

An Iron-Based Dehydration Catalyst for Selective Formation of Styrene

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ABSTRACT: We	report the synthesis and crystal	structure of [Fe(OTf) ₂ (FOX)] (A).	Гhis	о Чон о

robust iron(II) complex was successfully applied as a homogeneous catalyst for the dehydration of 1-phenylethanol to styrene. Even at low catalyst loadings and moderate reaction temperatures, A showed a high catalytic efficiency. It was found to selectively activate the benzylic alcohol group of 1-phenylethanol. This is challenging since the vinyl system of styrene is highly reactive. In contrast to most of the other dehydration processes, the use of a Brønsted acid was not necessary. Furthermore, mechanistic insights into this E_1 -type



transformation and its competing S_N^1 -type side reactions are reported. [Fe('HexOH)(OTf)(FOX)][OTf] (B), an alcohol adduct of A, [Fe(H₂O)₂(FOX)][OTf]₂ (C), the completely hydrated derivative of A, and [μ -O{Fe(OTf)(FOX)}₂][OTf]₂ (D), a dinuclear oxidation product of A, were also characterized and are discussed.

KEYWORDS: catalysis, dehydration, iron, industrial chemistry, kinetics, isotopes, reactive intermediates

■ INTRODUCTION

Catalytic dehydration processes present an opportunity to access valuable olefins from abundant alcohols as found in biomass.¹ Since nucleophilic substitution reactions compete with the desired elimination of water, finding olefin-selective catalysts is still a major challenge.² Despite the potential for higher conversion rates, homogeneous catalytic processes using Brønsted acids are less common in industrial settings as they lead to the corrosion of equipment and the production of aggressive wastes.³

Styrene (2) is an important olefin widely used in organic synthesis and industrial polymerization reactions. The world's styrene supplies are commercially produced via the dehydrogenation of ethylbenzene and, to a lesser extent, the dehydration of 1-phenylethanol (1).⁴ These dehydration reactions are typically catalyzed by Brønsted acids.⁵ It is of interest to find catalytic conditions under which 1 is converted to 2 at high rates without oligomerization or polymerization. This is challenging since the vinyl group of 2 is very reactive. A simple dimer of 2 is compound 5, which is a common byproduct along with α -methylbenzyl ether (AME) stereoisomers 3, 4, and 4' (Scheme 1).^{6,7} Under harsher conditions, heavier oligomers and polymers are formed.

The liquid-phase dehydration of 1 is typically performed at temperatures around 170 °C with Brønsted-acidic heterogeneous catalysts.⁸ Klein Gebbink and co-workers showed that suspended Re_2O_7 is an excellent dehydration catalyst that selectively converts 1 to 2 in toluene at only 100 °C without the use of a Brønsted acid.⁹ There are few studies on the use of truly homogeneous, non-Brønsted-acidic catalysts for this transformation. Espenson and Zhu demonstrated that methyltrioxorhenium can be used to catalyze various

Scheme 1. Catalytic Dehydration of 1-Phenylethanol (1) to Styrene (2) with Achiral α -Methylbenzyl Ether (AME) 3, Chiral AMEs 4 and 4', and Styrene Dimer 5 as Major Byproducts



dehydration reactions, including a relatively low-yielding conversion of 1 to 2.10^{10}

RESULTS AND DISCUSSION

Catalyst Design. The aim of this study was to develop an efficient process for the selective dehydration of 1 that does not require the use of precious metals or Brønsted acids and that is based on homogeneous catalysis. Iron(III) chloride and triflate are common Lewis acids that are often applied in

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catalysis. However, in the presence of water or alcohols, iron(III) ions tend to aggregate into polyalkoxo/hydroxo/oxo iron(III) clusters. Such aggregation processes often lead to a rapid decrease in catalytic activity and cause precipitation. This is a reason why simple iron(III) salts are typically used in relatively high loadings in catalysis, ranging from 5 to 15 mol %.¹¹ Since iron(III) ions are also known to activate vinyl systems, their use in the selective formation of **2** is less favorable.¹² Iron(II) chloride and triflate are less Lewis-acidic but are also considerably less soluble in organic media.¹³ Recently, the oxidative conversion of **1** to benzaldehyde was reported to be catalyzed by a molecular iron(II) scorpionate-type catalyst, which was immobilized on Fe₃O₄/TiO₂ core–shell particles.¹⁴ Styrene (**2**) was detected to be an intermediate in this oxidation reaction.

We have found that fused oxazolidine (FOX) bicycles are ideal ligands for iron-based dehydration catalysts that selectively convert 1 to 2. Figure 1 shows the homogeneous



Figure 1. Depictions of the dehydration catalyst $[Fe(OTf)_2(FOX)]$ (A). (1) Crystal structure of A. Color code: iron, blue; oxygen, red; nitrogen, green; carbon, gray; sulfur, yellow; fluorine, violet; hydrogen, white. (2) Simplified drawing highlighting the coordination geometry of A.

catalyst $[Fe(OTf)_2(FOX)]$ (A). The tetradentate FOX ligand inhibits the aggregation of the iron ions in the presence of water and improves their solubility in organic media. It also favors the formation of octahedral high-spin complexes, such as A or its previously published chloride and bromide analogs, with two neighboring reactive sites.¹⁵

Reaction Optimization. NMR experiments showed that the conversion of 1 catalyzed by A occurs at relatively constant rates. No induction period was observed, which implies that no catalytically active nanoparticles had to be formed. Instead, the smooth kinetic reaction profiles are indicative of a homogeneous process.

Already 1 mol % of the catalyst A converts 1 to approx. 95% at only 100 °C (Figure 2). At this temperature, no formation of dimers or higher oligomers was observed. This means that A does not activate the vinyl system of 2 but rather selectively targets the benzylic alcohol 1. However, the amount of the AMEs 3, 4, and 4' produced and the reaction rate were found to depend on the concentration of 1.

At a 1.64 M concentration of 1 in *o*-dichlorobenzene (ODCB), 2 was only obtained in an approx. 20% yield at 95% conversion. The main products were the chiral AMEs 4 and 4' as well as the achiral AME 3. Recently, an iron-catalyzed conversion of styrenes into ketones with 1-arylethanols as byproducts was reported, and related α -methylbenzyl ethers were observed as minor byproducts.¹⁶ As the reaction progressed, 3, 4, and 4' began to be consumed. Interestingly,



Figure 2. Plots of NMR data recorded during conversion of 1-phenylethanol (1) to styrene (2) at different concentrations of 1 in deuterated *o*-dichlorobenzene (ODCB- d_4) in a total volume of 0.5 mL and with 1 mol % [Fe(OTf)₂(FOX)] (A) at 100 °C. The α -methylbenzyl ethers (AMEs) **3**, **4**, and **4**' were the only detected byproducts.

the consumption of 3 was measured to be faster than the consumption of 4 and 4'. To our knowledge, this observation has not been reported in the literature before. The different reactivity of the AME isomers can be explained by the shielding of the central oxygen atom. While the methyl groups in *meso* compound 3 point to the same direction and shield only one side of the ether bridge, the methyl groups in the enantiomers 4 and 4' are staggered and shield both sides.

The selectivity for 2 and the conversion rate of 1 were maximized at a 164 mM concentration (Scheme 2). 2 was

Scheme 2. Optimal Conditions for the Selective Conversion of 1-Phenylethanol (1) to Styrene (2) in *o*-Dichlorobenzene (ODCB) with $[Fe(OTf)_2(FOX)]$ (A) as a Homogeneous Catalyst



obtained in a 74% yield. Based on the consumption of 1 after the first 2 h, the turnover frequency (TOF) of the catalyst A doubled from approx. 10 to 20 h⁻¹ by decreasing the concentration of 1 from 1.64 M to 164 mM. This indicates a substrate inhibition at high concentrations. The selectivity for 2 was even further increased at a 16.4 mM concentration, but the reaction rate decreased drastically under these highly dilute conditions. The TOF was found to be around 0.4 h⁻¹. The decrease implies second-order kinetics for this catalytic dehydration process.

The NMR experiments revealed that the formation rates of the AMEs 3, 4, and 4' are affected differently by the changing concentration of 1 compared to the formation rate of 2. This observation opposes the hypothesis that the AMEs are formed as intermediates of the dehydration of 1 that finally yields $2.^{8b17}$ Instead, it implies that the AMEs are more likely reversibly formed byproducts.

Mechanistic Investigations. To elucidate the reaction mechanism further, we performed experiments with a mixture of equal amounts of deuterated 1-phenylethanol $(1-d_5)$ and nondeuterated styrene (2) (Scheme 3). The GC-MS results in Table 1 show that the AMEs formed after 1 h were almost

Scheme 3. Reaction of Deuterated 1-Phenylethanol $(1-d_5)$, Nondeuterated Styrene (2), and $[Fe(OTf)_2(FOX)]$ (A) in *ortho*-Dichlorobenzene (ODCB) at 120 °C^{*a*}



^{*a*}Nondeuterated 1-phenylethanol (1), deuterated styrene (2- d_5), the deuterated α -methylbenzyl ethers (AMEs) 3- d_{10} , 4- d_{10} , and 4- d_{10} , the partially deuterium-labeled AMEs 3- d_5 , 4- d_5 , and 4- d_5 , traces of the nondeuterated AMEs 3, 4, and 4' (faded and in parentheses), and the nondeuterated, partially deuterated, and deuterated styrene dimers 5, 5- d_{5} , and 5- d_{10} were observed as products.

exclusively derived from $1-d_5$. Therefore, it does not appear that these ethers are formed via an addition mechanism from 1-phenylethanol and styrene. However, small amounts of partially deuterated AMEs $(3-d_5, 4-d_5)$ and $4'-d_5$) and traces (<0.1%) of nondeuterated 3, 4, and 4' were also found in the reaction mixture. This can be explained by the hydration of 2 to 1, which was observed after the first hour of the reaction at $120 \ ^{\circ}C (\approx 0.12\%)$.¹⁸ Another possibility is the activation of 2 to a cationic intermediate that connects 1, 2, 5, and the AMEs.^{7b,11,12b,18} This intermediate could react with another equivalent of either 2 to yield 5, 1 to yield an AME, or with water to yield 1.^{7,18,19} The fact that nondeuterated 1phenolethanol and the partially deuterated AMEs were only observed in low concentrations shows that catalyst A is selective for alcohol substrates even if the concentration of 2 is high and the reaction temperature is elevated.

After a total reaction time of 4 h, 1-phenylethanol was completely consumed. Interestingly, the nondeuterated species 5 was the least abundant styrene dimer. Also, the completely deuterium-labeled compound $5-d_{10}$ was considerably less abundant than the partially deuterated dimer $5-d_5$. This implies that the dimer is neither exclusively formed from 2 nor from $1-d_5$. Consequently, 5 cannot simply be considered as the product of a dimerization of styrene. Since the selectivity of A for 2 as a substrate is low, it is most likely that 5 is produced via an activation of 1 by A followed by an attack of 2 at the activated intermediate.

Next, we tried to characterize the activated species of 1 in the presence of the catalyst **A**. In the NMR spectra, a broadening of the aromatic and aliphatic signals of 1 was observed. This can be attributed to a binding of 1 to the paramagnetic high-spin complex **A**. Unfortunately, we could not isolate this adduct. Instead, it was possible to crystallize and structurally characterize the cyclohexanol (^cHexOH) complex [Fe(OTf)(^cHexOH)(FOX)][OTf] (**B**).²⁰ Cyclohexanol is less reactive than 1 but can also be dehydrated by [Fe(OTf)₂(FOX)] (**A**) to cyclohexene.²⁰ Figure 3 shows that



Figure 3. Depictions of [Fe(HexOH)(OTf)(FOX)][OTf] (B). B is an adduct of complex I and cyclohexanol. (1) Extract of the crystal structure of B including relevant hydrogen bond networks. Color code: iron, blue; oxygen, red; nitrogen, green; carbon, gray; sulfur, yellow; fluorine, violet; hydrogen, white. (2) Simplified drawing highlighting the coordination geometry of B.

the equatorial triflate ligand is displaced by the alcohol. This was surprising since the equatorial Fe-OTf bond length of 2.06 Å in A is much shorter than the axial Fe-OTf bond length of 2.24 Å. A similar difference was previously reported for the axial and equatorial M–X bonds in $[M(X)_2(FOX)]$ $(M(X)_2 = Mn(Br)_2, Fe(Cl)_2, Fe(Br)_2, or Co(Br)_2)$. Methanol was found to preferentially occupy the axial positions in the complexes [Co(Cl)(CH₃OH)(FOX)][Cl] and [Ni-(Cl)(CH₃OH)(FOX)][Cl].¹⁵ Since the axial position is sterically less shielded, it should also provide more space for the relatively bulky cyclohexyl moiety. However, the equatorial displacement appears to be thermodynamically favored in $[Fe(OTf)_2(FOX)]$ as the Fe–O bond strength is increased in this position. In addition, the crystal structure of complex B shows strong hydrogen bonding. The coordinated cyclohexanol is hydrogen-bridged to the displaced triflate ion. The same triflate ion is connected via an uncoordinated cyclo-

Table 1. Composition of the Reaction Mixture Shown in Scheme 3 Determined via GC-MS at Different Time Points^a

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	time		
compound (isotope ratio)	0 h	1 h	4 h
$1 + 1 - d_5 (1 + 1 - d_5)$	51.5% (0:1)	3.7% (1:29)	0%
$2 + 2 - d_5 (2:2 - d_5)$	48.5% (1:0)	70.7% (27:10)	89.9% (11:10)
$3 \cdot d_5 + 3 \cdot d_{10} (3 \cdot d_5 \cdot 3 \cdot d_{10})$	0%	8.4% (1:42)	0.6% (1:5)
$4 \cdot d_5 + 4' \cdot d_5 + 4 \cdot d_{10} + 4' \cdot d_{10} \left(\{4 \cdot d_5 + 4' \cdot d_5\} : \{4 \cdot d_{10} + 4' \cdot d_{10}\} \right)$	0%	17.2% (1:50)	1.6% (1:10)
$5 + 5 - d_5 + 5 - d_{10} (5 - 5 - d_5 - 5 - d_{10})$	0%	0%	7.9% (1:8:3)

"Total amounts of deuterated, partially deuterated, and nondeuterated species of the same compound are given in percent. Ratios between deuterated, partially deuterated, and nondeuterated species are in parentheses. The trace amounts of 3, 4, and 4' are not included in the AME ratios.

hexanol molecule to the hydroxy group of the FOX ligand. This hydrogen bond network could be another reason for the equatorial displacement. Halide analogs of A, namely, $[M(X)_2(FOX)]$ $(M(X)_2 = Mn(Br)_2$, Fe(Cl)₂, Fe(Br)₂, or Co(Br)₂),¹⁵ did not catalyze the dehydration of 1.

The reaction mechanism depicted in Scheme 4 summarizes the findings of the NMR, GC-MS, and crystallographic

Scheme 4. Proposed Mechanism of the Conversion of 1-Phenylethanol (1) by the Catalyst $[Fe(OTf)_2(FOX)] (A)^a$



^{*a*}(I) Displacement of the equatorial triflate ligand of **A** by **1**. (II) Formation of a cationic intermediate. (III) Elimination of a proton from a cationic intermediate yielding styrene (**2**). (IV) Recovery of **A** via water elimination. (V) Nucleophilic attack of **1** at a cationic intermediate resulting in formation of α -methylbenzyl ethers **3**, **4**, and **4'**. (VI) Formation of a styrene dimer (**5**) caused by nucleophilic attack of **2** at a cationic intermediate. (III), (V), and (VI) are competing reaction pathways. Water formed in the dehydration process may displace triflate ligands at iron centers in the catalytic cycle.

experiments. In step (I), the equatorial triflate ligand of A is displaced by the alcohol 1. The activation of 1 by the Lewis acid A leads to the formation of a cationic intermediate (Scheme 4, step (II)). This benzylic carbocation can undergo an elimination of a proton yielding styrene (2) (Scheme 4, step (III)). The E₁-type conversion of 1 to 2 competes with the S_N1-type transformation of 1 to 3, 4, 4', or 5. Another molecule of 1 can attack the cation to form the α -methylbenzyl ethers (AMEs) 3, 4, or 4' (Scheme 4, step (V)). The side reaction yielding the styrene dimer (5) likely proceeds via a nucleophilic attack of a styrene molecule (2) at the cationic intermediate (Scheme 4, step (VI)). While the formation of 5 was only observed at a temperature of at least 120 °C, 2, 3, 4, and 4' were already obtained at 100 °C. This is probably due to the lower nucleophilicity of 2 than that of 1. No rearrangement of the disubstituted olefin **5** was observed during step (VI). This indicates that the cationic intermediate formed after the nucleophilic attack of **2** is short-lived. In similar reactions, the positive charge can migrate via a [1,3]hydride shift from a secondary carbon to a tertiary carbon. Since the cationic intermediate is converted into an alkene by proton elimination, Brønsted acid conditions extend the lifetime of such intermediates and favor this rearrangement process. However, the NMR data indicates that no [1,3]hydride shift occurred during the formation of **5**.²¹ This confirms that the reaction conditions are not Brønsted-acidic. The complete mechanism shown in Scheme 4 was tentatively formulated before but was not supported with the substantial amount of evidence gained during this study.²²

Reaction Scale-Up. Since the formation rates of all byproducts are increased at high concentrations of 1, we decided to feed 1 slowly to a larger-scale reaction at a constant addition rate (Scheme 5). 2 was continuously distilled from the

Scheme 5. Conversion of 1 to 2 via Reactive Distillation



reaction mixture. Such reactive distillation setups are common for liquid-phase transformation processes in industrial productions.⁸ The solvent, *o*-dichlorobenzene (ODCB), and the starting material 1 have higher boiling points than the product 2. The challenge is to distill 2 from the reaction mixture before it reacts with the cationic intermediate to form 5 or before it polymerizes at the relatively high reaction temperature. The high-temperature polymerization of 2 can occur independently of a catalyst and involves free radicals.²³

The optimization of such distillation processes is complex and involves sophisticated equipment and engineering skills. Our experiment was aimed to demonstrate the potential for the chemical optimization of this process. After only 1 h of operation, common Brønsted-acidic catalysts, such as zeolites and silica-aluminas, show signs of significant deactivation.^{8,24}

In contrast, A was proven to be very robust. The turnover number of 310 is high for a homogeneous iron catalyst. Also, the reaction rate did not notably decrease over the course of the reaction, and even higher turnover numbers could have been achieved. This is possible because the FOX ligand inhibits the aggregation of the iron catalyst. After the completion of the distillation, $[Fe(H_2O)_2(FOX)][OTf]_2$ (C) was crystallized from the reaction mixture (Figure 4). In this off-white compound, the two triflate ligands of A are displaced by water molecules. The equatorial Fe-OH₂ bond length (2.06 Å) is significantly shorter than the axial $Fe-OH_2$ bond length (2.13 Å). The water did not induce oxidation or oligomerization, and the catalytic activity was retained. It is likely that water completely displaces the triflate ligands at A in the catalytic cycle depicted in Scheme 4 as the water content in the reaction mixtures increases during the dehydration of 1phenylethanol (1). Therefore, complex C could replace complex A in Scheme 4.

At high temperatures, **A** was found to react with air to form the dinuclear iron(III) complex $[\mu$ -O{Fe(OTf)(FOX)}₂]-



Figure 4. Depictions of $[Fe(H_2O)_2(FOX)][OTf]_2$ (C). (1) Extract of the crystal structure of C. Color code: iron, blue; oxygen, red; nitrogen, green; carbon, gray; sulfur, yellow; fluorine, violet; hydrogen, white. (2) Simplified drawing highlighting the coordination geometry of C.

 $[OTf]_2$ (**D**) (Figure 5). **D** is similar to the dinuclear iron(III) catalyst $[\mu$ -O{FeCl(FOX)}₂][Cl]₂, which was recently used for



Figure 5. Depictions of $[\mu$ -O{Fe(OTf)(FOX)}₂][OTf]₂ (D). (1) Extract of the crystal structure of **D** not including two noncoordinated triflate counteranions. Color code: iron, blue; oxygen, red; nitrogen, green; carbon, gray; sulfur, yellow; fluorine, violet; hydrogen, white. (2) Simplified drawing highlighting the coordination geometry of **D**.

water oxidation.^{15,25} However, as found in the alcohol adduct **B**, the equatorial triflate of **A** was displaced to form the dinuclear complex **D**, while its chloride analog is oxide-bridged via the axial positions. To minimize the formation of complex **D**, reactive distillation was performed under a constant stream of inert gas.

CONCLUSIONS

In summary, we have developed a homogeneous dehydration catalyst that is stabilized and solubilized by a fused oxazolidine (FOX) ligand. While previous catalysts were based on Brønsted acids or precious metals, our iron-based catalyst operates without additives. It selectively converts 1-phenylethanol to styrene in good yields at moderate temperatures, and only low catalyst loadings are needed. Furthermore, the catalyst allowed us to study the different reaction pathways of this industrially relevant dehydration process. The results presented in this study partially revise prevalent mechanistic assumptions and provide more detailed insights into the styrene production. Since selective alcohol-to-olefin transformations are also important for the conversion of biomass to fine chemicals, these findings are potentially of broad relevance.

EXPERIMENTAL METHODS

Elemental compositions were determined on a PerkinElmer 2400 Series II analyzer. Nuclear magnetic resonance data was recorded on a Bruker Avance 400 spectrometer. GC–MS data was recorded on a Hewlett-Packard 5890 GC Series II equipped with a Hewlett-Packard 5970 Series mass selective detector. NMR spectra, chromatograms, and selected MS data are provided in the Supporting Information.

Crystallography. A Rigaku Synergy-S diffractometer with dual PhotonJet-S microfocus X-ray sources (Cu K α and Mo K α) and a HyPix-6000HE HPC detector was used for crystallographic experiments. CCDC 2086601–2086604 contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Bond lengths and angles as well as additional plots of the crystal structures are also provided in the Supporting Information.

Synthesis. All commercial reagents were used as received without further purification. Diethyl ether was distilled from sodium metal and benzophenone ketal. Acetonitrile was distilled from phosphorus pentoxide. Reactions requiring anhydrous conditions were performed in a Vacuum Atmospheres nitrogen-filled glovebox or under an argon atmosphere using Schlenk techniques.

 $[Fe(OTf)_2(FOX)]$ (A). $[Fe(Cl_2)(FOX)]^{15}$ (1.00 g, 2.35 mmol) was charged in a 20 mL scintillation vial with a Teflon stir bar and suspended in anhydrous acetonitrile (2 mL) under a nitrogen atmosphere. A solution of silver triflate (1.21 g, 4.71 mmol) in anhydrous acetonitrile (2 mL) was added to the stirred suspension. Silver chloride precipitated immediately from the reaction mixture. After the suspension was stirred for 2 min at room temperature, the precipitate was filtered off. Anhydrous diethyl ether (10 mL) was added to the clear solution. Colorless crystals of A, suitable for X-ray crystallography, were collected by filtration after 30 min. The crystals were rinsed with diethyl ether. Anhydrous n-hexane (5 mL) was added to the mother liquor, and more crystals of A were collected after 1 day and washed with diethyl ether. The combined crystal batches were dried in vacuo to yield A as a colorless solid (1.24 g, 1.90 mmol, 81%). C, H, and N (%) = 33.10, 2.61, and 6.48 (calc. 33.09, 2.62, and 6.43 for $C_{18}H_{17}F_6Fe_1N_3O_0S_2$). The effective magnetic moment (μ_{eff}) of 5.05 was determined by NMR using the Evans method and indicates a high-spin electronic configuration.²⁶

Kinetic Study. Under a nitrogen atmosphere, a stock solution of A (16.0 mg, 24.5 μ mol) in 1-phenylethanol (300 mg, 2.46 mmol) was prepared at room temperature and quickly transferred to NMR tubes with J. Young valves containing deuterated *o*-dichlorobenzene (ODCB-*d*₄). The following concentrations were used: 1.64 M, 100 μ L of stock solution in 400 μ L of ODCB-*d*₄; 164 mM, 10 μ L of stock solution in 490 μ L of ODCB-*d*₄; 16.4 mM, 1 μ L of stock solution in 499 μ L of ODCB-*d*₄. The ¹H NMR spectra of all solutions were recorded before the reaction mixtures was followed by ¹H NMR, and no lock signal was used.

Mechanistic Study. In a nitrogen-filled glovebox, A (22.4 mg, 34.3 μ mol) was charged into a 2 mL Schlenk tube, along with a Teflon stir bar. The flask was sealed, removed from the glovebox, and attached to a Schlenk line. Under a stream of nitrogen, *o*-dichlorobenzene (0.97 mL), which had previously been purged with nitrogen, 1-phenylethanol- d_5 (106 mg, 833

 μ mol), and styrene (85 mg, 816 μ mol) were added. A 50 μ L aliquot of the reaction mixture was taken, and then the flask was sealed and heated under stirring to 120 °C. Two more 50 μ L aliquots were taken after reaction times of 1 and 4 h. All aliquots were analyzed by GC–MS.

Reactive Distillation/Catalytic Reaction. Under a constant stream of argon, A (1.61 g, 2.46 mmol) and 1-phenylethanol (1.00 mL, 8.28 mmol) were dissolved in ODCB (49 mL). The solution was stirred and heated to 150 °C. Water and styrene were continuously distilled from the reaction mixture, while more 1-phenylethanol (99.0 mL, 820 mmol) was added at a rate of 1 mL/h with a syringe pump. After 110 h, the reaction was stopped, and aliquots of the reaction mixture and the organic phase of the distillate (55.9 g of styrene, 537 mmol, 65%, 59.1 g of ODCB) were analyzed by ¹H NMR. Upon cooling to room temperature, a few colorless crystals of $[Fe(H_2O)_2(FOX)][OTf]_2$ (C), suitable for X-ray crystallography, were obtained from the pale yellow reaction mixture.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c03037.

Properties of catalyst A, details of kinetic studies, isotope labeling and GCMS data, and reaction scale-up (PDF) Details of X-ray crystal structure determinations of A-D (CIF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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