ORGANOMETALLICS

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Oxo-Rhenium-Catalyzed Deoxydehydration of Polyols with Hydroaromatic Reductants

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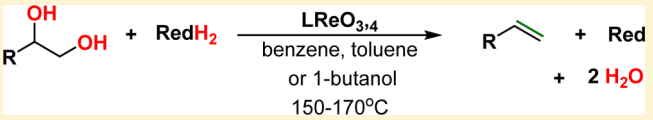
Supporting Information

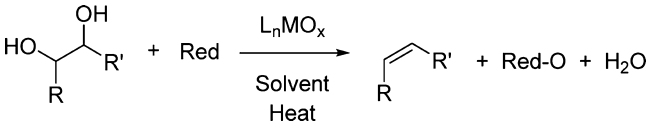
ABSTRACT: Several dihydroaromatic compounds are shown to be effective reducing agents in the oxo-metal-catalyzed deoxydehydration of diols and polyols to produce olefins and the corresponding arenes. NH_4ReO_4 and $MeReO_3$ are active catalysts for the reactions. The most effective of the hydroaromatic reductants is indoline, which is oxidized to indole. Yields for a variety of diols and polyols range from 35% to 99%. Two hydrogen donors, 1,3-cyclohexadiene and dihydroanthracene, engage in tandem DODH/cycloaddition reactions. Competition experiments show that indoline is more reactive than representative alcohols in H-transfer. Indoline is shown to reduce $MeReO_3$ to $MeReO_2$ via an isolable adduct, $MeReO_3$(indoline) (**4**), which has been structurally characterized and is suggested to be an intermediate in the catalytic DODH process.



INTRODUCTION

The finite supply, fluctuating prices, and uneven worldwide distribution of fossil-derived resources have stimulated interest in new processes for the chemical conversion of renewable feedstocks. Renewable plant-derived cellulose and triglycerides can be transformed into carbohydrates and polyols by hydrolysis and hydrogenation processes.[1] Three oxygen-altering processes have been considered to increase the value and diversity of these biorefinery inputs: dehydration,[2] hydrodeoxygenation,[3] and, most recently, deoxydehydration (DODH). In the DODH reaction vicinal diols (glycols) are converted into alkenes by the action of a reducing agent and an oxo-metal catalyst (Scheme 1).[4]

Scheme 1. DODH Catalyst/Reductant Systems



Several studies have focused on the development of catalysts and reductants for the DODH reaction. Oxo-rhenium compounds have largely been employed as catalysts, e.g., Cp^*ReO_3, TPB^*ReO_3, $MeReO_3$, and $Z^+ReO_4^-$, in combination with triphenylphosphine,[5] hydrogen,[6] sulfite,[7] and elements, e.g., zinc, iron, manganese, and carbon,[8] as reductants. Recently, oxo-molybdenum[9] and oxo-vanadium[10] complexes have been reported as inexpensive DODH catalysts with phosphine or sulfite reductants.

The use of alcohols as H-transfer reductants in DODH has also received attention.[11−14] Typically, secondary alcohol-reducing agents have been used, often as the reaction solvent.[11,12] The activated primary alcohol, benzyl alcohol, has been employed stoichiometrically together with $MeReO_3$ or NH_4ReO_4 for the DODH of organic-soluble glycols.[13] Shiramizu and Toste found 1-butanol to be effective as a reducing agent and solvent in combination with perrhenic acid as catalyst.[14] The mechanistic details of the alcohol-driven DODH have been the subject of some debate regarding which Re-intermediates react with the reductant and how the hydrogens are transferred.[15]

Hydroaromatics, several of which are abundant in fossil resources, have been employed as liquid organic hydrogen carriers for hydrogenation reactions and for hydrogen storage.[16] The catalytic activity of redox-active solid metal oxides, e.g., V_2O_5 and Fe_xO_y, for the dehydrogenation of alkyl aromatics, used for the production of styrene from ethylbenzene,[17] suggested to us the potential use of these reductants in homogeneous oxo-metal-catalyzed reactions. However, rather little is known about their reactivity with soluble oxo-metal species.[18] In the first report of ostensibly heterogeneous catalytic DODH reactions using perrhenate supported on carbon,[19] the primary reductant employed was hydrogen, but a few examples of H-transfer reductants, e.g., benzyl alcohol and tetrahydronaphthalene, were also noted. Here we report the development of efficient homogeneous catalytic DODH reactions with hydroaromatic hydrogen donors and provide insights into the nature of the reactive intermediates involved.

RESULTS AND DISCUSSION

A set of seven potential hydrogen donors were tested for efficacy under typical DODH conditions with diethyl tartrate (DET) and 1,2-octanediol as representative glycols. In these reactions (Table 1) we obtained moderate to excellent yields of

Received: March 18, 2015

DOI: 10.1021/acs.organomet.5b00226
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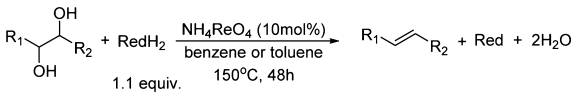
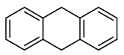
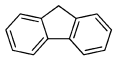
Table 1. Screening Hydroaromatic Reductants for DODH



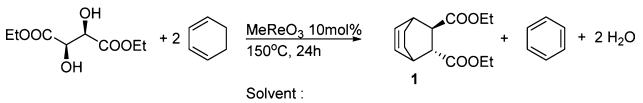
DET : R_1=R_2=COOEt
1,2-Octanediol : R_1=C_4H_9, R_2=H

Entry	Reducing agent	Glycol	Yield (%)[a]
1		DET	90
2a		DET	92
2b			73[b]
2c		1,2-octanediol	60
2d			48[b]
3a		DET	99 (99% indole)
3b		1,2-octanediol	70
4		DET	70
5a		DET	**1** (Scheme 2)
5b		1,2-octanediol	52[c]
6a		DET	**2** (Scheme 3)
6b		1,2-octanediol	64
7[d]		DET	82

[a]Yield determined by ^{1}H NMR with internal standard. [b]17 h reaction time with 0.55 equiv of reducing agent. [c]$MeReO_3$ used as catalyst and the reductant as solent. [d]The oxidized product of fluorene not characterized.

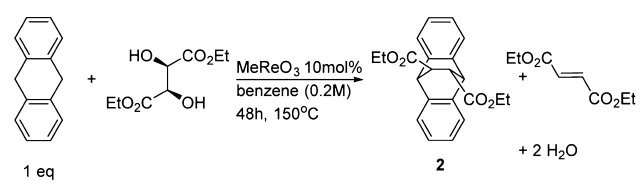
the alkene, from 70% to 99% from DET and 40% to 70% from octane diol. In the cases of entries 5a and 6a (Table 1), we could couple the DODH product, diethyl fumarate (DEF), in a tandem Diels–Alder (DA) reaction[14] (Schemes 2 and 3). In

Scheme 2. Tandem DODH/DA with DET and 1,3-Cyclohexadiene



Solvent :
Cyclohexane.....78% (38% benzene)
1,3-Cyclohexadiene.....90% (99% benzene)

Scheme 3. Tandem DODH/DA with DET and 9,10-Dihydroanthracene



40% (25% Diethyl fumarate)

the first case (entry 5a) 1,3-cyclohexadiene serves both as the reducing agent for the DODH reaction and as the diene for the Diels–Alder reaction, providing the *trans*-cycloadduct 1[20] in 78–90% yield depending on the solvent used. In the second case (entry 6a), 9,10-dihydroanthracene was employed as the reductant for DET, expecting to generate anthracene and fumarate, which would engage in cycloaddition. Indeed, the *trans*-adduct 2[21] was formed, albeit in a modest 40% yield, with about 25% of fumarate remaining.

Tetrahydronaphthalene (THN) from coal has been studied as a hydrogen donor.[22] An attractive feature of this abundant hydroaromatic is that it could provide two equivalents of hydrogen. We further investigated its efficacy using a half or one equivalent on diethyl tartrate and octanediol (Table 1, entries 2a–d). After only 17 h the yields were moderate using half an equivalent of THN, improving somewhat after 48 h; use of one equivalent of THN increased the yield further.

The results in Table 1 show that indoline is the most effective hydroaromatic hydrogen donor for DODH of the model substrates. Not only did it provide the highest yields of olefin, but its coproduct, indole, is easily detected and formed with high efficiency; typically the ratio of alkene to indole is close to 1:1.

Accordingly, indoline was utilized in DODH reactions with a broader range of polyols (Table 2). While the DODH reactions of diols are efficient employing NH_4ReO_4 (APR) or $MeReO_3$ (MTO)/indoline in aromatic solvents (Table 1, entries 3a,b), to effectively convert poorly soluble higher polyols, we turned to 1-butanol as a solvent.[14] The reaction utilizing indoline in combination with APR or MTO as catalysts in 1-butanol solvent proved to be effective for the DODH of several polar diols and polyols (Table 2, entries 2–10). We were pleased to obtain a quantitative yield (99%; 90% isolated) of *N*-allyl purine 3[23] from diprophylline (Table 2, entry 2). By comparison, a 70% yield of **3** was obtained from this substrate using the benzyl alcohol/NH_4ReO_4 system.[13] *N*-Allyl heterocycles such as **3** have diverse biological activity, including as modulators of drug-induced sleep and spontaneous activity,[24] as selective binders to the A2 adenosine receptor,[25] and as anticancer and antiviral agents.[26] Glycerol and its ester and ether derivatives (Table 2, entries 3–5) gave similarly high yields. Erythritol and xylitol (Table 2, entries 6 and 7) afforded moderate yields of the corresponding diene products. The three polyhydroxy carboxylic acids glyceric acid, tartaric acid, and mucic acid (Table 2, entries 8, 9, and 10) each provided an esterified alkene product; tartaric acid yielded 78% dibutyl fumarate (60% isolated), while mucic acid gave 57% of the corresponding *trans,trans*-diene ester. Glyceric acid gave a fairly low yield of butyl acrylate, which may be the result of competing reactions. The same reaction as Table 2, entry 8, using APR as catalyst showed no acrylate product, and GC-MS analysis revealed indoline- and indole/fumarate-coupled products (Scheme 4).[27]

Several observations indicate that indoline is a superior H-transfer agent relative to primary and secondary alcohols. In the indoline-driven reactions with 1-butanol as solvent, neither butanal nor the butanal/1-butanol acetal were detected in appreciable amounts. Two competition experiments were conducted to determine the relative H-transfer reactivity of indoline vs *sec*-alcohol reductants (Scheme 5). Conducting the same reaction as entry 3 (Table 2) with 2-butanol *as solvent* provided a lower yield of allyl alcohol, 46%, but a 1:1 ratio of allyl alcohol to indole and no detectable amount of butanone. In a fairer competition using conditions of entry 3a Table 1 the reaction of DET and 1.1 equivalents each of indoline and of 3-pentanol provided an 82% yield of diethyl fumarate with an appreciable amount of 3-pentanol remaining.

DOI: 10.1021/acs.organomet.5b00226
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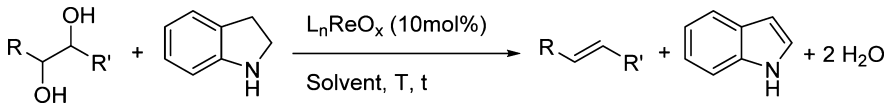
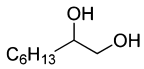
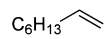
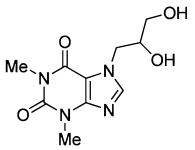
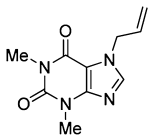
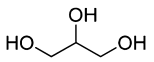
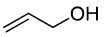
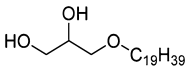
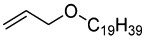
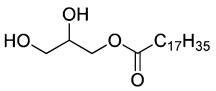
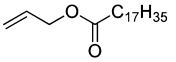
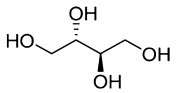
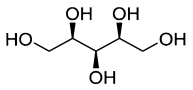
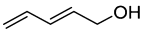
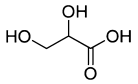
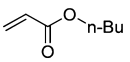
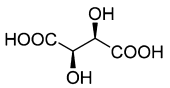
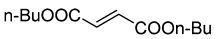
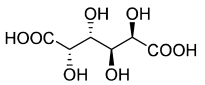
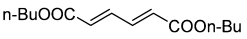
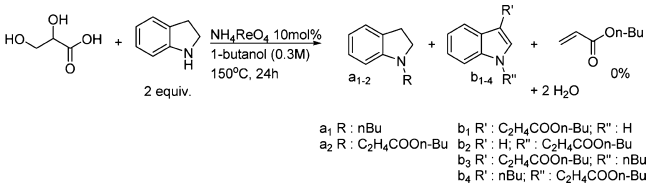
Table 2. DODH with Indoline as Reductant[e]



Entry	Substrate	Product	Conditions	Yield (%)[a] olefin/indole
1			A	70/90[b]
2		 **3**	B	99/50 (90)[c,b]
			E	62/54[d]
3			B	80/75
			D	66/67
4			C	78/80
5			C	80/56
6			C	43/61
7			B	56/55
8			C	35/64
9			D	78/65 (60%)[c]
10			D	57/88

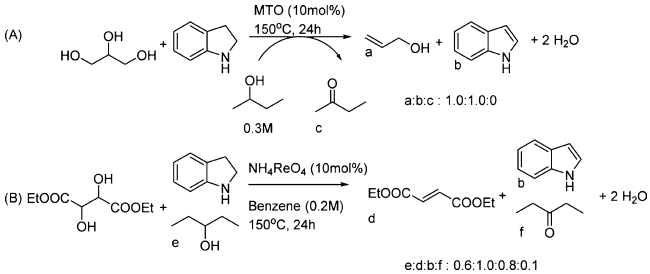
[a]Yield determined by ^{1}H NMR. [b]100% conversion. [c]Isolated yield. [d]65%. [e]Conditions: (A) NH_4ReO_4, benzene (0.2 M), 48 h, 150 °C; (B) $MeReO_3$ (MTO), 1-butanol (0.3 M), 24 h, 150 °C; (C) MTO, 1-butanol (0.3 M), 4 h, 170 °C (entry 7, 4.5 h); (D) NH_4ReO_4, 1-butanol (0.3 M), 24 h, 150 °C; (E) MTO 2.5 mol %, 1-butanol (0.3 M), 24 h, 150 °C.

Scheme 4. DODH of Glyceric Acid Using Indoline as Reducing Agent



Several of the hydroaromatics in Table 1 have been used in H-transfer reactions, including heterogeneous hydrogenation,[28,29] hydrogenolysis of aralkyl− and aryl−oxygen and −nitrogen bonds,[30] and light-driven alkane dehydrogenation.[31] In most of these studies indoline also showed high activity as a hydrogen donor. Computational and thermodynamic studies indicate an energetic driving force for the indoline/indole

Scheme 5. Reducing Agent Competition: (A) Indoline vs 2-Butanol; (B) Indoline vs 3-Pentanol



conversion ascribed to the gain of heteroaromatic stabilization, but little is known about the mechanism of H-transfer.[16,30]

The high efficiency of indoline-driven DODH reaction and the established affinity of amines for MTO[32] prompted us to

DOI: 10.1021/acs.organomet.5b00226
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investigate the interaction of MTO with indoline. The addition of a stoichiometric amount of indoline to a MTO solution at room temperature results in a rapid color change from colorless to yellow or green (λ 656 nm) depending on the concentration. The ^{1}H NMR spectrum of the mixture shows significant shifting of the indoline and Me-Re resonances, and the Re═O IR absorption is also shifted lower by 33 cm^{-1}. The MTO-indoline adduct **4** was isolated and structurally characterized by X-ray diffraction (Figure 1). The structure of **4** features a

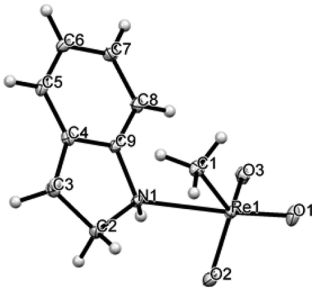


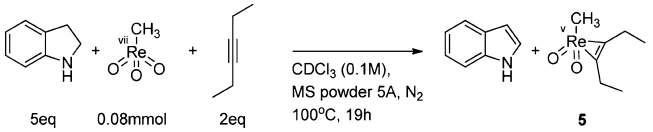
Figure 1. X-ray ORTEP diagram of $MeReO_3$(indoline) (**4**). Selected bond lengths (Å) and angles (deg): Re−O2 1.719(2), Re−O1 1.719(2), Re−O3 1.724(2), Re−C1 2.102(3), Re−N1 2.395(2), N−H 0.85(4); O2−Re−O1 105.01(10), O2−Re−O3 117.32(10), O1−Re−O3 106.26(10), O2−Re−C1 116.28(10), O1−Re−C1 90.03(11), O3−Re−C1 116.53(11), O2−Re−N1 78.62(9), O1−Re−N1 168.12(9).

distorted trigonal bipyramidal Re center with the N-coordinated indoline unit occupying an apical position and the Me-Re in an equatorial position.

After heating a solution of **4** for an hour at 150 °C, the ^{1}H NMR spectrum showed the formation of indole (ratio indoline:indole, 1.0:0.4); the indoline was entirely consumed after 4.5 h. From these observations it is clear that indoline coordinates to MTO at room temperature and, upon heating, is oxidized to indole. The less basic indole does not appreciably associate with MTO, given that after 20 h at room temperature there was no change in the ^{1}H NMR spectrum of an equimolar mixture of the two.

Because the corresponding reduced Re-species, $MeReO_2$ (MDO), will be highly reactive under the reaction conditions,[33] to test for its intermediacy, we conducted a trapping reaction with 3-hexyne.[12] Heating a mixture of indoline, 3-hexyne, and MTO (5:2:1) at 100 °C for 19 h fully consumed the MTO;[34] the ^{1}H and ^{13}C NMR spectra of the resulting mixture showed the formation of $MeReO_2$(3-hexyne) (**5**) (Scheme 6).

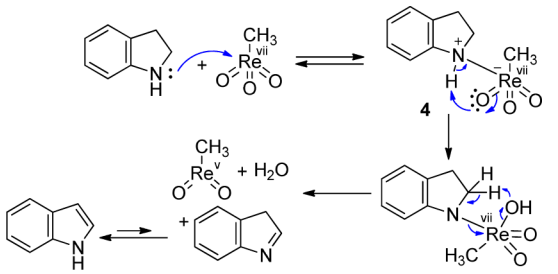
Scheme 6. MDO-Trapping Experiment



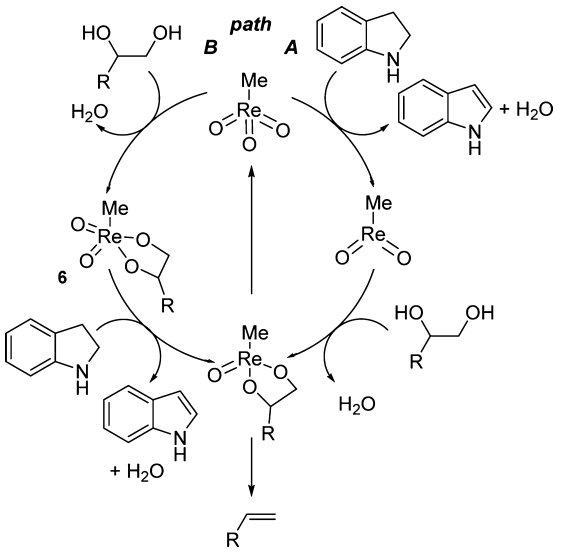
In Scheme 7 we suggest a possible mechanism for the formation of MDO and indole involving complexation, proton transfer of the acidified N−H to a Re═O unit, α-C-H transfer with H_2O loss, and isoindoline tautomerization.[35]

In the DODH system two pathways (A, B, Scheme 8) are viable, differing in the sequence of the reduction/condensation steps. In sequence A the rhenium(VII) species is first reduced, followed by condensation with glycol to form the Re^v-glycolate

Scheme 7. Possible Mechanism of MTO-Indoline H-Transfer Redox Reaction



Scheme 8. Potential MTO Catalytic Cycle with Indoline as Reductant



and fragmentation, while in path B the rhenium(VII) species first forms the glycolate, which is then reduced and fragments to the alkene. The affinity of MTO for indoline and the subsequent H-transfer redox reaction that proceeds at moderate temperatures indicate that path A (Scheme 8), involving initial reduction of MTO by indoline, is viable. To assess the relative affinity of indoline vs the diol substrate for MTO, we prepared an equimolar mixture of these reactants to which was added an equivalent of MTO at room temperature. The resulting NMR spectrum showed a 1.0:0.1 ratio of Me-ReO_3-(indoline) (**4**) to Re-glycolate (**6**)[7] (Scheme 8, R = H) and remained unchanged after 20 h, showing that indoline has a greater binding affinity than the glycol for MTO. This result also suggests a preference for pathway A, but does not exclude the operation of path B.

In conclusion we have demonstrated the ability of hydroaromatic compounds to serve as reductants in oxo-metal-catalyzed deoxydehydration of polyols. From a practical perspective the value of this transformation will depend on the cost/availability of the particular polyol and hydroarene co-reactants and the respective olefinic and aromatic co-products. Indoline is particularly efficient for these reactions, being more reactive than representative primary and secondary alcohols. Its effectiveness may be ascribed to its ability to coordinate to electrophilic oxo-metal species, to then effect entropically favored intramolecular H-transfer, and to form the stable, weakly coordinating aromatic, indole. Atom-economical tandem DODH/Diels−Alder reactions are also illustrated. The use of 1-butanol as solvent allows expansion of the range of

DOI: 10.1021/acs.organomet.5b00226
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polyols that are effectively converted to unsaturated products. The efficacy and availability of the hydroaromatic reductants could lead to their use in other oxo-metal-catalyzed reductions.

EXPERIMENTAL SECTION

General Information. All reactants and catalysts were obtained commercially and used without further purification. All solvents were ACS grade and were used directly (unless otherwise described in the procedures). ^{1}H, ^{2}H, and ^{13}C NMR spectra were collected on Varian VX300 MHz or VNMRS 400 MHz instruments. The NMR data were processed using SpinWorks[36] and ACD[37] software. GC-MS-EI analyses were performed on a Thermo-Finnigan instrument using a Stabilwax capillary column.

Representative Procedure for DODH Reactions. Diethyl tartrate (1.00 mmol, 0.17 mL), NH_4ReO_4 (0.10 mmol, 26.8 mg), indoline (1.10 mmol, 0.123 mL), and benzene (5 mL) were added to a thick-walled Ace glass reactor tube. A N_2 flow was bubbled into the mixture for at least 60 s before the Teflon seal was closed. The purge was made to avoid any oxidation of the hydrogen donors by O_2. The reactor was placed in an oil bath at 150 °C for 48 h while stirring magnetically. After cooling to rt, a 100 μL aliquot of the reaction mixture was removed and added to $CDCl_3$ and 2.0 μL of DMSO as internal standard for NMR analysis. This product and the others listed were characterized and quantified using ^{1}H NMR spectroscopy. Some of them were isolated and analyzed by NMR. The isolation of selected products was accomplished by column or preparative TL chromatography. The eluents varied according to the different polarity of the alkene product; hexane/ethyl acetate or chloroform/ethyl acetate mixtures were used. All olefinic products from the DODH reactions have been previously reported and were identified by comparison of their NMR spectra with authentic samples or published data (see the Supporting Information).

DODH/Diels−Alder Tandem Reaction with Diethyl Tartrate and 1,3-Cyclohexadiene. Diethyl tartrate (0.33 mmol, 0.057 mL), NH_4ReO_4 (0.033 mmol, 9.0 mg), and 1,3-cyclohexadiene (1.1 mL) were added to a thick-walled Ace glass reactor tube. The Teflon seal was closed, and the reactor was placed in an oil bath at 150 °C for 24 h while stirring magnetically. After cooling to rt, a 100 μL aliquot of the reaction mixture was removed and added to $CDCl_3$ and 2.0 μL DMSO as internal standard for NMR analysis. The product was identified and quantified by ^{1}H NMR spectroscopy and by comparison with an authentic sample of the separately prepared D−A adduct from the corresponding diene and diethyl tartrate (see the Supporting Information).

DODH Reaction of Glyceric Acid with Indoline. This reaction was conducted in the same way as the other DODH reactions. The NMR and GC-MS spectra of the crude product mixture after solvent evaporation indicated the presence of indole- and indoline-acrylate adducts (see the Supporting Information).

Reducing Agent Competition between 3-Pentanol vs Indoline. Diethyl tartrate (1.0 mmol, 0.17 mL), NH_4ReO_4 (0.10 mmol, 27 mg), 3-pentanol (1.1 mmol, 0.12 mL), indoline (1.1 mmol, 0.12 mL), and benzene (5 mL) were added to a thick-walled Ace glass reactor tube. A nitrogen flow was bubbled into the mixture for at least 60 s before the Teflon seal was closed, and the reactor was placed in an oil bath at 150 °C for 24 h while stirring. After cooling to rt, a 100 μL aliquot of the reaction mixture was removed and added to $CDCl_3$ and 2.0 μL of DMSO as internal standard for NMR analysis. The product composition was determined and quantified using ^{1}H and ^{13}C NMR spectroscopy.

Preparation of the $MeReO_3(\eta^1$-indoline) (4). MTO (0.040 mmol, 10 mg) was added to 3 mL of a 0.05 M solution of indoline in hexanes; the color change to yellow-green occurred instantaneously. The mixture was warmed to 40 °C in order to dissolve all the material. At 3 °C, a yellow precipitate formed in 10 min. Crystals for X-ray analysis were obtained by slow evaporation of the solvent at room temperature. IR: ν(Re═O) 933 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): 1.28 (s, 3 H), 2.60 (t, 2 H, J = 8.2 Hz), 2.93 (t, 2 H, J = 8.2 Hz), 6.59 (d, 1 H, J = 7.8 Hz), 6.77 (t, 1 H, J = 7.4 Hz), 6.96 (d, 1 H, J = 7.2 Hz), 7.02 (t, 1 H, J = 7.8 Hz). ^{13}C NMR (C_6D_6, 100 MHz): 150.7, 130.8, 127.8, 125.2, 120.9, 111.9, 47.7, 30.1, 19.3.

X-ray Crystal Analysis of 4. A yellow, plate-shaped crystal of dimensions 0.460 × 0.240 × 0.050 mm was selected for structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker APEX ccd area detector[38] and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The sample was cooled to 100 K. Cell parameters were determined from a nonlinear least-squares fit of 6810 peaks in the range 2.32° < θ < 28.32°. A total of 21 419 data were measured in the range 2.318° < θ < 28.333° using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method,[39] giving minimum and maximum transmission factors of 0.069 and 0.575. The data were merged to form a set of 2432 independent data with R(int) = 0.0395 and a coverage of 100.0%.

The monoclinic space group $P2_1/c$ was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2.[40] The positions of hydrogens bonded to carbons were initially determined by geometry and were refined using a riding model. The hydrogen bonded to the nitrogen was located on a difference map, and its position was refined independently. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the isotropic equivalent displacement parameters of the bonded atoms. A total of 131 parameters were refined against 2432 data to give $wR(F^2)$ = 0.0476 and S = 1.012 for weights of $w = 1/[\sigma^2(F^2) + (0.0280P)^2 + 1.4600P]$, where $P = [F_o^2 + 2F_c^2]/3$. The final $R(F)$ was 0.0162 for the 2340 observed, $[F > 4\sigma(F)]$, data. The largest shift/su was 0.003 in the final refinement cycle. The final difference map had maxima and minima of 0.840 and −0.873 e/Å^3, respectively. Further details on crystal data, data collection, and refinements are summarized in Table S1 (Supporting Information).

MTO/Indoline Reactivity Study. MTO (0.04 mmol, 10 mg) was dissolved in 800 μL of d_6-benzene in a high-pressure NMR tube. Indoline (0.04 mmol, 4.5 μL) was added, and the tube was flushed with N_2. ^{1}H NMR spectra were collected before and after placing the tube in an oil bath at 150 °C for 1 h. The reduction of MTO by indoline was set up similarly at a 0.20 mmol scale with protio-benzene in a thick-walled Ace glass reactor tube. A N_2 flow was bubbled in the mixture for 60 s, and after sealing the reactor the tube was placed in an oil bath at 150 °C for 4.5 h while stirring. After cooling at room temperature, the mixture was transferred to an NMR tube for analysis by no-D solvent NMR (see the Supporting Information). The two CH_2 group absorptions from indoline (3.1 and 3.6 ppm) were absent after the reaction, being replaced by the peaks for indole (with no overlap; 6.5 and 7.8 ppm). The mixture changed from colorless to yellow upon the addition of indoline at room temperature, then turned green. At 150 °C the solution turned blue then brown-black.

MDO Trapping. In a high-pressure NMR tube, 63 mg of MS 5 Å powder and 20 mg of MTO (0.08 mmol) were added to an 800 μL solution of 3-hexyne (2 equiv, 0.16 mmol, 18 μL) in d-chloroform (dried over 4 Å molecular sieves). The tube was flushed with N_2. ^{1}H and ^{13}C NMR spectra were collected at rt and after placing the tube in an oil bath at 100 °C. The reaction was completed after a total of 19 h.

Competition between Indoline and Ethylene Glycol for MTO. MTO (0.02 mmol, 5 mg) was added to 800 μL of a 0.03 M equimolar solution of indoline and ethylene glycol in d_6-benzene. ^{1}H NMR spectra were collected directly and confirmed after standing overnight at room temperature.

ASSOCIATED CONTENT

Supporting Information

NMR spectra of the reaction mixtures and isolated products. X-ray crystallographic files (CIF) for complex **4**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00226.

DOI: 10.1021/acs.organomet.5b00226
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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful for the support provided by the U.S. Department of Energy (DE-11ER16276). We thank Dr. Douglas Powell for determination of the X-ray structure of **4**.

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DOI: 10.1021/acs.organomet.5b00226
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