step of reaction.[30] Additionally, DFT calculations show that olefin extrusion appears to proceed through formation of a metal-oxetane consistent with the work of Gable and co-workers on Re(V) diolate systems.[31–34]

Herein we synthesize Mo-dioxo complexes bearing a chelating pincer ligand. These complexes are active DODH catalysts under milder reaction conditions than those previously reported.

Results and discussion

Synthesis and structure

We considered the following criteria when designing our catalyst system: ligand bulk and cost of the metal. Abu-Omar and co-workers found that one of the off-cycle reactions of the MeReO$_3$ catalyst system was the formation of oxo-bridged-Re dimers.[6] We chose a bulky ligand scaffold to discourage cata-

lyst dimerization and deactivation by comproportionation. Furthermore, the greater earth abundance of Mo compared to Re and the commercial availability of low-cost starting materials led us to choose a Mo complex.

We synthesized and screened two Mo(vi)-dioxo-pincer complexes for DODH activity. Treatment of MoO₂(acac)₂ in methylene chloride with equimolar amounts of 2,6-bis-(3,4-di-*tert*butyl-2-phenol)pyridine (L) in the presence or absence of triphenylphosphine oxide affords **1** and **2**, respectively, (Scheme 2) in good yield.

X-Ray crystallography revealed that **1** and **2** bear a *cis*-dioxo-Mo fragment supported within the ONO pincer ligand. Six-coordinate **1** was found to be octahedral at Mo, and **2** was isolated as a base-free complex showing a trigonal bipyramidal structure at the Mo center with the oxo-ligands occupying the equatorial plane of the complex (Fig. 1 and 2). Six coordinate *cis*-dioxo-Mo(vi) complexes are well known in the literature (*vide supra*). Most of these systems are structurally analogous to **1**. Of the known five coordinate systems, many are related to the structure of **2** in that they contain tri-dentate ONO ligands.
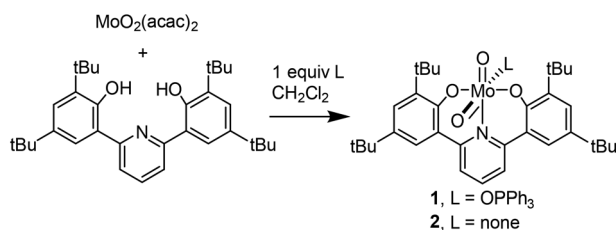
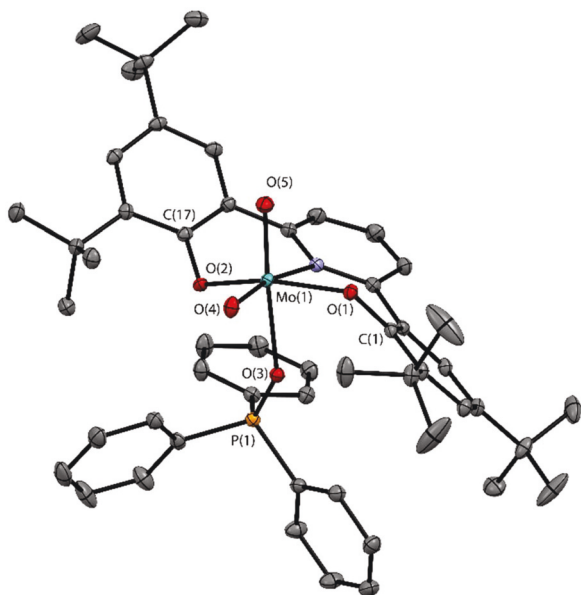Scheme 2 Synthesis of ONO–Mo complexes.

Fig. 1 Thermal ellipsoid plot of **1** shows an octahedral *cis*-dioxo bipyramidal Mo center. Selected bond lengths (Å) and angles (°): Mo=O4 = 1.714, Mo=O5 = 1.701, Mo−O1 = 1.961, Mo−O2 = 1.963, M−N = 2.341; ∠O4−Mo−O5 = 104.46, ∠O1−Mo−O2 = 154.85.
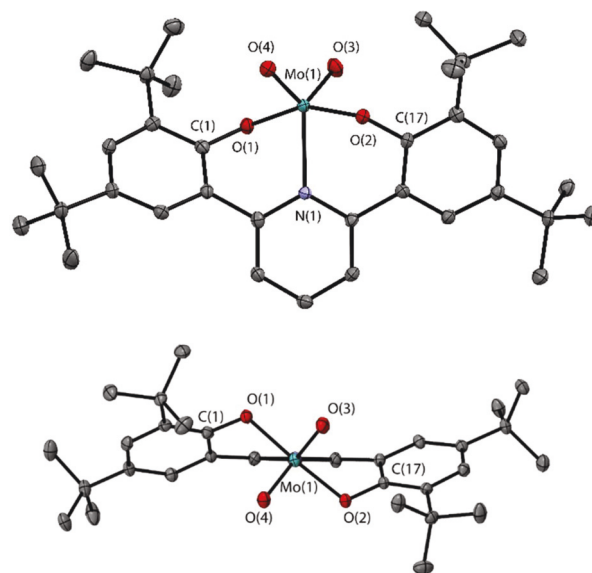

Fig. 2 Thermal ellipsoid plot of five coordinate compound **2** shows a trigonal bipyramidal Mo center. Selected bond lengths (Å) and angles (°): Mo=O3 = 1.689, Mo=O4 = 1.693, Mo−O1 = 1.951, Mo−O2 = 1.947, Mo−N = 2.223; ∠O3−Mo−O4 = 111.68, ∠O1−Mo−O2 = 156.69. Top viewed normal to the plane of the pyridine ring, bottom viewed along the Mo−N bond axis.

The Mo=O distances of **2** are 1.689 and 1.693 Å, comparable to the literature values ranging from 1.69 to 1.70 Å.[20–25]
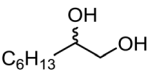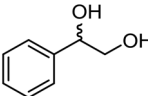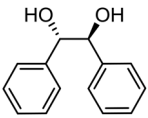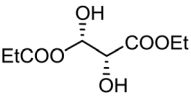
Elemental analysis of **1** shows the presence of water in the pure compound owing to the complex's hygroscopic nature. ³¹P NMR of **1** shows no signal for the bound OPPh₃ likely due to the signal being broadened into the baseline. ¹H NMR shows broadened aryl peaks for both the phenolate ligand and OPPh₃. These data imply that OPPh₃ is weakly bound to the Mo center in solution and that the rate of dissociation/reassociation is approximately that of the NMR time scale.

DODH catalyzed by 1 and 2

The catalytic activity of **1** and **2** were screened using 10 mol% catalyst at 150–190 °C for 48 h (Table 1). Catalytic reactions of **1** with 1,2-octanediol at 190 °C using PPh₃ as reductant in chlorobenzene formed 1-octene in 59% yield with only 6% yield of deformylation products. The reaction shows complete conversion by NMR.

Reaction of **1** and **2** with 1-phenyl-1,2-ethanediol also gave appreciable styrene yields using a variety of reductants including PPh₃, Na₂SO₃, Zn, C, 3-octanol and isopropyl alcohol. PPh₃ showed lower yields (21%) under the same conditions as 1,2-octanediol but afforded similar yields at 150 °C. Other reductants gave similar alkene yields (29%–37%) with 1-phenyl-1,2-ethanediol (ESI†). NMR analysis of the product mixtures revealed that **1** forms alkene and aldehydes in approximately a 3 : 1 ratio for 1-phenyl-1,2-ethanediol. The yield of this reaction remains modest at 48% (alkene + aldehyde), with conversions typically ranging from 42–64%. The ratios of alkene to aldehyde observed in the products implies that both reduction of

Table 1 Summary of catalytic activity of **1** and **2**

Substrate	Reductant	% Yield.1[a] C=C (C=O)	% Yield.2[a,c] C=C (C=O)
C6H13—CH(OH)—CH2OH	PPh3	59 (6)[b]	25 (8)[b]
	3-Octanol	4 (4)[b]	14 (20)[b]
	Carbon	18 (18)[b]	Trace[b]
Ph—CH(OH)—CH2OH	PPh3	31 (9)	31 (5)
	3-Octanol	10 (13)	1 (22)
	Carbon	37 (11)	46 (14)
	Zinc	36 (9)	30 (12)
	Na2SO3	29 (9)	27 (11)
	2-Propanol	10 (13)	18 (16)
HO—CH(Ph)—CH(Ph)—OH	PPh3	62 (21)	46 (41)
	Carbon	54 (42)	40 (40)
	Zinc	48 (44)	38 (38)
	Na2SO3	48 (46)	39 (40)
	2-Propanol	42 (18)	—
EtOOC—CH(OH)—CH(OH)—COOEt	PPh3	18 (0)	—
	Carbon	9 (0)	—
	Zinc	6 (0)	—
	Na2SO3	5 (0)	—
	2-Propanol	26 (0)	—

[a] Unless noted, reactions are run at 150 °C in toluene with 10 mol% catalyst loading for 48 h. Yields reported are an average of two reactions. Yields were determined by ^{1}H NMR using an internal standard (ESI†). [b] Reactions run at 190 °C in chlorobenzene 10 mol% catalyst loading for 48 h. These conditions correspond to a pressure of ~5 atm in the reaction tube. [c] In some preparations of **2**, Hacac was observed. The presence of Hacac does not appear to affect the overall DODH yields for 1-phenyl-1,2-ethanediol (ESI Table S2†).

Mo *via* oxo-abstraction and *via* deformylation are competitive for 1-phenyl-1,2-ethanediol (Scheme 1, red/blue paths and green path respectively). Notably, DODH reactions using the bulkier tri-ortho-tolyl phosphine as reductant resulted in an alkene yield of 15% with the formation of 10% yield of aldehydes for catalyst **2**, implying that DODH occurs primarily *via* the deformylation mechanism shown in Scheme 1 (green path) for bulkier reductants. Additionally, **1** can perform sub-stoichiometric DODH of 1-phenyl-1,2-ethanediol in the absence of other reductants.

(R,R)-(+)-Hydrobenzoin showed good yields for the major products *trans*-stilbene and benzaldehyde and nearly complete conversion using **1** and a variety of reductants. These findings imply that oxidation of reductants (Scheme 1, red path) is likely *not occurring* and that the oxidation of diol (Scheme 1, green path) is the dominant reduction pathway for DODH.

In reactions where isopropyl alcohol was used as reductant with **1** or **2**, we observed nearly equimolar amounts of acetone (the product of catalyst reduction) and the DODH products, demonstrating that the secondary alcohol was being oxidized in the course of the reaction. In some cases, one or two excess equivalents of acetone are observed by NMR, indicating transfer hydrogenation from iPrOH to aldehydes could be a competing reaction as observed previously.[13]

1 and **2** show poor catalytic conversion of aliphatic diols to alkenes at lower temperatures (1,2-octanediol and *cis*-1,2-cyclo-hexanediol) (ESI Table S1†). (L)-(+)-Diethyltartrate was examined as a model substrate for DODH of biomass materials (Table S1†). The greatest yield, 26%, was obtained using iPrOH as reductant. These results demonstrate that **1** and **2** afford greater reaction yields for aromatic substrates over aliphatic substrates at low temperatures, likely due to a lower barrier to olefin extrusion. We hypothesize this lower reaction barrier results from stabilization of the transition state for C=C bond formation. At the transition state, the pi electron density of the forming C=C bond is partially delocalized into the adjacent aromatic rings, lowering the overall energy of the orbital. The preference for deformylation of aromatic diols can be explained in an analogous manner. The transition state of deformylation can be considered a [2 + 2 + 2] retro-cyclo-addition reaction. At the transition state, the orbitals corresponding to the forming C=O bonds are likely delocalized into the adjacent aromatic rings, again lowering the overall transition state energy. Additionally, the starting diolate is destabilized because the relatively weak benzylic–benzylic C–C bond of the starting material also lowers the relative transition state energy.

1 and **2** were found to be sensitive to water under catalytic conditions. Crystallographic data shows that a stable inner sphere hydrate forms when **2** is recrystallized in atmosphere (ESI†). However, over the course of a catalytic reaction, protonated free ligand is detected by ^{1}H NMR. Addition of water to a toluene solution of **1** at elevated temperature shows partial decomposition of **1** and formation of free ligand. Use of common desiccants, such as molecular sieves, P_2O_5, and anhydrous $MgSO_4$ in the catalytic reaction did not afford product formation. Other methods to mitigate the influence of water on the reaction are currently being investigated, including the addition of bases.

Mechanistic insights

Solutions of **1** or **2** in aromatic solvent are light yellow in color. Upon heating in the presence of one equivalent of PPh3 these solutions become deep purple. ^{1}H NMR of these solutions shows a set of broad low intensity resonances indicative of paramagnetic species in addition to a mixture of diamagnetic components. Formation of paramagnetic species could be the result of dimerization of a reduced mono-oxo-Mo(IV) species with a second equivalent of either mono-oxo-Mo(IV) or the parent *cis*-dioxo-Mo(VI) compound. These results imply the steric bulk of the pincer ligand does not prevent dimerization and formation of dimers analogous to those observed by Abu-Omar and co-workers.[6] After longer reaction times in the presence of substrate, the reaction changed from purple to an intense red color. Further studies are underway to examine the identity of the species in solution during catalysis.

Addition of 10 equivalents of exogeneous OPPh3 to DODH reactions of 1-phenyl-1,2-ethanediol under typical reaction conditions catalyzed by **1** and **2** resulted in an overall product yield of ~10% after 48 h. This observation is consistent with OPPh3 acting as an inhibitor for product formation. This

further implies that dissociation of OPPh₃ is required to form the active catalytic species.

Preliminary kinetics. Preliminary kinetics studies were performed *via* ¹H NMR by monitoring the formation of the major product, styrene, and the consumption of 1-phenyl-1,2-ethanediol substrate using **1** as catalyst. The growth of styrene shows an early, relatively rapid, non-linear growth of product. After 15 hours, we observe a plateau in the concentration of styrene. The concentration of diol *vs.* time shows an apparent zero-order dependence on diol during this period. During this same period, the profile for styrene concentration *vs.* time does not correspond to first- or second-order production of styrene. This implies several species may be competent catalysts for DODH and the rate of production is not dependent solely on the concentration of reductant and catalyst (ESI†). These kinetics data suggest more complicated kinetics are present in this reaction, and further studies are underway to better understand the mechanism of DODH in these systems.

Comparison to other Mo catalysts

Comparison of these results to the literature shows that yields for the alkene DODH product are similar or higher than those reported using ammonium heptamolybdate as catalyst in the absence of base.[15] However, the bulk of our reactions are performed at a lower temperature. Additionally, our data here shows 44% to >99% conversion (see ESI†) where it is previously not reported for the same reductants.[15] Our results for aliphatic diols are superior to those currently in the literature with one exception.[16] These results show promise for future development. Reactions with (+)-diethyl ʟ-tartrate showed comparably lower yields when compared to current published systems.[15] When our results are compared to those of Fristrup and coworkers[13] we see similar conversions. As is observed in the literature, some DODH reactions show >99% conversion and yields of 70% and below. It is noteworthy that recent reports have shown the benefits of manipulating the ligand environment. Stalpaert and coworkers reported similar yields to those reported here using a mixture of *in situ*-generated catalysts. Additionally, they obtained higher yields for aliphatic diols at slightly higher temperatures in the presence of excess ligand.[16]

Conclusions

We have synthesized d⁰ Mo-dioxo catalysts with a bulky pincer ligand that are active for deoxydehydration. We have shown that these catalysts are active for DODH with many reductants. Using 1,2-octandiol as substrate, they afford alkene yields of 59% with relatively low yield of aldehydes formed *via* diol oxidation at 190 °C. Modest to good yields are obtained for aromatic diols at 150 °C through a combination of reaction pathways including diol oxidation. PPh₃ is a competent oxo acceptor to catalyze these reactions, but greener reductants, including isopropyl alcohol, also show appreciable yields when used with these catalysts. Bulky phosphines do not appear to be

competent reductants implying that the steric bulk of the ligand and reductant are of critical importance. OPPh₃ was found to be an inhibitor of alkene formation implying that generation of a five coordinate species is likely involved in formation of the active catalyst species. Current efforts are underway to explore the mechanism of reaction and to better understand the possible reaction pathways and the metal-based intermediates.

Experimental details

General comments

Reagents were obtained from common commercial sources and were used without further purification. Solvents were obtained anhydrous from Aldrich and were placed over 3 Å molecular sieves. All reactions were performed under inert atmosphere using standard Schlenk or glovebox techniques unless otherwise noted. The preparation of the ligand is a modified version of literature procedures.[35] ¹H NMR was referenced to solvent residual signals (chloroform-*d*, δ = 7.26, methylenechloride-*d*₂, δ = 5.32). DODH reaction yields were determined by use of an internal standard: (1,3,5-trimethoxybenzene, δ = 3.32 (s, 9H, OCH₃) δ = 6.13 (s, 3H, aryl H)) or (hexamethyl-cyclotrisiloxane, δ = 0.17 (s, 18H, CH₃)). Elemental analysis was performed by either the CENTC Elemental Analysis Facility at the University of Rochester or Midwest Microlabs (Indianpolis, IN).

Ligand synthesis

The synthesis of the dianionic ONO pincer ligand is modified from the literature procedure[1] and is shown in Scheme 3.

***O*-Methoxyethyl-2,4-di-*tert*-butyl-6-bromophenoxide (A).** 2,4-Di-*tert*-butylphenol (2.09 g, 10.13 mmol) was dissolved in CH₂Cl₂ (26 mL). Bromine (0.5 mL, 10.14 mmol) was added *via* syringe, and upon addition, the solution became colorless.
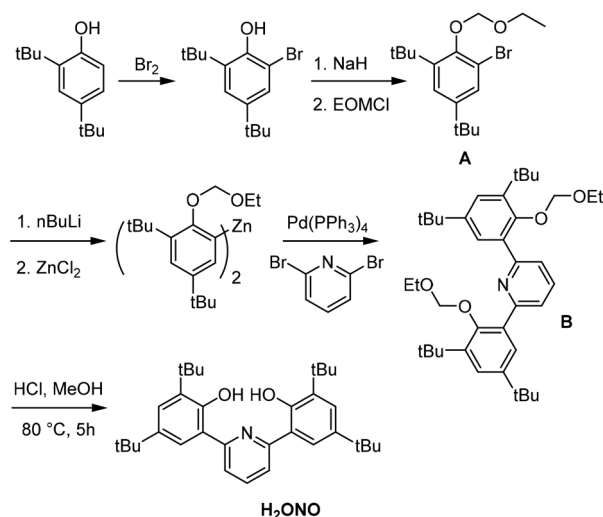
Scheme 3 Synthesis of H₂ONO pincer ligand.

The organic mixture was washed with water, dried with MgSO$_4$, and filtered. The solution was dried *via* rotary evaporation resulting in a golden oil. Under inert atmosphere, this oil was dissolved in dry tetrahydrofuran (30 mL) and treated with sodium hydride (270.1 mg, 11.26 mmol). This reaction was stirred for 1 h at room temperature and chloromethylethylether (1.1 mL, 11.86 mmol) was added *via* syringe. The reaction mixture was stirred for 9 h at room temperature and then quenched with H$_2$O (30 mL), the mixture was extracted with DCM three times, dried with MgSO$_4$, and then dried *in vacuo* overnight resulting in a viscous oil (3.03 g, 87% yield). ^{1}H NMR (400 Mhz, CDCl$_3$) δ = 1.31 (s, 9H, *t*-butyl), 1.35 (t, 3H, CH$_3$, *J* = 7.1 Hz), 1.43 (s, 9H, *t*-butyl), 3.95 (q, 2H, CH$_2$, *J* = 7.1 Hz), 5.25 (s, 2H, OCH$_2$O), 7.30 (s, 1H, aryl H, *J* = 2.4 Hz), 7.39 (s, 1H, aryl H, *J* = 2.4 Hz).

2,6-Di(2-*O*-methoxyethyl-3,5-di-*tert*-butyl-phenoxide)pyridine (B). A (3.41 g, 9.93 mmol) was dissolved in THF (16 mL) in a threaded Teflon-capped Schlenk tube and was cooled to −35 °C. To this vigorously stirring cold solution was added 2.5 M *n*-butyllithium in hexanes (8.34 mL, 20.86 mmol) dropwise *via* syringe. The solution bubbled slightly as the *n*BuLi was added. The lithiated mixture was stirred and allowed to warm to room temperature over 3 hours forming a white precipitate. After stirring, ZnCl$_2$ was added (947.7 mg, 6.95 mmol), and the mixture stirred for 30 minutes. Upon addition of ZnCl$_2$, the white precipitate dissolved into solution. To this yellow mixture was added 2,6-dibromopyridine (1058.7 mg, 4.47 mmol) and Pd(PPh$_3$)$_4$ (114.8 mg, 0.10 mmol) with aid of minimal THF. The reaction was heated to 75 °C for 16 hours. The reaction was quenched with water (5 mL) and concentrated by half under vacuum. The solution was extracted three times with Et$_2$O. The organic layer was dried with MgSO$_4$, filtered, and the solvent removed under vacuum. This residue was recrystallized from minimal methanol at −25 °C. The resulting white precipitate was collected *via* filtration and washed with cold methanol (5 mL) (4.49 g 75% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 1.15 (t, 3H, CH$_3$, *J* = 7 Hz), 1.35 (s, 18H, *t*-butyl, *J* = 10 Hz), 1.50 (s, 18H, *t*-butyl, *J* = 10 Hz), 3.62 (q, 4H, CH$_2$, *J* = 7 Hz), 4.66 (s, 4H, OCH$_2$O), 7.43 (s, 2H, aryl-H, *J* = 2.5 Hz), 7.58 (s, 2H, aryl-H, *J* = 2.5 Hz), 7.71–7.80 (m, 3H, pyr-H).

Synthesis of H$_2$ONO. The protected bis-phenol **A** (2.0 g 3.3 mmol) was suspended in a mixture of 80 mL of methanol and 80 mL of concentrated hydrochloric acid. This mixture was stirred and heated at 80 °C for 5 hours in air. The mixture was extracted three times with 50 mL of methylene chloride and the volatiles were removed under vacuum on a rotary evaporator. The remaining material was dried on a Schlenk line yielding a yellow solid. (1.3 g 80% yield). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ = 1.37 (s, 18H, *t*-butyl), 1.47 (s, 18H, *t*-butyl), 7.44 (s, 2H, aryl H, *J* = 2.4 Hz), 7.51 (s, 2H, aryl H, *J* = 2.4 Hz), 7.75 (d, 2H, pyr H, *J* = 8 Hz), 8.05 (t, 1H, pyr H, *J* = 8 Hz).

(ONO)MoO$_2$(OPPh$_3$) (1). Equimolar amounts of MoO$_2$(acac)$_2$, (726 mg 2.23 mmol), H$_2$ONO (1.09 g 2.23 mmol) and OPPh$_3$ (620 mg 2.23 mmol) were combined in a round bottom flask with 15 mL of dichloromethane. The solution was stirred for

48 hours at room temperature. The mixture was filtered to remove unreacted solids, and the solution was dried under vacuum, resulting in a yellow solid. This solid was purified by trituration in 15 mL pentane and was recrystallization from acetonitrile affording yellow crystals (1.68 g 84% yield). ^{1}H NMR (400 MHz, CH$_2$Cl$_2$) δ = 1.32 (s, 18H, C(CH$_3$)$_3$), 1.36 (s, 18H, C(CH$_3$)$_3$), 7.28 (br m, 15H, OPPh$_3$), 7.39 (s, 2H, aryl H), 7.52 (s, 2H, aryl H), 7.61 (d, 2H, pyr H, *J* = 8 Hz), 7.74 (t, 1H, pyr H, *J* = 8 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) δ 30.2 (C(CH$_3$)$_3$), 31.8 (C(CH$_3$)$_3$), 34.6 (C(CH$_3$)$_3$), 35.5 (C(CH$_3$)$_3$) 122.8, 123.8, 126.3, 128.5, 132.1, 132.5, 138.3, 141.7, 154.9, 155.1, 160.5 (aryl). Elemental analysis was attempted 6 times and in each case the sample was found to absorb two equivalents of water from the environment in transit. Anal. calcd for C$_{51}$H$_{62}$MoNO$_7$P C, 66.01; H, 6.73; N, 1.51. Found: C, 66.208%; H, 6.40%; N, 1.41%.

(ONO)MoO$_2$ (2). Equimolar amounts of MoO$_2$(acac)$_2$, (1.17 g 3.59 mmol), H$_2$ONO (1.75 g 3.58 mmol) were combined in a round bottom flask with 25 mL of dichloromethane. The solution was stirred for 48 hours at room temperature. The mixture was filtered to remove unreacted solids, and the solution was dried under vacuum, resulting in a yellow solid which was recrystallized from dichloromethane and pentane to afford yellow crystals (1.58 g, 72% yield). ^{1}H NMR (500 MHz, C$_6$D$_6$) δ = 1.36 (s, 18H, C(CH$_3$)$_3$), 1.64 (s, 18H, C(CH$_3$)$_3$), 6.92 (t, 1H, pyr H, *J* = 8 Hz), 7.09 (d, 2H, pyr H, *J* = 8 Hz), 7.34 (s, 2H, aryl H), 7.77 (s, 2H, aryl H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125 MHz) δ = 30.3 (C(CH$_3$)$_3$), 31.6 (C(CH$_3$)$_3$), 34.7 (C(CH$_3$)$_3$), 35.8 (C(CH$_3$)$_3$), 122.9, 123.1, 125.4, 128.5, 138.9, 139.9, 143.5, 154.2, 157.5. Anal. calcd for C$_{33}$H$_{43}$MoNO$_4$ C, 64.59%; H, 7.06%; N, 2.28%. Found: C, 64.60%; H, 7.02%; N, 2.38%.

General procedure for catalytic reactions and workup

A pressure tube with a threaded Teflon cap was charged with catalyst (65 mmol), 10 equivalents of reductant, 10 equivalents of diol, a known amount of internal standard, and 10 mL of solvent (toluene or chlorobenzene). The reaction was stirred at constant temperature in an oil bath pre-heated to either 150 °C or 190 °C. The reactions were cooled to room temperature before analysis. NMR samples were prepared by taking a 0.35 mL aliquot of solution that was diluted with NMR solvent (CD$_2$Cl$_2$) to a final volume of 0.7 mL. Diol conversion was determined by GC/MS analysis and samples were prepared by separating diol from metal species by column chromatography of a 0.5 mL aliquot of the reaction mixture. The non-volatile components of the column fractions containing diol, were then dissolved in 0.4 mL acetone and 0.8 mL of a standard solution of pentane and naphthalene for a measured total volume of 1.1 mL. Yields were calculated by comparison with previously obtained calibration curves of analytes. Quantification of E-stilbene was performed by NMR of the non-volatile components of a 0.5 mL aliquot of reaction mixture.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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